

Defects and Transport Mechanisms in Solid Electrolytes and Mixed Conductors

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July 18 - July 22, 2022

Symposium Organizers

George Harrington, Kyushu University / MIT
Rotraut Merkle, Max Planck Institute for Solid State Research
Alexander Opitz, Technische Universität Wien

* Invited Paper

SESSION DT01: Grain Boundaries
Session Chair: George Harrington
Monday Morning, July 18, 2022
Mezzanine Level, Second Floor, Georgian

9:10 AM **DT01.01

Space-Charge-Mediated Phenomena at Oxide Interfaces for Electronics and Energy Applications Moritz L. Weber¹, Marc-André Rose¹, Lisa Heymann¹, Suqin He¹, Anton Kaus¹, Christian Lenser¹, Christoph Baeumer² and Felix Gunkel¹; ¹Forschungszentrum Jülich GmbH, Germany; ²Universiteit Twente, Netherlands

The properties of nanostructured complex oxides are often mediated by their rich ionic defect structure. Heterogeneous interfaces of oxides enable the exchange of ionic and electronic defect species between the neighboring materials, giving rise to electronic-ionic charge transfer and space charge formation. Such space charge regions typically possess distinctly different material properties as compared to the charge-neutral bulk of the materials and allow tailoring and tuning of ionic-electronic properties by intentional design of interfaces.

Here, we will discuss how dedicated design and understanding of interfacial space charge phenomena can be used to tailor electronic and ionic charge transport along and across oxide interfaces and surfaces. First, we will address the charge transfer at the solid-solid oxide interface between polar and non-polar oxides. In this case, the polarity mismatch of the neighboring materials enforces charge transfer across the interface, selectively triggering enhanced electronic conductivity or ionic conductivity along the interface depending on its chemical termination.

Second, we discuss the role of space charge at solid-liquid interfaces operating in electrochemical water splitting in alkaline media. As we will show the dedicated control of the surface band structure of oxide catalysts via space charge can be used to mediate activity for oxygen evolution reaction, while the mass transport across the interface is responsible for the degradation and limited lifetime of the catalysts. In this way, the control of space charge and electronic structure can be used to realize hybrid catalysts that attempt to break classical scaling relations of electrochemical activity and stability. Finally, we will address ionic processes during metal exsolution, which can be tailored by the ionic defect structure of the host oxide and provide catalytically active sites for gas exchange reactions.

9:40 AM DT01.02

Variability of Grain Boundary Defect Chemistry and Anion Conductivity in an Oxide-Conducting Ceramic Using Electron Microscopy and Electrical Measurements Hasti Vahidi¹, Alejandro Mejia², Shengquan Xuan¹, Angelo Cassiadoro², Abednego Abdi², David S. Mebane² and William Bowman^{1,3}; ¹University of California Irvine, United States; ²West Virginia University Eberly College of Arts and Sciences, United States; ³University of California Irvine Materials Research Institute, United States

Despite their promises in energy storage, conversion, catalysis, etc., non-stoichiometric polycrystalline oxides often suffer from the effect of internal interfaces called grain boundaries (GBs), which exhibit substantially lower ionic conductivity than the bulk in many solid-state ionic conductors. This is due to the existence of space charge layers (SCLs) at the GBs, where redistribution of the point defects (e.g., oxygen vacancies) affects the migration of charge carriers (e.g., oxygen anions) across the GBs. To date, modeling of the SCLs has been mainly focused on dilute solutions (< 1 at % of point defects), with few studies on concentrated solid solutions (which encompass most engineering materials) where defect-defect interactions are non-negligible, which is particularly important as it includes the most useful compositions for solid electrolyte applications. Oxygen conducting gadolinium-doped cerium oxide nanoparticles ($Gd_xCe_{1-x}O_{2-x}$) were synthesized and used to prepare sintered ceramic pellets. Ionic conductivity and conductivity activation energy for grain and grain boundary were resolved using AC impedance spectroscopy. The grain boundary point defects were measured using sub-nanometer spatial resolution electron energy-loss spectroscopy (EELS) in an aberration-corrected scanning transmission electron microscope (AC-STEM). A novel thermodynamic phase-field model was optimized by simultaneously fitting both experimental data sets and revealed that the various grain boundaries characterized here contribute differently to the overall conductivity. The grain, grain boundary, and total ionic conductivity values estimated using this model are in good agreement with experimentally measured values. A substantial variation in point defect concentrations was observed by nano-characterization and interpreted as a variation in the boundary-to-boundary ionic transport properties with the help of simulations.

9:55 AM *DT01.03

Direct Measurement of Local Oxygen Kinetics in Nanocrystalline Mixed Conductors by Isotope Exchange-Atom Probe Tomography Federico Baiutti^{1,2}, Francesco Chiabrera¹, David Diercks³, Alex Morata¹ and Albert Tarancón^{1,4}; ¹Institut de Recerca en Energia de Catalunya, Spain; ²Kemijski institut, Slovenia; ³Colorado School of Mines, United States; ⁴Institució Catalana de Recerca i Estudis Avançats, Spain

Enhancing mass transport by the introduction of an interface is a highly potential strategy for the fabrication of advanced energy materials, which find application in next-generation solid-state electrochemical devices such as batteries and solid oxide cells. In recent years, prominent successful examples of oxygen kinetics nanoengineering have been provided. In nanocrystalline Sr-doped lanthanum manganite (LSM) for instance, it has been shown that both the oxygen diffusivity and the surface exchange rate are strongly enhanced at the grain boundaries.^(1,2) The exact magnitude and the origin of such local effects, however, remain elusive also owing to the lack of specific tools with sufficient resolution to track the phenomenon. The introduction of methodologies capable of resolving local mass transport with nanometer resolution is therefore desired. In this work, we introduce novel atom probe tomography in combination with isotope exchange (IE-APT) to study the local oxygen kinetics in nanocrystalline thin films of LSM and Sr-doped lanthanum chromite (LSCr), previously annealed in an oxygen enriched atmosphere. IE-APT presents unique capabilities for mapping the atomic distribution in 3 dimensions, with nm-resolution and sensitivity towards isotopes. Applied to LSM and LSCr grain boundaries, IE-APT disclosed an unprecedented direct 3D imaging of highly conducting oxygen incorporation nanopathways, with reliable quantification of the local oxygen isotope distribution, independent ¹⁸O profiling for bulk and grain boundaries in 3-dimensions, correlation to the local stoichiometry and accessible information on the grain size and geometry.⁽³⁾ The combination with finite element simulations of the exact nanostructure allowed quantifying the grain boundary and bulk oxygen kinetic parameters with great precision. In both LSCr and LSM, an enhancement of several orders of magnitude for diffusivity and surface exchange coefficient with respect to the bulk is, in this way, highlighted and analyzed. Direct comparison with common local techniques, including TEM and IEDP-SIMS, is given, demonstrating the reliability of IE-APT for the analysis of the oxygen kinetics and the capability of the method for providing complementary, currently unaccessible, information. The possible origin of the observed grain boundary properties is critically discussed on the basis of the experimental data.

References

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- (2) F. Chiabrera, A. Tarancon et al., *Adv. Mater.* 2019, 31, 1805360
- (3) F. Baiutti, F. Chiabrera, A. Tarancon et al., *Adv. Mater.* 2021, 33, 2105622

10:15 AM DT01.04

Why We Should Not Trust (But Still Might Use) the Mott–Schottky Model for Grain-Boundary Impedance Adrian L. Usler and Roger A. De Souza; Rheinisch-Westfälische Technische Hochschule Aachen, Germany

Identifying the excess resistivity of grain boundaries with the presence of space-charge layers has become widely accepted in the context of high-purity oxide-ion conducting polycrystals: the considered space-charge models usually involve a positively charged grain-boundary core, surrounded and compensated for by negatively charged space-charge layers. A simplified description with closed-form expressions can be provided if the acceptor cations take a uniform concentration profile throughout the sample (*Mott–Schottky* case). This approximation may be justified with the typical range of measurement temperatures, in which the cation mobility is negligible, such that non-equilibrium configurations may be retained.

Nevertheless, the analysis of impedance data with the Mott–Schottky model is problematic in two aspects: first, this dilute-solution model is often applied to heavily substituted electrolyte materials, whose bulk-phase electrical conductivities are known to be largely determined by point-defect interactions. Second, ion-conducting ceramics are usually prepared by sintering at high temperatures, thus permitting the acceptor cations to attain electrochemical equilibrium before their movement is frozen-in upon cooling.

In this work, we have calculated impedance spectra from continuum-level simulations of a bicrystal geometry, with space-charge layers at the grain boundary. Different space-charge models for dilute and concentrated solid solutions are considered. Specifically, space-charge layers are simulated in the scope of the *restricted-equilibrium* model [1, 2] and the *Poisson–Cahn* model [3, 4] to account for thermal history and for point-defect interactions, respectively. Based on the simulation results, the common practice of analysing grain-boundary impedance with the standard closed-form expressions is assessed.

Our results indicate that, given a restricted-equilibrium scenario, the Mott–Schottky expressions may substantially underestimate the true space-charge potential, even though the results display a general qualitative agreement with the Mott–Schottky case. Furthermore, it is demonstrated that, in concentrated solutions, grain-boundary impedance must be considered as being virtually decoupled from the space-charge potential, owing to variations of ion mobility within the space-charge layer. Different consistency checks [5, 6] are discussed that require only the impedance-spectroscopic experimental setup and that can reveal cases not adequately described by the Mott–Schottky model.

References:

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SESSION DT02: Battery Materials, Cathode
Session Chair: Wolfgang Zeier
Monday Morning, July 18, 2022
Mezzanine Level, Second Floor, Arlington

9:10 AM **DT02.01

The Role of Ionic Transport in Controlling the Intercalation Mechanisms of Battery Electrode Materials—Magnetic Resonance, Diffraction and Optical Scattering Measurements Alice J. Merryweather, Christopher Schnedermann, Akshay Rao and Clare P. Grey; University of Cambridge, United Kingdom

Ni-rich layered cathode materials are among the most promising candidates for high energy density Li-ion batteries for EV applications, yet improvements in their capacity retention – particularly under conditions of stress (high/low temperature, fast charging) – are still required for their more widespread use. This talk will focus on recent studies aimed at understanding the initial first cycle capacity loss and capacity loss over more extended cycling in half and

full cells. Operando x-ray diffraction (XRD) and nuclear magnetic resonance (NMR) spectroscopy of $\text{Li}_x\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ is used to demonstrate that the apparent first cycle capacity loss is a kinetic effect linked to limited Li mobility at $x > 0.88$.¹ The use of a novel operando optical spectroscopy method coupled with continuum modelling to study intercalation processes, phase transitions and lithium-vacancy ordering processes will be described for LiCoO_2 and nickel manganese cobaltates (NMCs).² The method is applied, along with transport measurements³ to explore how changes of Li mobility as a function of state charge lead to the appearance of significant concentration gradients within individual particles and apparent two phase behaviour even within solid solution regimes when cycling the material, particularly at high rates.

- [1] "Intrinsic Kinetic Limitations in Substituted Lithium Layered Transition-Metal Oxide Electrodes", A. Grenier, P.J. Reeves, H. Liu, I.D. Seymour, K. Märker, K.M. Wiaderek, P.J. Chupas, C.P. Grey, K.W. Chapman, *J. Am. Chem. Soc.*, **142**, 7001-7011 (2020)
 [2] "Operando optical tracking of single-particle ion dynamics in batteries", A.J. Merryweather, C. Schnedermann, Q. Jacquet, C.P. Grey, A.K. Rao, *Nature*, **594**, 522–528 (2021).
 [3] "Evolution of Structure and Lithium Dynamics in $\text{LiNi}_{0.8}\text{Mn}_{0.1}\text{Co}_{0.1}\text{O}_2$ (NMC811) Cathodes during Electrochemical Cycling," K. Märker, P.J. Reeves, C. Xu, K.J. Griffith, C.P. Grey, *Chem. Mater.*, **31**, 2545 (2019)

9:40 AM DT02.02

Investigation of Lattice Oxygen Stability of Lithium-Ion Battery Cathode $\text{Li}(\text{NiMn})\text{O}_2$ Takashi Nakamura¹, Xueyan Hou¹, Yuta Kimura¹, Yusuke Tamenori², Kiyofumi Nitta², Hirona Yamagishi³ and Koji Amezawa¹; ¹Tohoku Daigaku, Japan; ²Kokido Hikari Kagaku Kenkyu Center, Japan; ³Ritsumeikan Daigaku, Japan

Introduction

To utilize renewable energies in larger scale, high-energy-density and safe energy storage technologies like advanced Li-ion batteries is vitally important. Although some high-energy-density cathodes are proposed such as high-Ni cathode and Li-rich cathodes, gas generation from oxide-based cathodes remained as an unsolved issue for the reliable battery operation [1]. To design robust cathode materials, it is important to understand the mechanism of oxygen release and decisive factors for the lattice oxygen stability. For that, we developed the methodology for the evaluation of oxygen release from oxide-based cathode materials [2]. In this work, we applied the methodology we developed to a promising Li-ion battery cathode $\text{LiNi}_x\text{Co}_y\text{Mn}_{2-d}\text{O}_{2-d}$ and discussed lattice oxygen stability based on their oxygen release behavior, the charge compensation and thermodynamic analyses.

Experimental

$\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ (NCM111), $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$ (NCM523) and $\text{LiNi}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}\text{O}_2$ (NCM622) were synthesized by solid-state reactions from LiOH H_2O and Ni-Co-Mn mixed carbonate precursors obtained by a co-precipitation method. Oxygen release behavior was evaluated by the coulometric titration using yttria stabilized zirconia (YSZ) tube as an oxide-ion conductor. The sample was placed in the YSZ tube and sealed in Ar atmosphere. Electrochemical cell was fabricated as Pt/sample/YSZ/Pt. The relation between the amount of released oxygen and equilibrium $P(\text{O}_2)$ was investigated until the total oxygen loss reached 5 mol% ($2-d = 1.9$). Charge compensation by oxygen release was investigated by X-ray absorption spectroscopy (XAS) at BL27SU, Spring-8 and SR center of Ritsumeikan-University.

Results and discussion

The order of equilibrium $P(\text{O}_2)$ for 5 mol% oxygen release was $\text{NCM111} < \text{NCM523} < \text{NCM622}$, meaning that increasing the Ni content enhanced oxygen release. This tendency is well consistent with earlier reports that high-valent Ni destabilizes lattice oxygen [2, 3]. Until the amount of the released oxygen reached 5 mol%, XAS revealed that only reduction of Ni^{3+} was observed in NCM622, while the selective reduction of Co^{3+} was observed after slight reduction of Ni^{3+} in NCM111. The difference of reduction species, Ni^{3+} or Co^{3+} , caused the difference in lattice oxygen stability. For more quantitative discussion, we calculated partial molar enthalpy of oxygen of NCMs which represents the binding energy of lattice oxygen, in other words, necessary energy for oxygen release. According to the thermodynamic analysis, obtained partial molar energy can be classified into two groups depending on reduction species. The partial molar enthalpy of oxygen by Ni reduction (-150 to -50 kJ mol^{-1}) is much smaller than that by Co reduction (-270 to -200 kJ mol^{-1}). This quantitative comparison provides deeper understanding of the stability of cathode active materials and leads to a flexible tuning of electrochemical performance and robustness of cathode active materials.

Summary

To understand lattice oxygen stability in Li-ion battery cathode $\text{LiNi}_x\text{Co}_y\text{Mn}_{2-d}\text{O}_{2-d}$, we carried out coulometric titration and X-ray absorption spectroscopy, and succeeded to quantitatively evaluated the lattice oxygen stability by calculating partial molar enthalpy of oxygen which represents the binding energy of lattice oxygen. The combination of defect chemical evaluation and XAS revealed that necessary energy for oxygen release by Ni reduction is much smaller than that by Co reduction in $\text{LiNi}_x\text{Co}_y\text{Mn}_{2-d}\text{O}_{2-d}$.

References

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9:55 AM *DT02.03

Designing Hysteresis Free High-Valent Redox Cathode Materials for Electrochemical Application Iwnetim I. Abate^{1,2}; ¹University of California Berkeley, United States; ²Massachusetts Institute of Technology, United States

Advances in electrochemical devices such as batteries, fuel cells, and water-splitting membranes are making the global transition towards clean and renewable energy more possible than ever. Foundational to (electro)chemical and catalytic transformations in these devices are stable and reversible high-valent redox couples in mixed ionic-electronic conductors. In particular, the phenomenon of high-valent oxygen redox (anionic redox) in lithium- and sodium-ion positive electrodes has the potential to significantly improve cell energy density by providing additional high voltage capacity beyond that of most transition metal redox couples. However, the additional capacity from (anionic redox) has come at the expense of reduced reversibility in the form of voltage hysteresis and voltage fade. As a result, high valent redox couples have been historically avoided. In this talk, first, I will outline the mechanism and the framework for understanding the source of poor electrochemical reversibility in high-valent redox and the role defects play. Second, I will demonstrate a mechanism where structural disorder and voltage hysteresis can be completely avoided through defect engineering. Third, I will provide a set of actionable design rules involving tuning of defect formation energy landscape to engineer materials with high-valent redox couples for various applications.

10:15 AM DT02.04

Enhancing Capacity Retention of $\text{Na}_2\text{Mn}_3\text{O}_7$ Using Ti Dopants—A Density Functional Theory Study Yong-Seok Choi^{1,2,3}, Stephanie Linnell^{4,2}, Eun Jeong Kim^{4,2}, A. Robert Armstrong^{4,2} and David O. Scanlon^{1,2,3}; ¹University College London, United Kingdom; ²The Faraday Institution, United Kingdom; ³Thomas Young Centre, United Kingdom; ⁴University of St Andrews, United Kingdom

Despite their high energy density, Li-ion batteries (LIBs) suffer the intrinsic drawback of the rarity of its raw materials, inhibiting the development of future large-scale energy storage devices. As a promising alternative for LIBs, Na-ion batteries (NIBs) have emerged with practically ubiquitous and

inexhaustible sodium resources. However, the commercialization of NIBs remains as a challenge as the less negative redox potential and larger ionic radius of Na makes the overall electrochemical performance of NIBs inferior to LIBs^[1,2]. To enhance the energy density and cycle life of NIBs, major efforts have been devoted to design high performance Na-ion cathodes. An effective approach is to introduce anionic redox couples. The anionic redox, which was first discovered in LIBs with extraordinary energy densities^[3], has been reported to endow long cyclability and high energy density on Na-ion cathodes as well, as can be shown from Na₂Mn₃O₇^[4].

In addition to introducing anionic redox reactions, another method to promote the cycle lives of Na-ion cathodes is doping redox-inactive cations. Of all dopants reported to date, Ti dopant has drawn attention in recent years due to its chemical stability and widespread distribution in the earth's crust. The Ti-substituted Na-ion cathodes are reported to display higher working potential and improved cycling stability^[5-7]. Above two strategies imply that the combination of Ti dopants and anionic redox-based Na-ion cathodes will further enhance the electrochemical performance suitable for future cathodes. Despite such promising aspects, doping strategies have mostly been employed mostly for NaTMO₂ (TM = transition metal elements) stoichiometries, where cationic redox prevails over anionic redox.

Here, using first-principles calculations, we study the effect of Ti dopants on the electrochemical performances of Na₂Mn₃O₇. Based on Generalized Quasi-Chemical Approximation^[8], we predicted that the amount of Ti that can be doped to Na₂Mn₃O₇ is 0.5 per unit formula at typical synthesis temperature of 600 °C. The Ti-doped Na₂Ti_{0.5}Mn_{2.5}O₇ showed higher anionic redox voltages than pristine Na₂Mn₃O₇, which is beneficial for high energy density batteries. Furthermore, the resultant TiO₆ octahedra after Ti doping is predicted to stabilize the cathode structure, enhancing its capacity retention. Lastly, by employing Al dopants with opposing properties to Ti, we also discuss the relationship between the dopant properties (e.g. electronegativity, oxidation state) and electrochemical performance (e.g. cyclability, voltage), which can enable the development of high performance sodium manganese oxide cathodes.

References

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SESSION DT03: Interfaces
Session Chair: Federico Baiutti
Monday Morning, July 18, 2022
Mezzanine Level, Second Floor, Georgian

11:00 AM **DT03.01

Linking Oxide Electronic Structure and Electrocatalytic Activity via X-Ray Spectroscopies Kelsey A. Stoerzinger^{1,2}; ¹Oregon State University, United States; ²Pacific Northwest National Laboratory, United States

Perovskite oxides (ABO₃) are highly active for the oxygen evolution reaction (OER). I will present studies of model oxide electrodes grown by pulsed laser deposition (PLD) and molecular beam epitaxy (MBE) on single crystal substrates that display a known crystallographic orientation, strain, surface area, and path for charge transport. Activity is observed to correlate with changes in bulk electronic structure parameters, such as metal-oxygen covalency and transition metal oxidation state, obtained via X-ray based spectroscopies. Many surface science techniques, such as X-ray photoelectron spectroscopy (XPS), collect information from inherently surface-sensitive low-energy processes, requiring operation in ultrahigh vacuum. This constraint is lifted for ambient pressure XPS, which can probe the surface in equilibrium with the gas phase at pressures up to ~a few Torr, or with thin liquid layers using a higher incident photon energy. This presentation will discuss the insights obtained with this technique regarding the electronic structure of oxide electrocatalysts in an oxidizing or humid environment, as well as the reaction intermediates of relevance to electrocatalysis.

11:30 AM DT03.02

A Lithium Dendrite Inhibiting Strategy by Metallic Coatings in Solid Electrolytes via Operando Study Xin Xu, Geoff McConohy, Edward Barks, Sunny Wang, Emma Kaeli and William C. Chueh; Stanford University, United States

As a next-generation battery technology, solid state batteries, though promising, still face barriers that limit their practical application. Lithium dendritic growth, a main limitation for cell life, is receiving urgent attention within the scientific community because: 1) Li dendrites are easily generated in solid electrolytes and cause early-onset cell shorting and failure; and 2) the understanding of the lithium dendrite mechanism^{1,2} remains unsatisfactory. To develop high-performance solid state batteries with long cyclability, inhibiting lithium dendrites is a must. This requires deep knowledge and further study of the dendrite mechanism: when and exactly where Li nucleation occurs, how Li dendrites propagate through solid electrolytes, and what steps will be required to protect solid electrolytes from dendrite penetration. Recognition of this gap in understanding has driven efforts to study the electro-chemo-mechanical effect of dendrites by local characterization which allows immediate observation and direct characterization at the regions of interest. Here we developed an operando microprobe platform with pressure control, in combination with cryo electron microscopy (Cryo EM) and nanoscale secondary ion mass spectrometry (NanoSIMS), to address this need. We examined a leading solid electrolyte Li_{6.6}La₃Zr_{1.6}Ta_{0.4}O₁₂ (LLZTO) of wide interest to the materials community due to its fast ionic conductivity and wide electrochemical stability window³. The highly dense LLZTO sample (>99% relative density) was fractured in an Ar-filled glove box and transferred to SEM by a mechanical air-free transfer cell. The as-fractured surface provides a clean surface without carbonate/hydroxide contamination. A tungsten probe was touched to the as-fractured surface with a controlled contact force, from 0.1 mN to ~5 mN, measured by a well-calibrated spring table. A negative electrical potential was applied between the probe (working electrode) and a counter electrode of lithium metal. We observed that the sample surface under high probe contact force (>2 mN) was cracked by lithium dendrites at a low cell voltage (< 500 mV) while the sample under low probe contact (~0.1 mN) can survive at a higher voltage. The surface nanoscale cracks were shown to be largely responsible for the lithium dendritic deposition.

To inhibit the dendritic deposition, we sputtered the as-fractured surface with a variety of metals including Ag, Pt, and Cu without exposing the LLZTO to air. We then used a focused ion beam (FIB) to cut out microelectrodes between 5 and 20 microns in diameter. We observed that Ag coating of fractured surfaces induced uniform Li plating and high stability at (1) current density > 1000 mA/cm², and (2) cell voltage > 1000 mV at room temperature. In addition, the lithium penetration probability due to lithium dendrites was heavily decreased with only 20 μm² area fractured out of a total searching area of ~2500 μm², in comparison with nearly 100% fracture probability of the uncoated surfaces under the same conditions. The metal-coated surfaces were then examined with Cryo EM and NanoSIMS. The cryo EM analysis showed that the sputtered Ag was able to fill surface nano cracks to a depth of 20-200 nm.

The high lithium diffusivity in Ag may circumvent lithium plating at the cracks and avoid hydrostatic stress build-up. In addition, NanoSIMS depth profiling of the isotopes of ^{109}Ag , ^{139}La , ^{90}Zr showed that the interface experienced inter-diffusion of cations in compliance with the cryo EELS results which might improve surface energy to prevent dendritic cracks. These insights suggest a strategy of surface defect control and effective coating to inhibit lithium dendrites in solid electrolytes which enables long cyclability of solid state batteries.

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11:45 AM *DT03.03

Relating the Varied Composition and Oxide Ion Conductivity of Ceramic Grain Boundaries Using Electron Microscopy and Electrical Measurements William Bowman¹, Hasti Vahidi¹, Huiming Guo¹, Shengquan Xuan¹, David S. Mebane², Alejandro Mejia², Angelo Cassiadoro² and Abednego Abdi²; ¹University of California Irvine, United States; ²West Virginia University, United States

Polycrystalline ionic conducting oxides such as $\text{Gd}_x\text{Ce}_{1-x}\text{O}_{2-d}$ and $\text{Y}_x\text{Zr}_{1-x}\text{O}_{2-d}$ can suffer from negative effects of grain boundaries (GBs) and internal heterointerfaces, which exhibit substantially lower ionic conductivity than the grain bulk particularly at lower temperatures. This is due to space charge layers and zones of significant local point defect redistribution near the interface plane, where a depletion of mobile charge carriers is often observed by high spatial resolution characterization ¹. Modeling of these phenomena has highlighted the importance of defect-defect interactions, which are more pronounced at interfaces in concentrated solid solutions that offer useful functional properties ^{2,3}. Moreover, polycrystalline materials can by nature have a distribution in the local defect chemistry and thus transport properties from boundary to boundary ^{4,5}. This talk will focus on our efforts to better understand the local point defect accumulation and depletion at GBs in concentrated solid solution oxygen ion conductors. Our hypotheses focus on roles of defect segregation and GB variability within polycrystalline ceramics on defining GB electrical transport in oxides.

First, we have correlated direct observations of local GB defect chemistry with the average oxygen anion conductivity of GBs in a bulk $\text{Gd}_{0.25}\text{Ce}_{0.75}\text{O}_{2-d}$ (GCO) ceramic. Ionic conductivity and conductivity activation energy for grain and GB were resolved using AC impedance spectroscopy. The GB point defects were measured using sub-nanometer spatial resolution electron energy-loss spectroscopy (EELS) in an aberration-corrected scanning transmission electron microscope (AC-STEM). A novel thermodynamic phase field model was optimized via simultaneously fitting both experimental data sets and revealed that the various GB characterized likely contribute differently to the overall conductivity. Second, we are directly correlating (Y_2O_3 - ZrO_2 , YSZ) bicrystal interface characterization in the AC-STEM with measured electrical conductivity across the interfaces. Customizable model bicrystal interfaces are being synthesized by two methods: a conventional ‘top-down’ approach of hot pressing of single crystals, and a novel ‘bottom-up’ approach leveraging pulsed laser deposition (PLD). Both approaches should offer unique opportunities and advantages to isolate critical aspect of interface character and local chemistry to better understand their role on charge transport.

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12:05 PM DT03.04

Molecular Dynamics Study of Oxygen-Ion Diffusion in Ytria-Stabilized Zirconia Grain Boundaries Jose C. Madrid Madrid and Kulbir K. Ghuman; Institut national de la recherche scientifique, Canada

SOFC technology currently suffers from material interaction, insulating phase formation, and thermal stresses as it operates at high temperatures, which results in rapid degradation, low reliability, and high cost for commercialization. One of the approaches to reduce the operating temperature of SOFCs is the use of thin-film electrolytes to reduce the ohmic losses experienced at a reduced temperature while offering high thermal stability. That been said, the nanoscale thin films are generally polycrystalline and contain a high density of Grain Boundaries (GBs), which can substantially affect the ion diffusion in electrolytes. Experimentally, the atomistic structure of GBs can be analyzed and observed via high-resolution scanning STEM, but unfortunately, it does not provide sufficient information about the atomic-level structure of these boundaries. Molecular Dynamics (MD) simulations have been used for studying Grain Boundaries’ atomic structure and oxygen-ions transport across YSZ electrolyte over the last decades. However, high symmetry GBs have been commonly targeted even though most boundaries found in polycrystalline samples are a mix of twisted and tilted denominations- commonly named “mixed” GBs. A mixed grain boundary (GB) was modelled at the atomic level using MD in this work. The structure was built from a TEM image of an 8YSZ thin film sample using the amorphization and recrystallization (A&R) technique. Oxygen-ion self-diffusion was studied for a range of temperatures between 700 K and 2300 K and Y_2O_3 concentration between 4-14 mol%. It was found that Y_2O_3 does not segregate toward the GB core for one of the grain orientations. On the contrary, Y prefers to accumulate in this particular grain after the A&R process. As a result, it allows a better distribution of oxygen vacancies inside the grain interior what leads to obtaining a higher oxygen-ion self-diffusion for this region.

12:20 PM DT03.05

Investigation of Defect Behavior near the Interfaces of Au(111)/ Li_3PO_4 Using Neural Network Potential Koji Shimizu¹, Yasunobu Ando², Emi Minamitani³ and Satoshi Watanabe¹; ¹The University of Tokyo, Japan; ²National Institute of Advanced Industrial Science and Technology, Japan; ³Institute for Molecular Science, Japan

Li_3PO_4 based materials are used for solid electrolytes in thin film Li batteries. Recently, its application as a non-volatile memory is also being explored: Au/ Li_3PO_4 /Li as well as Ni/ Li_3PO_4 /Li stacked structures were found to exhibit a few different voltage states, which can be controlled by applied voltages with low energy consumption [1, 2]. To develop novel memory devices using this phenomenon, understanding of Li-ion distribution near the metal/ Li_3PO_4 interfaces is crucially important. The knowledge may be applied in all-solid-state batteries, considering the similarity of the device structures. In our previous study, we conducted the combined calculations of density functional theory (DFT) and continuum models, suggesting that interstitial Li-ions were accumulated at Au (Ni)/ Li_3PO_4 with a few Å depth from the interface [3]. In the present study, we aim to further understand interface phenomena of Au/ Li_3PO_4 system on the atomic scale, employing one of the machine-learning interatomic potentials, the high-dimensional neural network potential (NNP) [4], which is expected to achieve high reliability and low computational costs simultaneously.

We constructed four-element (Au-Li-P-O) NNPs using the dataset obtained from DFT calculations, which included bulk structures of Au and Li_3PO_4 , and Au/ Li_3PO_4 interface systems. We created 24,164 structures in total, and the root-mean-square-errors of the predicted total energies and atomic forces of the test dataset (randomly chosen 10%) were 5.78 meV/atom and 114 meV/Å, respectively. Next, using the constructed NNP, we analyzed Li defect behavior with an interface model containing 5,520 atoms (Au: 1,200 atoms and crystalline Li_3PO_4 : 4,320 atoms, where the lattice mismatch was as small as 1.6%). From the defect formation energies of a single Li defect (vacancy and interstitial) at various positions inside Li_3PO_4 , we found that both defect species showed the lower energies near the interface in comparison to those in the middle of Li_3PO_4 region. In addition, we investigated the density dependence on the formation of Li defects. The calculated formation energies indicated that the Au/ Li_3PO_4 interface could accommodate a large number of interstitial Li-ions, which qualitatively agreed with the continuum-model results [3]. At the conference, we will also discuss the DFT verification of the above results.

Acknowledgements

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SESSION DT04: Battery Materials, Theory
 Session Chair: Martin Wilkening
 Monday Morning, July 18, 2022
 Mezzanine Level, Second Floor, Arlington

11:00 AM **DT04.01

The Complex Mechanisms that Create High Li-Ion Mobility in Oxides and Sulfides [Gerbrand Ceder](#)^{1,2}; ¹University of California Berkeley, United States; ²E O Lawrence Berkeley National Laboratory, United States

The exciting development of solids with extremely high Li-ion conductivity, higher than that in traditional liquid electrolytes, in the last decade has forced us to rethink the processes that make cations move in solids. Super-ionic Li conductors typically have very high Li concentration so that their conductivity behavior cannot be explained with simple point defect mechanisms. Instead, ideas of concerted motion or highly correlated motion have been proposed. I will discuss our current understanding of the mechanisms that provide high Li-ion conductivity. We find that due to the high screening power of S^{2-} Li mobility in sulfides is mostly determined by local anion coordination and its variation along the migration pathway, making anion topology the main determinant of Li-ion conductivity. As a result, we find that there is little coordinated or concerted motion in sulfides. In contrast, due to the lower screening power of oxides and their lower Li-Li distances, Li-ion conductivity is much more determined by the electrostatic interaction with the other cations, setting the stage for possible concerted motion of multiple ions. I will show how this leads to very specific, but precise rules for selecting structures that may accommodate very fast Li-ion motion.

While fast motion of divalent cations is much less likely, I will show computational results that indicate that even super-ionic motion of ions such as Mg^{2+} and Ca^{2+} may be possible in the right framework.

11:30 AM DT04.02

Theoretical and Experimental Studies of Ion Transport in Mixed Polyanion Solid Electrolytes [Zeyu Deng](#)¹, Tara P. Mishra^{1,2}, Eunike Mahayoni^{3,4,5}, Qianli Ma⁶, Olivier Guillon^{6,6}, Jean-Noël Chotard^{3,4,5}, Vincent Seznec^{3,4,5}, Anthony K. Cheetham¹, Christian Masquelier^{3,4,5}, Sai Gautam Gopalakrishnan⁷ and Pieremanuele Canepa^{1,1}; ¹National University of Singapore, Singapore; ²Singapore-MIT Alliance for Research and Technology, Singapore; ³Universite de Picardie Jules Verne, France; ⁴FR CNRS 3459, France; ⁵FR CNRS 3104, France; ⁶Forschungszentrum Julich GmbH, Germany; ⁷Indian Institute of Science, India

Lithium and sodium (Na) mixed polyanion solid electrolytes for all-solid-state batteries display some of the highest ionic conductivities reported to date. However, the effect of polyanion mixing on ion transport properties is still debated. Here, we focus on $\text{Na}_{1+x}\text{Zr}_2\text{Si}_3\text{P}_{3-x}\text{O}_{12}$ ($0 \leq x \leq 3$) NASICON electrolyte to elucidate the role of polyanion mixing on Na-transport properties. Although there is a large body of data available on this NASICON system, transport properties extracted from experiments or theory vary by orders of magnitude, signifying the need to bridge the gap between different studies. Here, more than 2,000 distinct *ab initio*-based kinetic Monte Carlo simulations have been used to map the statistically vast compositional space of NASICON over an unprecedented time range and spatial resolution and across a range of temperatures. We performed impedance spectroscopy of samples with varying Na compositions revealing that the highest ionic conductivity ($\sim 0.1 \text{ S cm}^{-1}$) is achieved in $\text{Na}_{3.4}\text{Zr}_2\text{Si}_{2.4}\text{P}_{0.6}\text{O}_{12}$, in line with our predictions ($\sim 0.2 \text{ S cm}^{-1}$). Our predictions indicate that suitably doped NASICON compositions, especially with high silicon content, can achieve high Na^+ mobilities. Our findings are relevant for the optimization of mixed polyanion solid electrolytes and electrodes, including sulfide-based polyanion frameworks, which are known for their superior ionic conductivities.

11:45 AM *DT04.03

The Role of Anion Dynamics in Controlling Ion Mobility in Solids [Don Siegel](#); The University of Texas at Austin, United States

Ion mobility in solids is important for the development of solid state batteries that employ solid electrolytes. Early studies have argued that the rotational dynamics of complex (or cluster) anions play a role in fostering cation motion, typically at temperatures above a volume-increasing polymorphic phase transformation. This talk will discuss the impact of anion dynamics on cation mobility across several ion-conducting solids. Detailed atomic-scale simulations are performed to map out the nature of anion motion and to quantify correlations with cation mobility in space and in time. Analyses are conducted to identify the circumstances under which anion rotations are beneficial. With this knowledge it may be possible to design solid electrolytes whose cation mobility is intentionally enhanced by anion dynamics.

SESSION DT05: Mixed Conductors I
 Session Chair: Nicola Perry
 Monday Afternoon, July 18, 2022
 Mezzanine Level, Second Floor, Georgian

2:00 PM **DT05.01

Oxygen Surface Exchange Kinetics of Sm-Doped Ceria Catalyzed by Co-Based Oxides [Hitoshi Takamura](#); Tohoku Daigaku, Japan

Cobalt is one of the magic elements to improve oxygen surface exchange kinetics of high-temperature electrochemical devices such as SOFCs. Co-based mixed ionic and electronic conductors (MIECs) including La-Sr-Co- and Ba-Sr-Co-Fe-based oxides are excellent materials with respect to use as electrodes and oxygen separation membranes. Cobalt cations in such the mixed conductors plays an important role on the formation and migration of oxygen vacancies. The effect of cobalt doping or addition on the surface exchange reaction can be seen not only in the single-phase-type but also dual-phase-type MIECs such as Sm-doped ceria mixed with CoFe_2O_4 or Co_3O_4 . Recently, our group has reported that cobalt in simple oxides with rock-salt-type or spinel-type structures themselves also enhances dissociative adsorption of oxygen on oxides at high temperatures. For example, the catalytic activity of Co-Fe-based spinel-type and Co-Mg-based rock-salt-type oxides was measured by a modified pulse isotopic exchange technique and was found to increase exponentially as the Co concentration increased regardless of the crystal structure. The catalytic activity of cobalt and other transition metals in such the simple oxides is firstly presented and discussed from percolation and electronic structural aspects.

In addition to those oxides, the surface exchange kinetics of Sm-doped ceria catalyzed by Co-based oxides was investigated. Sm-doped ceria mixed with Co-based MIECs or Co-rich oxides has been attracting much attentions as an active layer of cathode in SOFCs. To clarify the rate-limiting factor of the surface exchange kinetics in the Sm-doped ceria with Co-based oxides, e.g. Co_3O_4 , the pulse isotopic exchange technique was utilized. Their oxygen surface exchange kinetics will be discussed with respect to defects and their transport properties in Sm-doped ceria.

2:30 PM DT05.02

Defect Structure and Iso/Non-Isothermal Transport Properties of $\text{Ba}_{0.95}\text{La}_{0.05}\text{Co}_{0.8}\text{Fe}_{0.12}\text{Nb}_{0.08}\text{O}_{3-\delta}$ [Hohan Bae](#)¹, Jong Hoon Joo² and Sun-Ju Song¹; ¹Chonnam National University, Korea (the Republic of); ²Gwangju Institute of Science and Technology School of Earth Sciences and Environmental Engineering, Korea (the Republic of)

Over the past decades, studies on various solid state electrochemical devices based on ceramic mixed ionic-electronic conducting (MIEC) materials in which mass/charge transport phenomena occurs under isothermal and non-isothermal conditions are attracting huge attention. Among them, the $\text{BaCo}_{0.8}\text{Fe}_{0.12}\text{Nb}_{0.08}\text{O}_{3-\delta}$ perovskite-based mixed conductor showing high ambipolar conductivity is in the spotlight as a component of high permeable oxygen transport membrane and a fuel cell cathode material by applying an irreversible chemical diffusion phenomenon due to a chemical potential gradient. In this study, $\text{Ba}_{0.95}\text{La}_{0.05}\text{Co}_{0.8}\text{Fe}_{0.12}\text{Nb}_{0.08}\text{O}_{3-\delta}$ (BLCFN) was confined to the target system and its defect structure and transport properties of ionic/electronic charge carrier were investigated. Correlation between the flow of two different charge carrier (ion and hole) and the three independent driving forces (electrochemical potential gradient of oxygen ion, hole and temperature gradient) was defined by 2×3 Onsager matrix. The isothermal transport coefficients were measured through an ion-blocking polarization cell with partial electrons and ion probe, and the non-isothermal transport coefficients was also measured as a function of the partial ionic/electronic thermopowers under Soret equilibrium condition. Oxygen nonstoichiometry and total electrical conductivity was measured as a function of temperature and oxygen partial pressure by thermo-gravimetric analysis (TGA) & coulometric titration and DC 4-probe method, respectively. Investigation on the defect structure of the target system was performed by using its transport coefficient under isothermal/non-isothermal conditions, oxygen non-stoichiometry and total electrical conductivity.

2:45 PM *DT05.03

Tailoring the Mixed Ionic/Electronic Conductivity in Mesoporous CeO_2/YSZ Nanocomposites by Surface Engineering [Erdogan Celik](#)¹, [Yanjiao Ma](#)², [Torsten Brezesinski](#)² and [Matthias T. Elm](#)^{1,1,1}; ¹Justus Liebig Universitat Giessen, Germany; ²Karlsruher Institut fur Technologie, Germany

Mixed ionic and electronic conductors (MIECs) represent a highly relevant material systems for electrochemical device applications in the field of energy storage and conversion, e.g. as intercalation electrodes, permeation membranes or sensors. Unfortunately, most materials with a high electronic conductivity exhibit a negligible ionic one and vice versa. Thus, the development of artificial composites with tailored mixed ionic and electronic conductivity is highly desired. A common approach is the preparation of mixed-conducting composites by mechanically mixing of an electronic conductor with an ionic conductor to enable transport paths for both the electrons and ions. However, a sufficient electronic conductivity is achieved only by adding a comparably large amount of electronically conductive material to generate percolation pathways for the electrons. Furthermore, the composites exhibit a random network of interfaces, which may significantly alter the transport properties of both the electronic and ionic charge carriers in the system. Here, we present a different approach for the preparation of mixed ion- and electron-conducting nanocomposites with a well-defined morphology by facile surface modification. Thermally stable ordered mesoporous 8 mol-% yttria-stabilized zirconia (YSZ) thin films with different pore sizes were synthesized using an evaporation-induced self-assembly process. The free surface of the YSZ thin films was modified with either 3 or 7 nm ceria coatings using atomic layer deposition (ALD). ALD is the method of choice, as it allows uniform coating of even complex surfaces. The transport properties of the CeO_2/YSZ nanocomposites were characterized using electrochemical impedance spectroscopy. Interestingly, the pore size has no effect on the ionic conductivity of the pristine YSZ thin films, which is probably due to the high interconnectivity of crystallites of identical size. However, the characterization of the conductivity for varying oxygen partial pressure reveals that the electronic transport properties strongly depend on the thickness of the ceria coating. While a mixed ionic and electronic conductivity is observed for the nanocomposites with a 3 nm surface layer, those with a 7 nm ceria coating exhibit a dominant ionic conductivity over the whole oxygen partial pressure range investigated. The results reveal that the electronic conductivity contribution can be manipulated by the coating thickness. This opens new possibilities for the design of nanocomposites with tailored ionic and electronic transport properties for next-generation electrochemical devices.

3:05 PM DT05.04

Elucidating Oxygen Ion and Proton Transport in the Triple-Conducting Oxide $\text{BaCo}_{0.4}\text{Fe}_{0.4}\text{Zr}_{0.1}\text{Y}_{0.1}\text{O}_{3-\delta}$ (BCFZY4411) and Tuning the Co/Fe Ratio in the BCFZY System to Boost Electrolysis and Fuel Cell Performance [Yewon Shin](#)¹, [Youdong Kim](#)¹, [Michael D. Sanders](#)¹, [Steve Harvey](#)², [Michael Walker](#)¹ and [Ryan O'Hayre](#)¹; ¹Colorado School of Mines, United States; ²National Renewable Energy Laboratory, United States

$\text{BaCo}_{0.4}\text{Fe}_{0.4}\text{Zr}_{0.1}\text{Y}_{0.1}\text{O}_{3-\delta}$ (BCFZY4411) has been identified as a promising protonic ceramic fuel cell (PCFC) cathode material primarily due to its good electrochemical activity and its ability to support simultaneous triple-conduction of protons, oxygen ions, and electron holes. The low-activation energy for proton migration enables a decrease in the operating temperature of ceramic electrochemical devices, while heavy transition metal doping ensures adequate electrical conductivity and electrochemical reactivity. Moreover, the multiple oxidation states of Co and Fe assist the electrocatalytic and redox ability of BCFZY4411, while Zr and Y provide structural and chemical stability. Despite the considerable role of Co and Fe transition metal doping in BCFZY4411, the study of alternative BCFZY compositions with various Co/Fe ratios has not yet been investigated. In order to further support the use of this material in

relevant device applications, kinetic studies of both the surface reaction and bulk transport processes are needed.

The isotope exchange technique is a powerful method to obtain kinetic properties, primarily the diffusion coefficient and surface exchange coefficient, using appropriate isotopically-labeled tracer species. Decoupling the incorporation kinetics of both oxygen ions and protons is possible by exchanging only one isotopic species at a time. To do so, dense samples are annealed under enriched isotope atmospheres at various temperatures followed by a rapid thermal quench to room temperature. Isotope depth profile/line scans are then collected by time-of-flight secondary ion mass spectrometry (ToF-SIMS) and fit to an appropriate transient diffusion solution to obtain values for the surface exchange coefficient (k^*) and the tracer diffusivity (D^*). In this work, we apply the isotope exchange technique to decouple and quantify oxygen ion transport in selected compositions of $\text{BaCo}_{0.8-x}\text{Fe}_x\text{Zr}_{0.1}\text{Y}_{0.1}\text{O}_{3-\delta}$ ($x = 0.1, 0.2, 0.4, 0.6, \text{ and } 0.7$) and proton transport in BCFZY4411. $^{18}\text{O}/^{16}\text{O}$ and $\text{H}_2\text{O}/\text{D}_2\text{O}$ line-scanning analyses were performed by ToF-SIMS to determine the tracer diffusion coefficients and surface exchange parameters. Additionally, symmetric cell and full cell tests were conducted to examine the performance of selected BCFZY cathode compositions.

This work provides critical knowledge on the surface incorporation kinetics and bulk diffusion of oxygen ions and protons in BCFZY4411, thereby enabling further optimization and modeling of these materials for various electrochemical applications, including fuel cells and electrolyzers. Additionally, we found that the surface exchange kinetics and bulk diffusion of oxygen tracer strongly depend on Co/Fe ratio. Finally, the symmetric and full cell performance tests show behavior consistent with the results from the isotope exchange experiments, highlighting opportunities to tune electrochemical behavior in the BCFZY system for specific applications (e.g., electrolysis vs. fuel cell mode operation). Based on this work, we suggest promising alternative BCFZY compositions for further PCFC cathode development.

3:20 PM DT05.05

Hexagonal Rare-Earth Manganites—From Materials Development to Practical Application of Oxygen Production in Temperature Swing
Proces Kacper Cichy¹, Alicja Klimkiewicz², Katarzyna Jarosz¹ and Konrad Swierczek^{1,3}; ¹Akademia Gorniczo-Hutnicza imienia Stanislaw Staszica w Krakowie Wydział Energetyki i Paliw, Poland; ²Shibaura Kogyo Daigaku, Japan; ³Akademia Gorniczo-Hutnicza imienia Stanislaw Staszica w Krakowie, Poland

Currently, most of the oxygen gas for industrial uses is produced by cryogenic distillation of air. Despite that this process is well-known and at TRL 9 level, it is still an expensive method, due to the associated high energy consumption. As reported by The Business Research Company, the demand for oxygen gas grows each year by several percent. Especially today, oxygen use in healthcare has a vital share in this demand, as a consequence of the COVID-19 pandemic. With this continuous increase in O_2 demand and the potential of its use in modern energy technologies (e.g. oxy-combustion), there is a need to develop alternative methods of O_2 production, which include temperature swing absorption (TSA) or the use of ceramic oxygen permeable membranes.

In the TSA application, hexagonal rare-earth manganites ($\text{RMnO}_{3+\delta}$) are of interest, as they operate at exceptionally low temperatures (ca. 200-300 °C, compared to 500-700 °C for other material groups). However, most of the research reported so far for $\text{RMnO}_{3+\delta}$ did not document the anticipated high effectiveness for the operation in air, but rather showed ability for oxygen release/intake in pure O_2 . This obviously hinders the practical application. In a search for the practically-applicable materials, the series of rare-earth-substituted $\text{Y}_{1-x}\text{R}_x\text{MnO}_{3+\delta}$ (R: Pr, Nd, Sm, Gd, Yb; x: 0.05, 0.1) oxides was prepared via a sol-gel auto-combustion method followed by annealing at high temperatures in argon. The phase composition and crystal structure of the synthesized materials were examined by X-ray diffractometry (XRD). The absorption/release of oxygen in air and O_2 was evaluated with thermogravimetry (TG). The structure and phase composition of samples oxidized during TG were also investigated by XRD. The morphology of powders was examined by scanning electron microscopy. For Pr- and Nd-substituted materials, X-ray absorption spectroscopy (XAS) was utilized to determine oxidation states of Mn, Pr, and Nd in the reduced and oxidized samples. XAS measurements were done at the SOLARIS National Synchrotron Radiation Centre (Cracow, Poland). $\text{Y}_{0.95}\text{Pr}_{0.05}\text{MnO}_{3+\delta}$ oxide was also in-depth studied in terms of its TSA operation – additional TG and XRD experiments were done (e.g. TSA cycling stability, the influence of redox temperatures on the absorption/release rate, etc.). Additionally, a series of Nd-substituted samples ($\text{Y}_{0.95}\text{Nd}_{0.05}\text{MnO}_{3+\delta}$) was prepared by modifying the final annealing (temperature and dwell time). Those powders were used to evaluate the influence of the material's preparation route on its performance in the TSA process. Last, but not least, the demonstrator TSA equipment for O_2 separation from air was designed. The most promising oxides developed in this work (i.e., $\text{Y}_{0.95}\text{Pr}_{0.05}\text{MnO}_{3+\delta}$ and $\text{Y}_{0.95}\text{Nd}_{0.05}\text{MnO}_{3+\delta}$) were selected to be tested using that equipment, and to document the real utilization of the optimized hexagonal $\text{RMnO}_{3+\delta}$ for small scale O_2 production from air via TSA. For the first time, chemical composition tweaking and powder morphology manipulation were both used to boost oxygen separation performance of $\text{Y}_{1-x}\text{R}_x\text{MnO}_{3+\delta}$ during TSA operation. The developed materials were found to exhibit excellent oxygen storage-related properties and ability for the effective production of O_2 in air by the thermal swing process at exceptionally low temperatures. Thus, medium-/low-temperature industrial waste heat could be utilized for the production of oxygen. In addition, the oxygen content changes and oxidation rate in $\text{Y}_{1-x}\text{R}_x\text{MnO}_{3+\delta}$ oxides were correlated with the mean size of material's crystallites. Higher oxygen storage capacities were observed for the materials having a larger mean ionic radius introduced in the Y-sublattice. Also, oxygen intercalation in $\text{Y}_{0.95}\text{Pr}_{0.05}\text{MnO}_{3+\delta}$ and $\text{Y}_{0.95}\text{Nd}_{0.05}\text{MnO}_{3+\delta}$ was found to occur without a change in the Pr/Nd oxidation state – only Mn^{3+} is oxidized to Mn^{4+} to compensate charge introduced with the absorbed oxygen.

SESSION DT06: Mechanistic Aspects of Li+Transport
 Session Chair: Bettina Lotsch
 Monday Afternoon, July 18, 2022
 Mezzanine Level, Second Floor, Arlington

2:00 PM **DT06.01

Understanding (Effective) Ionic Transport in Solids and Solid-State Batteries Wolfgang Zeier; University of Muenster, Germany

The advent of solid-state batteries has spawned a recent increase in interest in lithium conducting solid electrolytes. However, many open questions remain when trying to optimize electrolytes and understand solid state battery chemistries.

In this presentation, we will show how an understanding of the structure-transport properties can help tailor the ionic conductivity. In an exemplary study on superionic lithium metal halides, we show that a cation site-disorder and the local structure of materials is important to study, especially as synthetic influences control materials properties.

Finally, we will show that it is not only important to find fast ionic conductors, but that fast ionic conduction is paramount within solid state battery composites. Measuring the effective ionic transport in cathode composites provides an avenue to explore transport and stability limitations that in turn provide better criteria for solid state battery performance

2:30 PM DT06.02**Study of Composition and Temperature Dependence of Li Dynamics in $\text{Li}_x\text{La}_3\text{Zr}_{x-5}\text{Ta}_{7-x}\text{O}_{12}$ with Machine-Learning Interatomic Potentials** Wei Lai and Jin Dai; Michigan State University, United States

Lithium garnet oxides are an important class of solid-state materials that support high Li ionic conductivity (10^{-3} - 10^{-2} S/cm at room temperature). While there have been many experimental studies of Li diffusion and conduction through impedance spectroscopy and nuclear magnetic resonance methods, atomic insights from complementary computational studies remain limited, which was caused by the tradeoff between accuracy and efficiency of common computational methods. On one hand, lithium garnet oxides are computationally exorbitant for density-functional theory (DFT) calculations due to the large number of atoms in the unit cell. On the other hand, the complex chemical, stoichiometric, bonding environments in lithium garnet oxides make it difficult to develop conventional interatomic potentials with high accuracy.

In this talk, we will present our recent work on applying machine-learning interatomic potentials (MLIP) to study the composition and temperature dependence of Li dynamics in $\text{Li}_x\text{La}_3\text{Zr}_{x-5}\text{Ta}_{7-x}\text{O}_{12}$ (LLZT). We will focus on (1) how does the accuracy and efficiency of MLIP compare with DFT and conventional interatomic potentials; (2) how does composition in LLZT influence Li diffusion and conduction; (3) the non-Arrhenius temperature dependence of Li conductivity.

2:45 PM *DT06.03**Modeling the Defect Chemistry, Transport Properties and Stability of Anti-Perovskite Materials** Francesco Ciucci; The Hong Kong University of Science and Technology, Hong Kong

Solid-state electrolytes with fast lithium conduction are the core of the all-solid-state Li-battery technology. By substituting the organic electrolyte with a piece of non-flammable ceramic material, we can achieve better safety, higher specific capacity, and a higher energy density. To date, the major bottleneck for this technology is the slow Li diffusion in the solid-state electrolyte and the interfacial incompatibility between the electrolyte and electrodes. To resolve these issues, several families of fast ionic conductors have been developed. Understanding Li diffusion in these materials is essential to the development of novel family fast ionic conductors. To this end, atomistic modeling provides us with a unique tool to obtain comprehensive information on atom motion, which is difficult to access with experimental techniques. In this talk, we showcase our group's atomistic simulations regarding a novel family of superionic conductors, Li-rich antiperovskites (LiRAPs)

LiRAPs are a promising family of solid electrolytes, which exhibit ionic conductivities above 1 mS/cm at room temperature, among the highest reported values to date. Here, we report on the defect chemistry and the associated lithium transport in Li_3OCl , a prototypical LiRAP, using DFT calculations and classical MD simulations [1]. We studied these materials' phase, interfacial, and voltage stability [2,3] with DFT, showing good agreement with experiments, further proposing low-dimensional superionic antiperovskites [3]. In addition, the interfacial properties were studied for both protonated and fluorinated materials [4]. Analogous simulations were also carried out for Na-rich antiperovskites [5].

Acknowledgments

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3:05 PM DT06.04**Native Defect Engineering in Solid Electrolytes Toward Reproducible High Ionic Conductivity** Saneyuki Ohno¹, Masaki Shimoda¹, Cheng-Wei Lee² and Prashun Gorai^{2,3}; ¹Kyushu Daigaku, Japan; ²Colorado School of Mines, United States; ³National Renewable Energy Laboratory, United States

Solid-state batteries are considered as safer and more energy-dense alternatives to conventional Li-ion batteries. The critical component of solid-state batteries is a solid electrolyte, which needs to possess high ionic conductivity. Countless studies have been conducted recently, and new candidate materials for solid electrolytes are found on a daily basis.

Nevertheless, there are still challenges for widespread usage. A reproducibility issue of high ionic conductivity of solid electrolytes is one of the critical challenges. A significant variation in measured ion transport has been observed even in nominally the same materials. Such variation remains even in the samples prepared via an identical synthetic route. For instance, reported ionic conductivities of Na_3SbS_4 synthesized by solid-state reaction at 550 °C vary from 1.1 mS cm^{-1} to 0.01 mS cm^{-1} .

Inter-laboratory reproducibility of ionic conductivity measurements has been evaluated through a round-robin test. The homogeneously prepared solid electrolyte powders were distributed to seven different groups worldwide, and the ionic conductivity of those electrolytes was measured with their standard protocols. Despite the same employed powders, the resulting ionic conductivity values significantly vary. Later, another study by Cronau et al. demonstrated that a variation in the sample pellets' fabrication pressure and the stack pressure upon measurements could further add the dispersion in the measured values. Whereas there is a significant error bar expected if the samples were handled and measured in different conditions, the latter study highlights that the results can be relatively reliable as long as one sticks to the same experimental condition to compare different materials.

However, an origin of a sample-dependent variation in ion transport and an assessment of its intrinsic range have not been systematically investigated yet. This is partly due to the requirement of a series of experiments performed under identical synthesis and measurement conditions. Inspired by the high but largely varied ionic conductivity of Na_3SbS_4 , we have investigated a degree of the sample-dependent variation in ionic conductivity and its thermodynamic origin by controlling the native Na vacancy concentration. By systematically changing the nominal composition of the target Na_3SbS_4 , we observed a stepwise change in the conductivity when the target phase equilibrated different sets of side phases. This indicates that the subtle change in the native defect formation energy can significantly impact transport. In other words, it is possible to suppress the sample-dependent variation as long as one stays in the same equilibrium.

3:20 PM DT06.05**Temperature Dependent Anion Rotational Dynamics Correlated to Cation Transport in Cluster Ion Anti-Perovskites** Sunil Mair¹, Ping-Chun

Tsai^{1,2}, Yiliang Li¹, Duhan Zhang¹, Kwangnam Kim³, Jeffrey Smith³, Alex Chien⁴, David Halat⁵, Yin Liang⁶, Jue Liu⁴, Lapidus Saul⁶, Nitash Balsara⁵, Jeffrey Reimer⁵, Don Siegel³ and Yet-Ming Chiang¹; ¹Massachusetts Institute of Technology, United States; ²National Taiwan University, Taiwan; ³University of Michigan, United States; ⁴Oak Ridge National Laboratory, United States; ⁵Lawrence Berkeley National Laboratory, United States; ⁶Argonne National Laboratory, United States

As fast-ion conductors, cluster-ion anti-perovskites (APs) are attractive for potential new mechanisms of conduction whereby cation and anion motion is highly correlated, referred to as the paddlewheel mechanism [1,2]. Cluster-ion APs, like perovskites, have a framework that accommodates diverse atomic substitutions. Furthermore, the potential for cluster-ion substitution onto one or both anion sites (A and B in X₃AB) provides additional compositional degrees of freedom. We have synthesized and characterized, using synchrotron XRD, neutron diffraction, NMR, and AIMD, a series of compositions Na_{3-x}O_{1-x}(NH₂)_x(BH₄) between the endmember compositions Na₃O(BH₄) and Na₂(NH₂)(BH₄). Ionic conductivity of Na_{3-x}O_{1-x}(NH₂)_x(BH₄) depends on both Na vacancy concentration and disorder, and NH₂ and/or BH₄ anion mobility. The limiting composition Na₂(NH₂)(BH₄) is shown to be a unique sodium ion conductor in which rotational mobility of both cluster anions contribute to cation migration. Extensions of this understanding to other multi-paddlewheel conductors will be discussed.

Acknowledgements: This work was supported as part of the Joint Center for Energy Storage Research, an Energy Innovation Hub funded by the U.S. Department of Energy, Office of Science, Basic Energy Sciences.

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SESSION DT07: Proton Uptake and Transport I
 Session Chair: WooChul Jung
 Monday Afternoon, July 18, 2022
 Mezzanine Level, Second Floor, Georgian

4:00 PM *DT07.01

Exploration and Diffusion Mechanism of High Oxide-Ion and Proton Ceramic Conductors Masatomo Yashima and Kotaro Fujii; Tokyo Kogyo Daigaku, Japan

Oxide-ion and proton conductors have numerous applications in various electrochemical devices, such as fuel cells, gas sensors, and separation membranes. Dion–Jacobson phases have attracted much attention due to their wide variety of properties; however, there are no reports on oxide-ion conduction in Dion–Jacobson phases. We report oxide-ion conduction in the Dion–Jacobson phase CsBi₂Ti₂NbO_{10-δ} (where δ represents the oxygen-vacancy content) [1]. The high conductivity of CsBi₂Ti₂NbO_{10-δ} is attributable to the large anisotropic thermal motions of oxygen atoms, the existence of carriers (oxygen vacancies), and the formation of oxide-ion conducting layers in the crystal structure. High oxide-ion and proton conductors with hexagonal perovskite related structures are rare. Here, we also report high oxide-ion conduction in Ba₇Nb_{3,9}Mo_{1,1}O_{20,05} [2] and Ba₇Ta_{3,7}Mo_{1,3}O_{20,15} [3], and high proton conduction in Ba₅Er₂Al₂ZrO₁₃ [4].

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4:20 PM DT07.02

Proton Uptake and Transport Properties of Self-Generated Ba(Ce,Fe,Y)O_{3-δ} Composites Christina Nader¹, Judith Lammer², Tolga Acartürk³, Christian Berger³, Edith Bucher¹, Andreas Egger¹, Werner Grogger², Rotraut Merkle³, Ulrich Starke³, Joachim Maier³ and Werner Sitte¹; ¹Montanuniversität Leoben, Austria; ²Technische Universität Graz, Austria; ³Max-Planck-Institut für Festkörperforschung, Germany

Mixed proton-, oxide-ion- and electron-conducting oxides (triple conducting oxides, TCOs) are promising materials as electrodes in protonic ceramic fuel and electrolyser cells, and for hydrogen separation membranes. Since the combination of these properties in a single-phase material is difficult, composite materials with a proton-conducting and a mixed oxide-ion- and electron-conducting phase are of interest. In this work, self-generated Ba(Ce,Fe,Y)O_{3-δ} composites prepared via a sol-gel process were investigated [1], which aim at increasing the proton uptake compared to BaCeO_{3-δ}-BaFeO_{3-δ} materials [2]. The local cation stoichiometry in the Fe-rich and Ce-rich perovskite phases of the self-generated composites was analysed by STEM-EDX. Y shows a strong accumulation in the Fe-rich phase (despite larger size mismatch), which is interpreted in terms of an acid-base reaction. The proton uptake measured by thermogravimetry decreases with increasing overall Fe-content from 1.6 mol-% for 20% Fe to 0.7 mol-% for 60% Fe (at 500°C in 17 mbar H₂O), and clearly exceeds that of respective Y-free compositions.

A comprehensive characterisation of the transport properties of Ba(Ce,Fe,Y)O_{3-δ} composites and separately prepared Fe- or Ce-rich single phases is carried out. Conductivity relaxation in van der Pauw geometry, applying pO₂-steps under dry conditions, yields oxygen chemical diffusion coefficients (e.g. for BaCe_{0,4}Fe_{0,4}Y_{0,2}O_{3-δ} D_{O₂}^δ = 9.7 × 10⁻⁶ cm² s⁻¹ at 800°C and pO₂ = 0.10 bar) as well as the electronic conductivities (e.g. for BaCe_{0,4}Fe_{0,4}Y_{0,2}O_{3-δ} σ = 0.028 S cm⁻¹ at 800°C and pO₂ = 0.10 bar). The mass and charge transport properties of composites are compared to those of the individual pure perovskite phases BaCe_{0,76}Fe_{0,04}Y_{0,2}O_{3-δ} and BaCe_{0,04}Fe_{0,76}Y_{0,2}O_{3-δ}.

Owing to the predominant electronic and still significant oxygen vacancy ionic conductivity, the proton conductivity and mobility cannot be accessed directly. Therefore, pore-free single-phase as well as composite samples are investigated by isotope exchange measurements. Pre-dried samples are hydrated in D₂O at 300–500°C, quenched, and the frozen-in deuterium profiles analysed by time-of-flight secondary ion mass spectroscopy (ToF-SIMS) line scans. This yields a D₂O chemical diffusion coefficient D_{D₂O}^δ, which under the present conditions of low hydration is close to the proton diffusivity D_{OH⁺}. For the Ce-rich sample D_{D₂O}^δ = 6 × 10⁻⁸ cm² s⁻¹ is found at 300°C, measurements on Fe-rich compositions are in progress. These experiments are extremely important, as hardly any proton mobility data in redox-active perovskites are available in the literature.

Based on the present results, mixed protonic-electronic transport will further be tuned along two lines: exploration of other acceptor dopants to foster proton uptake in the Ce-rich phase, and optimisation of the microstructure as well as the phase ratio (minimisation of Fe-rich phase while preserving electronic percolation) of the composite.

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4:35 PM *DT07.03

Computational Modeling and Simulation of Ion Transport in Oxides for Energy Conversion Manfred Martin; Rheinisch-Westfälische Technische Hochschule Aachen, Germany

Ion transport in oxides plays an important role in energy and environmental applications. Important examples are oxygen ion or proton conducting oxides for electrolytes in electrolyzers and fuel cells.

I will present our recent theoretical approaches to understand these ionic transport processes in detail. We use density-functional theory (DFT) to calculate on a microscopic level defect interaction energies and migration energies of the defects that enable ionic motion. By means of Kinetic Monte Carlo (KMC) simulations we then predict macroscopic ion mobilities and ion conductivities on an *ab initio* level, i.e. without any adjustable parameters. As first example we will discuss rare-earth doped ceria. We show that all interactions between defects contribute to the so-called conductivity maximum of the ionic conductivity [1]. The second example concerns BaZrO₃-based oxides which are proto-type proton conductors. We show that the proton mobility is determined by nanoscale percolation of dopant ions which enables high proton mobility along [2].

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4:55 PM DT07.04

High-Throughput Screening of Solid-State Proton Conductors Based on Physical Descriptors of Proton Conduction Konstantin Klyukin^{1,2}, Piotr Zguns¹, Ju Li¹ and Bilge Yildiz^{1,1}; ¹Massachusetts Institute of Technology, United States; ²Auburn University, United States

Fast proton transport is critical for such applications as proton-based neuromorphic computing hardware [1,2], enabling fast switching speed and reliability. Despite significant attention and intensive experimental investigations, most proton conductors still suffer from sluggish ion transport kinetics at low temperatures or are not compatible with current CMOS fabrication processes. Therefore, the solid-state proton conductors operating promptly at room temperature are much required for rapidly growing proton-based neuromorphic computing applications [1,2].

To identify potential conductors, we screened the Materials Project database [3] and pre-selected compounds which: 1) have H as a part of their nominal structure; 2) have a H-bonding network necessary for Grothuss transport; 3) have a large band gap to minimize possible electronic leakage; and 4) are predicted to be stable or were previously synthesized. We first employed a small subset of materials, including solid acids, inorganic hydrates, and other compounds, to run *ab initio* molecular dynamics calculations (AIMD) and investigate H⁺ transport. We then used this data to identify chemical and physical traits of proton conducting materials that control different steps of Grothuss transport. This mechanism consists of two equally important processes involving (i) the proton shuttling between donor and acceptor groups, and (ii) the reorganization of the environment to stabilize H⁺ transfer [4]. Several descriptors based on the structure, chemistry, and lattice dynamics were identified and used to further screen proton conductors.

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5:10 PM DT07.05

Dopant Configurations and Hydration Behavior in Heavily Sc-Doped BaZrO₃ from Machine-Learning Assisted First-Principles Statistical Thermodynamics Shusuke Kasamatsu¹, Akihito Kuwabara², Kenta Hoshino^{3,3}, Junji Hyodo³ and Yoshihiro Yamazaki^{3,3}; ¹Yamagata University, Japan; ²Japan Fine Ceramics Center, Japan; ³Kyushu University, Japan

Acceptor-doped BaZrO₃ is under intense research as a candidate for the proton-conducting electrolyte component in medium-temperature solid oxide fuel cells. In fact, some of the authors recently reported that 60% Sc-doped BaZrO₃ exhibits proton conductivities as high as 0.01 S/cm at 400 degrees Celsius [1], finally breaking the so-called “Norby gap” which refers to the lack of chemically stable electrolytes at intermediate temperatures.

In this class of materials, acceptor doping induces oxygen vacancies to satisfy charge neutrality; these vacancies then act as active sites for hydration reaction under humid atmosphere. This results in the incorporation of proton carriers which can rotate around and hop between oxide ions in the perovskite lattice. The local environment around the oxygen vacancies is expected to determine the activity of the hydration reaction, which is key to obtaining high proton conductivity. There are three possible environments considering nearest neighbors: M-V_O-M, M-V_O-Zr, and Zr-V_O-Zr, where M is the acceptor dopant. To clarify which of these is most active towards hydration, XAS [2] and NMR [3] have been utilized to probe the local structures around dopant cations; however, because of the difficulty of *in situ* measurements, and because the vacancies themselves cannot be probed directly, a clear picture of the active vacancy sites for the solid-state hydration reaction in this system remains elusive. On the other hand, first-principles calculations can provide atomistic insight [4], but it is quite challenging to properly handle the combinatorial explosion in the number of possible configurations of dopants, oxygen vacancies, and protons and obtain a thermodynamically relevant picture. To tackle this issue, we employ, in this work, a parallel statistical sampling method called replica exchange Monte Carlo method, combine it with first principles calculations, and accelerate the sampling using active learning of a neural network model that reproduces the first-principles configurational energetics [5,6].

Temperature-dependent configurational sampling of oxygen vacancies, Sc dopants, and protons were performed in a 3×3×3 cubic perovskite model with 8 Sc_{Zr} and 4 V_O corresponding to 30% Sc-doped BaZrO₃. Then, the same calculations were repeated with varying hydration levels, i.e., by varying the number of oxygen vacancies and protons. From the results, Sc-V_O-Sc is predicted to be most abundant below 1000 degrees Celsius, which is necessary for

hydration to occur under mildly hydrated atmospheres, followed by Sc-V₀-Zr. Zr-V₀-Zr was found to exist in almost negligible amounts. As hydration proceeds, the less abundant Sc-V₀-Zr is first occupied preferentially, followed by the more abundant Sc-V₀-Sc. Near full hydration, the Sc-V₀-Sc and Sc-V₀-Zr sites account for about 2/3 and 1/3 of the total hydration, respectively. The Zr-V₀-Zr site, which was proposed to be most active based on hydration energy calculations [3], is ruled out as the active site because it is too unstable and does not exist in significant amounts under realistic thermodynamic conditions.

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5:25 PM DT07.06

Proton Transport in Cubic Perovskite BaZrO₃ Solid Solutions with Concentrated Lattice Defects Lei A. Zhang; Carnegie Mellon University, United States

Unlike dilute lattice defects in semiconductor physics, those in solid state ionic conductors have high concentrations for the purpose of creating sufficient ionic charge carriers in the lattice. Typically, this is achieved by high levels of aliovalent doping, as a consequence, defects with the opposite charge form to maintain the global charge neutrality of the ionic conductors. Inevitably, strong Coulomb interactions between charged defects impede the charge carriers' mobility, making it below the upper limit of that in their "dilute" limits. Yttrium-doped BaZrO₃, one of the typical solid-state proton conductors at high temperatures, suffers from this detrimental effects.

From a classical thermodynamics point of view, Y dopants, O vacancies, and protons have interactions within and across their own sublattices, making the material a rich "defect-phase" matrix. Unlike a simple binary alloy, solid solutions in ionic conductors typically "dissolve" in multiple sublattices. Interactions of lattice defects include short-range elastic and long-range electrostatic kinds. Due to the drastic mobility differences between cation defects, anion defects and protons (main charge carriers), phase equilibration could be only partial, depending on the heat treatment protocol of the material. On the other hand, degradation of the material could occur after long periods of service at high temperatures. One can observe "nano-domains" under high-resolution transmission electron microscopy that is driven to form by the defect-phase segregation.

Classical thermodynamic models, although intuitively straight-forward and computationally efficient, suffer from the exclusiveness of the physical information, e.g., spatial-relevant, concentration-dependent, and chemical nature of defect interactions. To go beyond that, in this work I use the atomic-level cluster-based interaction model with *ab-initio* calculations to map out the thermodynamics and kinetics of lattice defects in BaZrO₃-based proton conductors. I will demonstrate the stable and metastable defect-phase transitions driven by defect interactions across multi-sublattices, illustrating the temperature and humidity effects on the material's thermodynamic stability. Furthermore, ionic conductivity under the manybody defect interactions in the three-dimensional lattice framework will be provided, correlating its functional properties (conducting ions) with its doping chemistries and service environment.

5:40 PM DT07.07

The Strategy of Improving Proton Conductivity Base on the Meyer-Neldel Rule Peng Du and Qianli Chen; Shanghai Jiao Tong University, China

Y-doped BaMO₃ (M=Zr/Ce) proton conductors have drawn numerous attentions from researchers as the electrolyte for intermediate temperature proton ceramics fuel cells^[1-4]. To improve the proton conductivity, it is still necessary to further understand the proton conduction mechanism^[2]. In this work, we found that the proton conductivity of Y-doped BaMO₃ (M=Zr/Ce) follows the Meyer-Neldel Rule^[3] when the material structure is tuned by applying pressure^[4] or by varying the Ce content. The Arrhenius behavior of proton conductivity meets at an isokinetic temperature, where the activation energy does not change the proton conductivity. The relationship between isokinetic temperature and lattice vibration reveals that the materials with stiff lattices, consisting of light atoms and small M-O bond length, have a high isokinetic temperature. The results of this work suggest that it is necessary to tune the material according to its activation energy for the designing of new perovskite type proton conductor with high conductivity at low temperature^[1].

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SESSION DT08: Battery Electrolytes I
Session Chair: Wei Lai
Monday Afternoon, July 18, 2022
Mezzanine Level, Second Floor, Arlington

4:00 PM *DT08.01

Ion Polarization Mechanisms and Dendrite Initiation Dynamics in Li-Conducting Ceramic Electrolytes Peng Bai; Washington University in St Louis, United States

Solid-state electrolytes, by stabilizing thin lithium metal anodes, hold the promise to significantly increase the energy density of current lithium-ion batteries. However, similar to their liquid counterparts, these hard and stiff electrolytes can still be penetrated by soft Li metal, above a critical current density (CCD). The prevailing method to determine the CCD employs step-wise galvanostatic cycling, which suffers from inconsistent active interfacial

areas due to void formations after repeated stripping and plating. The large variance in the reported CCD data precludes precision understandings of the underlying mechanisms. Here, we combine a one-way polarization technique with electrochemical impedance spectroscopy to uncover, for the first time, the transient ion polarization dynamics mainly through grain boundaries of ceramic electrolyte, which leads to a *limiting* current peak. Thus determined limiting current densities are consistent with the traditional CCD but do not induce the metal penetration. The results suggest a self-consistent theoretical analysis that reveals that the physical mechanisms of ion transport preceding dendrite initiation in ceramic electrolytes are unifiable with those in liquid electrolytes.

4:20 PM DT08.02

Modulating Grain Boundary Chemistry to Mitigate Li Filament Formation in Garnet-Type Solid-State Electrolytes [Hyunwon Chu](#), Thomas Defferriere, Kunjoong Kim, Haemin Paik, Lingping Kong, Harry Tuller and Jennifer Rupp; Massachusetts Institute of Technology, United States

Ceramic solid-state electrolytes are considered as the enabler of lithium (Li) metal batteries. However, Li metal penetration still takes place along various interfaces in polycrystalline LLZTO ($\text{Li}_{7-x}\text{La}_3\text{Zr}_{2-x}\text{Ta}_x\text{O}_{12}$), putting in question the efficacy of the solid electrolyte. Recently, the LLZTO grain boundary (GB) was claimed to be a major Li nucleation and growth site given its ionically-blocking and electronically-conducting nature. However, limited attention, both theoretical and experimental, has been focused on this feature of GB charge transport mismatch. We apply the grain boundary core-space charge layer model to explain Li filament initiation and growth at LLZTO GBs. Excess negative charge at the GB core triggers positive space charge compensation within the adjacent grains. The charge imbalance induces Li vacancy depletion and hole accumulation locally within the GB space charge regions, leading to locally reduced ionic conductivity and enhanced electronic conductivity. Both electrochemical and microscopic characterization tools were employed to investigate the defect chemistry and space charge formation at the characteristic GBs. This understanding suggested strategies to control Li filament formation. First, oxygen-rich sintering was used to decrease the GB space charge potential by suppressing negative charge accumulation at the grain boundaries. Second, higher Ta concentrations, with net positive charge, were examined as a means for compensating the negative GB core charge. Both approaches have proven to impede Li metal penetration, apparently by lowering the local electronic conductivity. We successfully achieved critical current densities (CCD) of $\sim 1 \text{ mA cm}^{-2}$, a two-fold increase over prior reports. The GB core-space charge model and the two GB engineering strategies pursued appear to aid in addressing an important source of Li metal penetration in LLZTO and can be expected to point to a promising new research direction for safe all-solid-state Li metal batteries.

4:35 PM DT08.03

Defect Models for Li-Ion Transport in Al- and Nb-Doped LLZO [Madecha K. Pedersen](#) and Truls Norby; Universitetet i Oslo Det Matematisk-naturvitenskapelige Fakultet, Norway

The cubic $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZO) garnet-type oxide is a promising electrolyte candidate in all-solid-state Li-ion batteries because of its relatively high ionic conductivity at room temperature and wide electrochemical stability window [1]. Although the defect chemistry of this class of materials is barely studied, it is critical for understanding the nature of Li-ion conductivity. Li-ion transport in LLZO utilises the disorder on the partially occupied Li site and is limited by the Li vacancy concentration and their distribution in the crystal structure. However, traditional defect chemistry does not describe cation disorder well, making it difficult to predict and interpret the effects of doping and defect concentration on Li-ion transport.

In the present contribution, defects and transport in LLZO are analysed using a defect notation developed for inherently disordered materials with partially occupied sites in a cation sublattice [2]. Moreover, as Li can occupy two different crystallographic sites in the LLZO, two defect models are developed: The first model is based on the assumption that all Li sites are energetically equivalent, i.e., the lattice structure is totally disordered. The second model considers the two different Li sites where one site is favourable, hence a partially ordered structure. Effects of doping and defects concentration on the Li-ion transport mechanism in LLZO garnet is investigated, and the model predictions are compared with own and literature results on the conductivity of Al^{3+} and Nb^{5+} -doped LLZO.

Acknowledgement:

This work has been supported by the Research Council of Norway (RCN) through the "Next-generation oxide electrolytes for solid-state batteries" OxiBat (287890) project.

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4:50 PM *DT08.05

Interface-Induced High Ionic Conductivities in Complex Hydride-Based Nanocomposite Materials [Peter Ngene](#) and Laura M. de Kort; Universiteit Utrecht Faculteit Betawetenschappen, Netherlands

Solid-state electrolytes are crucial for next generation batteries with improved safety, higher energy density and improved cycle life. The compatibility of most solid electrolytes with metallic anodes (such as Li and Na metals) and cathodes such as sulfur, makes them suitable for high-capacity batteries (e.g., Li-S). They also address the safety concerns of current batteries by eliminating the flammable organic solvents in liquid electrolytes and by preventing/limiting dendrite formation.

The lithium and sodium containing complex metal hydrides (e.g., LiBH_4 , NaBH_4 , $\text{LiCB}_{11}\text{H}_{12}$) have recently gained attention as solid-state electrolyte. They show high ionic conductivities, but only at elevated temperatures (typically above 120 °C). Therefore, extension of the high ionic conductivities down to ambient temperatures is pivotal to the application of this fascinating class of solid electrolytes [1].

In this contribution, we will use LiBH_4 and NaBH_4 as examples to show that the ionic conductivities of complex hydrides can be greatly enhanced through interface effects resulting from the formation of nanocomposites with metal oxides. This strategy can lead to a more than three orders of magnitude increase of the room temperature ionic conductivity [2]. Using DSC, DRIFT, solid-state NMR, and XRS (X-ray Raman scattering) measurements, we will discuss how the nanocomposite formation and presence of interfaces modifies the phase stability, defect concentration and the ion mobility of the complex hydrides. Systematic studies with different oxide nanoscaffolds and surface modified metal oxides, reveal that the conductivity can be optimized by tuning/engineering the nanostructure and interfaces in the nanocomposites. [3-4] Finally, the extension of this approach to non-hydride-based solid electrolytes, and the performance of the nanocomposite electrolytes in all-solid-state Li-ion batteries, will be highlighted [5]

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5:10 PM DT08.06

Can Substitutions Affect the Oxidative Stability of Lithium Argyrodite Solid Electrolytes? Ananya Banik¹, Yunsheng Liu², Saneyuki Ohno³, Yannik Rudel¹, Alberto Jiménez-Solano⁴, Andrei Gloskovskii⁵, Nella M. Vargas-Barbosa⁶, Yifei Mo² and Wolfgang Zeier¹; ¹Westfälische Wilhelms-Universität Münster, Germany; ²University of Maryland at College Park, United States; ³Kyushu Daigaku Kogakubu Daigakuin Kogakufu, Japan; ⁴Max-Planck-Institut für Festkörperforschung, Germany; ⁵Deutsches Elektronen-Synchrotron, Germany; ⁶Forschungszentrum Jülich Helmholtz-Institut Münster Institut für Energie- und Klimaforschung Elektrochemische Verfahrenstechnik, Germany

Lithium ion conducting argyrodites are among the most studied solid electrolytes due to their high ionic conductivities. A major concern in a solid-state battery is the solid electrolyte stability. Here we present a systematic study on the influence of cationic and anionic substitution on the electrochemical stability of $\text{Li}_6\text{PS}_5\text{X}$, using step-wise cyclic voltammetry, optical band gap measurements, hard X-ray photoelectron spectroscopy along with first-principles calculations.¹ It has been observed that going from $\text{Li}_6\text{PS}_5\text{Cl}$ to $\text{Li}_{6+x}\text{P}_{1-x}\text{M}_x\text{S}_5\text{I}$ ($\text{M} = \text{Si}^{4+}, \text{Ge}^{4+}$), the oxidative degradation does not change. Considering the chemical bonding shows that the valence band edges are mostly populated by non-bonding orbitals of the PS_4^{3-} units or unbound sulfide anions and that simple substitutions in these sulfide-based solid electrolytes cannot improve oxidative stabilities. This work provides insights on the role of chemical bonding on the stability of superionic conductors and shows that alternative strategies are needed for long-term stable solid-state batteries.

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5:25 PM DT08.07

Enhanced Mobility of Lithium and Sodium Ions in Phosphate Glasses Obtained by WO_3 and MoO_3 Addition Sanja Renka¹, Luka Pavić¹, Grégory Tricot², Tomáš Hostinský³, Petr Kalenda³, Petr Mošner³, Ladislav Koudelka³, Andrea Moguš-Milanković¹ and Ana Šantić¹; ¹Institut Ruder Boskovic, Croatia; ²Universite de Lille, France; ³Univerzita Pardubice Fakulta chemicko-technologicka, Czechia

Increased demand for stable and efficient electrolytes in batteries puts the focus of recent studies on the improvement of relatively low ionic conductivity in various families of oxide glasses containing alkali ions. A popular approach in achieving this goal is to add the second glass-forming oxide to the glass in order to induce structural changes which have a facilitating effect on the ionic transport. This phenomenon is well-known as the mixed glass-former effect. In this study, we show that a significant increase in ionic conductivity can be achieved by the replacement of glass-forming oxide P_2O_5 with WO_3 and MoO_3 which are not conventional glass-formers but conditional ones. For that purpose, four series of glasses $40\text{Na}_2\text{O}-x\text{MoO}_3-(60-x)\text{P}_2\text{O}_5$, $40\text{Na}_2\text{O}-x\text{WO}_3-(60-x)\text{P}_2\text{O}_5$, $40\text{Li}_2\text{O}-x\text{MoO}_3-(60-x)\text{P}_2\text{O}_5$ and $40\text{Li}_2\text{O}-x\text{WO}_3-(60-x)\text{P}_2\text{O}_5$; $x=0-50$ mol% were prepared by melt-quenching. The electrical characterization was performed by impedance spectroscopy in a wide frequency (0.01 Hz – 1 MHz) and temperature (-90 °C – 250 °C) range while the structural changes were followed by the ³¹P MAS-NMR and Raman spectroscopy.

Comparing the phosphate glasses with different conducting ions, it was found that an increase in DC conductivity with the addition of transition metal oxides was more pronounced in lithium series, being five and four orders of magnitude for WO_3 and MoO_3 , respectively. On the other hand, the enhancement of sodium ion conductivity was four orders of magnitude in the case of WO_3 and three in the case of MoO_3 . Such difference is related to a smaller ionic radius and therefore higher mobility of lithium ions which can be more easily facilitated by the incorporation of tungsten and molybdenum units in the glass network. The trend in conductivity of sodium phosphate glasses was found to be non-linear, which is typical for the mixed glass former effect, exhibiting the maximal value at 30 mol% of MoO_3 and 40 mol% of WO_3 . Similar compositional dependence was also found in the fraction of mixed molybdate/tungstate-phosphate units and the number of P-O-Mo/W linkages. These findings indicate that the fastest transport of sodium ions occurs at the maximally interconnected phosphate and molybdenum/tungsten units.

On the other hand, lithium containing phosphate glasses did not show the typical effect of mixed glass formers on the electrical conductivity, even though the addition of WO_3 and MoO_3 produced similar network modification as in sodium containing glasses. In both series, the enhancement of ionic conductivity was found to be continuous for glasses containing up to 40 mol% of WO_3 and MoO_3 but retained for a higher fraction of these oxides. Here, similarly as in the sodium phosphate series, the formation of mixed molybdenum/tungsten-phosphate units strongly facilitates the transport of ions. However, at the highest amounts of WO_3 and MoO_3 , smaller Li^+ ions are less affected by the hindering nature of the glass network composed predominantly of molybdate and tungstate units, so the characteristic maximum in conductivity was not observed rather high values were retained.

SESSION DT09: Poster Session I: Oxides

Monday Afternoon, July 18, 2022

6:00 PM - 8:00 PM

Mezzanine Level, Second Floor, Stadler

DT09.01

Numerical Simulations of the Hebb-Wagner Polarization Method of Perovskite-Type Oxides Nadja Ahr and Manfred Martin; Rheinisch-Westfälische Technische Hochschule Aachen, Germany

Ternary oxides ABO_3 are known for their mixed ionic and electronic conductivity, which is well investigated depending on temperature, oxygen partial pressure, and composition. A famous method that enables the determination of the partial conductivities is the Hebb-Wagner polarization introduced by Hebb and Wagner in the 1950s [1,2]. Depending on the type of electrodes used for the polarization, it is possible to measure the ionic or electronic conductivity of the material depending on the oxygen partial pressure. The kinetics of the polarization process and the corresponding relaxation time were not studied in detail in literature, although both are of utmost importance for a better understanding of electrochemical polarization processes. A prominent example is resistive switching of oxides, where the prevailing electronic conductivity is modulated by slow ionic motion caused by an applied AC voltage. The observed hysteresis in the I - V curve depends critically on the ratio of the above relaxation time and the typical time for a voltage sweep [3,4]. In this contribution, the kinetics of the relaxation process during the Hebb-Wagner polarization of a nominally undoped perovskite-type oxide ABO_3 is simulated by means of numerical methods and using SrTiO_3 as a model system. The advantages of the theoretical approach are the prediction of the expected relaxation time for experiments and the exact reproduction of the fluxes of all involved mobile species simultaneously. Thus, it is possible to investigate the dependence of the relaxation time on different experimental variables, such as the applied voltage, acceptor concentration, temperature, and external oxygen partial pressure. In addition, the influence of parameters such as sample length, equilibrium constants for defect equilibria and diffusion coefficients of the mobile species can be studied to identify the relaxation times of different parameter sets for practical experimental application of the Hebb-Wagner polarization method.

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DT09.02

Effect of Lanthanum Doping on Ceria Fluorite Structure and the Relation with Transport Properties Sergio Damasceno¹, Fabiane d. Trindade¹, Raphael A. Martins Pires de Oliveira^{1,2}, Fabio Fonseca², Daniel Z. Florio¹ and Andre S. Ferlauto¹; ¹Universidade Federal do ABC, Brazil; ²Instituto de Pesquisas Energeticas e Nucleares, Brazil

Rare-earth-doped ceria is a material widely investigated for applications in which oxygen ion transport is relevant, including fuel cells, catalysis, and resistive switching memory. Usually, CeO₂ is doped with ~10–20 at. % cations such as Gd and Sm with 3+ valence to generate oxygen vacancies by charge balance. Gd and Sm cations have ionic radius that are close to Ce⁴⁺ and therefore no significant changes are observed in the ceria cubic fluorite structure. On the other hand, doping with lanthanum, La³⁺, which is a cation with a larger ionic radius promotes significant disorder in the fluorite structure that can be beneficial for applications such as catalysis. In this work we investigate the correlation between transport properties, defect chemistry and crystalline structure of lanthanum-doped ceria dense pellets (Ce_{1-x}La_xO_{2-x/2}) with 0 ≤ x ≤ 70 at.%. Single-phase Ce_{1-x}La_xO_{2-x/2} powders prepared by a combustion route were compacted into pellets and sintered at 1500 °C for 5 hours. The transport properties were studied by electrochemical impedance spectroscopy and the results show that ionic conductivity increases with increasing La³⁺ concentration for x ≤ 5 at.%, remains constant up to 15 at.%, and decreases for x > 20 at.%. For low lanthanum-doping (<5 at.%), conductivity increases as a result of the increase in the number of oxygen vacancies, whereas, above 20 at.%, electrostatic and steric interactions between dopant and vacancies (defects) lead to clusters formation that are associated to lower mobility. This association process originates from the Coulomb interaction between vacancies and local relaxation in the crystal lattice. In this regard, the activation energies decreases for lower doping and for x > 20 at.% it increases, which indicates an increased electrical resistance for defect migration. X-ray diffraction was used to determine the strain evolution, lattice parameter expansion, and phase concentration, through Rietveld refinement. The crystallographic analysis was complemented by detailed Raman spectroscopy. Raman experiments provided insights on the structural changes on fluorite crystal structure, such as a disorder associated with a phonon correlation length, that can be assessed by the broadening of the main fluorite peak (F_{2g}), the appearance of a C-type phase, oxygen vacancy concentration, and vacancy-dopant interaction. Moreover, local symmetry breaking and vibrational changes on the compound structure due to formation of oxygen vacancies and the different positions of oxygen in the lattice can be detected. The results indicate that La doping at large concentration up to 50–70 at.% can be a useful strategy to impart novel properties to cerium based oxides.

DT09.03

Spark Plasma Sintering and Thermal Properties of Eu-Doped Yttria-Silicate Coupons Fernando J. López; Instituto Politecnico Nacional, Mexico

Spark plasma sintering technique was used to densify Eu-doped Y₂SiO₅ powders, at the temperatures range between 1300 and 1400 °C. Shrinkage rate and microstructure, as well as porosity were analysed of the Y₂SiO₅ coupons doped with Eu⁺³. The sintering rate was evaluated during spark plasma sintering of Eu-doped yttria silicate powder. It was identified a densification effect when content Eu⁺³ is present. The thermal characterization was performed using the photothermal infrared radiometry technique. Both thermal diffusivity and thermal conductivity display an effect sigmoidal (Boltzmann type) behavior with the Eu⁺³ level concentration was present in the yttria-silicate coupons.

DT09.04

Relaxation Dispersion of Ionic Conductivity of Doped Ceria Ceramics Studied by Impedance Spectroscopy Marcin Malys¹, Maciej Wójcik¹, Aleksandra Dziegielewska¹, Marzena Leszczynska-Redek¹, Wojciech Wrobel¹, Jan Jamroz¹, Franciszek Krok¹ and Isaac Abrahams²; ¹Politechnika Warszawska, Poland; ²Queen Mary University of London, United Kingdom

An increase in the a.c. conductivity with increasing frequency is observed in ionic conductors and accompanied by a finite decrease of the dielectric constant. The dielectric function can be well described by the empirical functions of Cole-Cole or Haviliak-Negami. The parameters, relaxation strength, Δε, dc conductivity, σ₀, and relaxation frequency, ω_C, obey the Barton-Nakajima-Namikawa relation: σ₀ = Pε₀Δεω_C, where P is a coefficient, whose value is characteristic for a given ionic conductor.

Despite the fact that materials based on cerium oxide have already been intensively studied for many years in the direction of applications in solid state ionics due to their high oxygen ion conductivity, information on dielectric relaxation in these materials is to date relatively rare [1].

In this work dense ceramic samples of general formula Ce_{1-x}Me_xO_{2-x/2} (x = 0.20, Me = Gd, Sm or Nd) were prepared by an oxalate co-precipitation or solid state reaction methods to obtain dense polycrystalline samples with different size of grains and grain boundaries. For full characterization of electrical properties in air, a.c. impedance spectroscopy was used over an extended frequency range and as a function of temperature supported by transport number measurements using a modified EMF method with external voltage source [2]. To more accurately measure the impedance, the impedance analyzer was supplemented by a suitable current voltage amplifier allowing precise measurements especially at low temperatures. The electrical properties of the samples were fitted using an appropriate electrical circuit model by the least squares fitting. During the data analysis, efforts were made to minimize, as much as possible, measurement uncertainties. The frequency dependence of conductivity and complex dielectric relaxation were combined in one model of the a.c. response. Cole-Cole and more general Haviliak and Negami relaxation functions were tested giving the opportunity to fit specific dielectric relaxation parameters as a function of temperature.

By analyzing the obtained results, it can be hypothesized that the onset frequency ω_{onset} (on increasing a.c. conductivity with increasing frequency) is a parameter that characterizes the jump frequency of active charge carriers. This makes it possible to estimate the concentration of these carriers. By adjusting the remaining parameters, the P_{BNN} parameter (Barton-Nakajima-Namikawa) can be evaluated to investigate its dependence on temperature. In general, the value of this parameter is observed to decrease for all doped ceria samples with increasing temperature. The parameter P_{BNN} can be related to the length scale of non-random hopping expressed in units of elementary jump distance [3]. The results suggest that due to the increase in the level of thermal vibrations with increasing temperature, this distance becomes slightly shorter. In addition, it seems that the level of the parameter varies depending on the size of the crystallite grains or the environment created by the intergrain material.

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Acknowledgements

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DT09.05

Relaxation Dispersion of Ionic Conductivity of Doped NBT ($\text{Na}_{0.5+x}\text{Bi}_{0.5-x}\text{Ti}_{1-y}\text{Me}_y\text{O}_{3-\delta}$) Ceramics Marcin Malys¹, Konrad Kwatek¹, Aleksandra Dziegielewska¹, Marcin Krynski¹, Wojciech Wrobel¹, Isaac Abrahams² and Franciszek Krok¹, ¹Politechnika Warszawska, Poland; ²Queen Mary University of London, United Kingdom

Materials based on $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ (NBT) are considered as a potential electrolyte candidates for solid-oxide fuel cells. In these materials even small variations of Na and Bi content may lead to a significant change in electrical conductivity. So far, the highest oxide-ion conductivity has been observed for the $\text{Na}_{0.50}\text{Bi}_{0.49}\text{TiO}_{2.985}$ composition [1]. Our work is focused on further enhancement of oxide-ion conductivity by introduction of dopants (Mg, Zn, Ca, V) to the B-site to partially replace the Ti^{4+} ions in the perovskite structure.

NBT powders were synthesized using standard solid state reaction. Dense ceramic samples were prepared and characterized by various methods to investigate the crystal structure and electrical properties as a function of temperature. For full characterization of electrical properties a.c. impedance spectroscopy and modified *EMF* [2] methods were used. The frequency dependence of conductivity and complex dielectric relaxation were combined in one model of the a.c. response. Cole-Cole and more general Haviliak and Negami relaxation functions were tested giving the opportunity to fit specific dielectric parameters as a function of temperature: relaxation strength $\Delta\epsilon$, high frequency permittivity ϵ_∞ , onset ω_{onset} and relaxation ω_C frequencies [3]. These fits also allowed investigation of the empirical relation of Barton-Nakajima-Namikawa ($\sigma_0 = P \epsilon_0 \Delta\epsilon \omega_C$). The parameter P_{BNV} can be related to the length of scale of non-random hopping expressed in units of elementary jump distance[3]

NBT materials (e.g. doped with Mg or Ca) show moderate ionic conductivity, while maintaining interesting properties of dielectric relaxation - high values of the parameter ϵ_∞ are observed, which increases significantly with increasing temperature. The second parameter in relaxation function, relaxation strength $\Delta\epsilon$, in turn slightly decreases with increasing temperature. The ϵ_∞ parameter may be related to the specific polarization properties of bismuth lone pair of electrons - this hypothesis is gradually verified by computer modeling and ab-initio simulations. It is worth noting that this polarization may be related to the movement of oxygen ions in the structure.

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Acknowledgements

This work was supported by the National Science Centre (Narodowe Centrum Nauki), Poland under grant number UMO-2018/30/M/ST3/00743.

DT09.06

Effect of Aid-Sintering Additives in Processing of Solid Oxide Fuel Cells Electrolytes Sofia Cuello^{1,2}, Joaquin Rodriguez^{1,2}, Laura Baque^{1,2} and Liliiana V. Mogni^{1,2}, ¹CONICET Patagonia Norte, Argentina; ²Comision Nacional de Energia Atomica, Argentina

Solid oxide fuel cells (SOFC) are devices that convert chemical energy into electrical energy with high efficiency and lower environmental impact than traditional technologies. They could produce fuels by H_2O or CO_2 electrolysis (H_2 , CO , CH_4). They can generate high-quality heat, which allows cogeneration. Additionally, they are modular allowing a wide range of applications. Despite the abundance of raw materials, the high cost of ceramic manufacturing is currently the limiting factor for its commercialization. A way to sort it out is by reducing the number of steps and the temperature of the heat treatments required for the fabrication of the multi-component membrane electrode assembly (MEA) by co-tape and co-sintering process. The Tape-Casting technique is a well-established technique to produce ceramic thin sheets. It consists in extending a ceramic powder-based slurry along a surface or carrier and controlling the thickness with a “doctor blade”. The green tape is dried and sintered to get the final layer of ceramic material. The SOFC components can be tape-casted as a single multi-layer sheet and be sintered together to simplify the manufacturing process. However, this is the biggest challenge we face because of the different microstructures (porous and dense ceramic) demand different sintering temperatures and can produce shrinkage and chemical reaction between the component materials.

This research aims to investigate the processing of the LSGM (Lanthanum Gallate doped with Strontium and Magnesium) as electrolyte material and the effect of additives on reducing its sintering temperature. For this purpose, we tested three different additives: Zn, V and Fe salts and oxides. TG-DSC analysis was performed to optimize the thermal treatment. In all cases, the slurry composition and thermal treatment were the same, being the green tapes sintered at 1300°C by 8h. Both, Fe and Zn additives allow obtaining dense electrolytes, with microstructure similar to those obtained for LSGM without additives at 1500 °C. On the contrary, The LSGM treated with V and without additives at 1300 °C shows incomplete sintering. Despite Fe and Zn act as sintering aids, we found by XRD the formation of secondary phases between LSGM and Zn. Once selected Fe as the best additive, we assayed different percentages of $\text{Fe}(\text{NO}_3)_3$, and Fe_2O_3 to determine the optimum type and amount of additive. In order to assess if the addition of additives affects the transport properties of the electrolytes, we measured its electrical properties as a function of temperature by conductivity measurements and electrochemical impedance spectroscopy (EIS). These results were analyzed in regard of the bulk and grain boundary conductivities and were correlated with grain size and grain boundary density studied by Scanning Electron Microscopy and Fe distribution through the electrolyte by TOF-SIMS characterization.

DT09.07

Partial Covalent Interactions Effect on Oxygen Diffusion in CeO_2 , ZrO_2 , and Bi_2O_3 Nguyen X. Thi and Aleksandar Staykov; Kyushu Daigaku, Japan

Reducing the dependence on fossil fuels requires more efficient Solid Oxide Fuel Cells (SOFCs). One of the determining factors of SOFCs' efficiency is the oxide ion conductivity within the electrolyte. Each electrolyte material has different oxide conductivity because of varying interactions between the oxide ion and surrounding cations. Understanding how oxygen interacts with these cations can guide the choice of electrolyte material and will lead to accurate models of oxide ion diffusion.

Two models of oxygen diffusion can be investigated: the classical ionic model and the partial covalent conduction model. The conventional model assumes that all ions in the lattice are fully ionized, and oxygen conduction is hindered by steric effects from cations and electrostatic interactions. According to this model, the most favorable scenario is oxygen traveling through cations with small radius and small positive charge. Such theory ignores oxygen-cation electronic interactions and the effect of the polarizability of cations. The partial covalent model involves partially ionized atoms with some degree of covalent bonding. This theory considers electronic interactions along with steric hindrance and electrostatic force. Including these partial covalent bonds is likely to produce different conclusions to those of the conventional ionic model [1]. The model has shown already its potential in the simulation and understanding of oxygen reduction reaction on oxide surfaces [2,3,4].

We examined the effect of partial covalent interactions on oxygen migration in CeO_2 , ZrO_2 , and Bi_2O_3 . Activation energy and electron density of all possible migration pathways were calculated using plane-wave Density Functional Theory. The results proved that the oxygen migration is influenced by the oxygen-cation partial covalent interaction in a non-intuitive manner. If oxygen at the transition state is stabilized by partial covalent interaction, the

activation energy is decreased. When oxygen at the initial state had higher partial covalent interaction with cations compared to the transition state, initial energy is stabilized, thus increasing bond breaking energy penalty and activation energy. The electron density data showed nonlinear oxygen migration trajectory of the oxygen inside $\delta\text{-Bi}_2\text{O}_3$. It moves in curved pathway, breaking bond with one Bi and forming bond with another Bi simultaneously. Oxygen also breaks bonds in succession in Y doped ZrO_2 and propagates in diagonalized pathway. These results indicate that maximizing partial covalent interaction in the vicinity of cations is preferable for oxygen migration.

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DT09.08

Enhancing the Total Ionic Conductivity of Gadolinia Doped Ceria Electrolyte for SOFC Using Co-Precipitation [Prerna H. Vinchhi](#)¹, Ranjan Pati², Abhijit Ray¹ and Indrajit Mukhopadhyay²; ¹Pandit Deendayal Energy University School of Solar Energy, India; ²Pandit Deendayal Energy University, India

Ceria has been extensively explored as an efficient electrolyte material for Low Temperature Solid Oxide Fuel Cell (LT-SOFC). The redox coupling $\text{Ce}^{4+}/\text{Ce}^{3+}$ in doped Ceria supports the enhanced ionic conduction. Gadolinia doped Ceria (GDC) has been extensively explored electrolyte material for low temperature SOFC applications. In the present article, facile co-precipitation method is employed to synthesize GDC composites with stoichiometric ratio of $\text{Gd}_x\text{Ce}_{1-x}\text{O}_{2-\delta}$, $x=0, 0.05, 0.10, 0.15$ and 0.20 , with a modification of using molecular water of the precursors to avoid agglomeration. The ionic radius compatibility and sintering at very high temperature resulted in highly dense electrolyte structure with about 96% of theoretical density. The thermal stability along fractional mass loss of as prepared powders were analyzed using thermogravimetric analysis (TGA). The structural formation of cubic phase were examined using X-Ray Diffraction (XRD) and Raman profile ascribing absence of other phases. The granularity of the samples were observed using FESEM with elemental mapping by EDS. The electrochemical behavior was investigated using Electrochemical Impedance spectroscopy (EIS) which was taken between the temperature range of $350\text{-}700^\circ\text{C}$. This work demonstrates the interrelationship of oxygen vacancy generation due to the doping effect of Gadolinia over Ceria which yields in improvement of ionic conductivity.

DT09.10

Systematic Investigation of Unsteady-State Redox Properties of CuO/Perovskite Materials [Giacomo Peron](#)¹, Donato Pinto², Giovanni Carollo¹, Atsushi Urakawa² and Antonella Glisenti¹; ¹Universita degli Studi di Padova, Italy; ²Technische Universiteit Delft, Netherlands

In this contribution several materials of the type $10\% \text{ wt CuO/La}_{1-x}\text{Sr}_x\text{BO}_3$ ($x=0;0.2;0.5$ and $B=\text{Mn;Fe}$) are characterized by XRD, XPS, SEM, EDX and TPR, and tested in unsteady-state regime for H_2 and CO oxidation (i.e. alternating pulses of fuel with pulses of oxygen) at the temperatures of 250°C , 350°C and 450°C . CuO/SrTiO_3 has also been studied in the same way.

The aim of the study is to clarify the nature of CuO-perovskite interaction and how it varies by including different percentages of A-site doping, or changing the B-site element. Generally, perovskite-related literature, indicates A-site doping with lower valence elements as a way to induce vacancies formation and improve the oxygen mobility [1]. However, while this is generally true at high-temperature applications, at low temperatures things are not so clear.

Hydrogen oxidation over the $10\% \text{ wt CuO/La}_{1-x}\text{Sr}_x\text{MnO}_3$, $x = 0; 0.2; 0.5$, helped to identify two different paths of activity: the first one is related to CuO reduction: a fast-kinetics process that is activated in CLSM20 much more than CLSM50, and a second, slow-kinetics one that is always present in CLM and lights-off on the other samples during the 350°C step. If the global reducibility of the perovskite is lower than that of Cu, copper will react with CO more quickly, constantly attracting oxygen from the support to replenish the active sites. If temperature or doping increase change the energy balancing at the interface, then we have direct reaction of the perovskite. In this case, the activity on the surface of the perovskite will attract oxygen in that direction. The data on CO oxidation were integrated over time. The mobility is particularly activated after 350°C for both B-site elements. If we consider Mn, the $20\% \text{ Sr}$ doped sample seems to be the best choice to get closer to the top of the volcano curve. Going at 50% doping seems to undermine the transport properties. The high content of Mn^{4+} does not allow complete oxygen exchange. In Fe the effect is much more linear, and the transport from the perovskite lattice can be activated at lower T with the highest degree of doping. This activation, as well as that of simple absorption of oxide species during the oxidant pulses, is found also in peak area data, that encompass both contributions previously analyzed. In manganites, CLSM20 locates in the middle between the two opposite behaviors displayed by CLM and CLSM50. The former relies on excess oxygen transport to Cu, the latter from one side can store more readily available oxygen on the surface sites, from the other needs to undergo a certain reduction process in order to achieve an efficient transport. The stability of the B-site redox couple can help to generate a great number of species M^{4+} after the doping treatment. Thus, stable Mn^{4+} hinders reactivity at low-T by retaining oxygen, whereas unstable Fe^{4+} is instead an active site of reaction, helps in creating vacancies and consents the hopping of oxide anions in the lattice as described by Ref. 2. The influence of the atmosphere is to continuously stimulate oxygen delivery by reacting, in this latter case, with CO, that “likes” to adsorb on more oxidized sites. If, at high temperature, or in the presence of softer cations, the reducibility of the support becomes comparable to that of copper, then oxygen may also transfer on the perovskite sites to directly react without involve Cu.

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DT09.12

Electrical Conductivity in Iron Phosphate Glasses—Insights into the Role of B_2O_3 and HfO_2 from Model-Free Scaling Analysis of Conductivity Spectra [Luka Pavić](#)¹, [Arijeta Baftić](#)², [Shiro Kubuki](#)³, [Hüseyin Ertap](#)⁴, [Mustafa Yüksek](#)⁵, [Mevlut Karabulut](#)⁶ and [Andrea Moguš-Milanković](#)¹; ¹Rudjer Bošković Institute, Croatia; ²Faculty of Chemical Engineering and Technology, University of Zagreb, Croatia; ³Tokyo Metropolitan University, Japan; ⁴Kafkas University, Turkey; ⁵Iskenderun Technical University, Turkey; ⁶Gebze Technical University, Turkey

Iron phosphate-based glasses (IPGs) belong to a family of electronically conducting amorphous materials. Due to the presence of transition metal (TM) ions, e.g. iron, in more than one valence state, small polaron hopping (SPH) conduction mechanism is observed. These materials are of boundless scientific interest due to their potential application as electrode materials for batteries, electronic circuits elements, etc.

In this work, we report the effect of the addition of modifiers and network formers on the polaronic transport in binary IPG in which up to 8 mol% of boron and hafnium oxide are added. The electrical properties of two glass systems $\text{HfO}_2\text{-B}_2\text{O}_3\text{-Fe}_2\text{O}_3\text{-P}_2\text{O}_5$ are studied in detail by Solid State Impedance Spectroscopy (SS-IS) in a wide frequency and temperature range, revealing interesting features behind the polaronic transport. The addition of oxides significantly alters the $\text{Fe}^{2+}/\text{Fe}_{\text{total}}$ ratio, which directly affects the polaron number density and consequently strongly controls the DC conductivity trends for both glass-series. Moreover, we found that short-range polaron dynamics are also under the influence of the induced structural changes. Therefore, we have studied them in detail using relatively simple but very informative model-free scaling procedures, Summerfield and Sidebottom scaling. Both scaling procedures of the conductivity spectra confirmed the validity of the time-temperature superposition principle for all glasses. An attempt to construct a super-master curve revealed that in addition to the change in polaron number density, the hopping lengths of the polarons also change, and Sidebottom scaling yields a super-master curve. In the next step, the spatial extent of the localized motion of the polarons is correlated with the polaron number density and two distinct regions containing glasses with low and high polaron concentration are observed. The transition between these regions is not only related to the polaron number density, but also to the combination of glass compositions and parameters that have an impact on the polaron motions. The large increase in the spatial extent of the polaron hopping jump could be related, either to the structural changes caused by the addition of HfO_2 and B_2O_3 and their effects on the formation of polarons, or to the inherent property of polaron transport in IP glasses with low polaron number density. The obtained results provide new valuable information about the resulting mixed glass network and its impact on the polaron formation and its dynamics.

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DT09.13

Electrochemical Observation of Compressive Strain Built-Up During Pulsed Laser Deposition Christoph Riedl¹, Matthäus Siebenhofer^{1,2}, Sergej Raznjivic³, Zaoli Zhang³, Markus Kubicek¹, Alexander K. Opitz¹ and Juergen Fleig¹; ¹Technische Universität Wien, Austria; ²CEST Kompetenzzentrum für elektrochemische Oberflächentechnologie GmbH, Austria; ³Erich Schmid Institute of Materials Science of the Austrian Academy of Sciences, Austria

In this study, lanthanum strontium ferrite (LSF) electrodes were grown on different single crystalline electrolyte substrates (yttria-stabilized zirconia (YSZ), $\text{La}_{0.95}\text{Sr}_{0.05}\text{Ga}_{0.95}\text{Mg}_{0.05}\text{O}_{3-\delta}$ (LSGM) and YSZ + 5 nm Gd doped ceria (GDC) buffer layer) and their electrochemical performance was tracked directly after deposition by *in-situ* PLD impedance measurements (i-PLD) in the vacuum chamber of the pulsed laser deposition (PLD). These measurements allowed us to stepwise grow the electrode and observe changes of the polarization resistance and chemical capacitance over the film thickness. In addition, i-PLD measurements benefit from a superb stability of the oxygen exchange activities due to the absence of surface contaminations.

While on YSZ substrates polycrystalline thin film growth of LSF was observed by means of XRD measurements, epitaxial thin film growth was founded on LSGM and YSZ-GDC. Most interestingly, also different electrochemical properties were measured: For polycrystalline LSF thin films the polarization resistance saturates after several ten nanometers of film growth, while, measurements on epitaxial LSF thin films measurements revealed a constant increase of the polarization resistance with film thickness. In order to explain this effect, high resolution transmission electron microscopy (HR-TEM) was conducted. The results indicate an increase of compressive strain with increasing LSF film thickness. Thus, we suggest that due to strain built-up the concentration of oxygen vacancies decreases, which leads to higher polarization resistances.

DT09.14

Oxygen Non-Stoichiometry and Mixed Conductivity of Ti and Mg Doped $\text{BaCo}_{0.4}\text{Fe}_{0.4}\text{Y}_{0.2}\text{O}_{3-\delta}$ Perovskite Md Saiful Alam^{1,2}, Isao Kagomiya¹ and Ken-ichi Kakimoto¹; ¹Nagoya Institute of Technology, Japan; ²University of Chittagong, Bangladesh

The perovskite materials exhibiting mixed ionic-electronic conductivity (MIEC) have been comprehensively researched as potential cathodes for solid oxide fuel cells. The Co and Fe containing MIEC perovskite oxides show high electrochemical performances as a result of enhanced electrochemical reaction sites. In the recent past, among the investigated mixed conducting oxides, $\text{BaCo}_{0.4}\text{Fe}_{0.4}\text{Zr}_{0.1}\text{Y}_{0.1}\text{O}_{3-\delta}$ (BCFZY) cathode material is pointed out to be compatible for the low-temperature proton-conducting solid oxide fuel cells with notable response [1]. Despite the worthwhile findings of this material, further analysis/modification is needed to obtain a potential cathode for practical application. As it is recognized that doping can modify the overall performance [2, 3], thus in this study Ti, and Mg were chosen independently as doping elements in place of Zr of BCFZY to prepare $\text{BaCo}_{0.4}\text{Fe}_{0.4}\text{Y}_{0.2}\text{O}_{3-\delta}$ (BCFY), $\text{BaCo}_{0.4}\text{Fe}_{0.4}\text{Ti}_{0.1}\text{Y}_{0.1}\text{O}_{3-\delta}$ (BCFTY), and $\text{BaCo}_{0.4}\text{Fe}_{0.4}\text{Mg}_{0.1}\text{Y}_{0.1}\text{O}_{3-\delta}$ (BCFMY) compositions, respectively. This study has been formulated to conduct comprehensive research on the prepared samples which expresses the characteristics of MIEC in terms of performing as a potential cathode in regards to solid oxide fuel cells. However, with a view to this context, no significant literatures are available to go through.

The stated compounds were prepared by following the steps of citrate-based liquid mixing technique process. BaCO_3 , TiO_2 , and MgO oxides; in addition to $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, and $\text{Y}(\text{NO}_3)_3 \cdot 6.09\text{H}_2\text{O}$ nitrates were required to complete the task; chemicals purities were 99.9%. We investigated the crystal phase perfectness, oxygen non-stoichiometry, total conductivity, and oxygen permeability of the prepared compounds. The prepared compounds belong to cubic perovskite with space group of *Pm-3m* without forming any secondary phase. It was confirmed that the elements of the composed combination distributed homogeneously using Energy-dispersive X-Ray spectroscopy. Microstructural and density studies suggest that the on-hand bulk samples are dense. The Mohr's salt titration was performed at room temperature using an automatic titrator and identified that BCFMY possesses the highest amount of oxygen non-stoichiometry. Contrarily, the BCFTY sample shows improved total conductivity among the prepared samples. Oxygen permeation properties were studied at temperatures as low as 600 °C and impressive oxide ion permeability was noticed. It is noteworthy that crystal structure modification, in addition to oxygen non-stoichiometry caused by doping, significantly affects the oxygen permeability of these materials. Details of the investigated results will be discussed during the presentation.

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DT09.15

Study of the Oxygen Reduction Reaction in the $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$ / CGO Composite SOFC Cathode Fatima-Ezzahra El Bassiri^{1,2}, Aurélie Rolle^{2,1}, Jean-Philippe Dacquin^{3,1}, Edouard Capoen^{3,1}, Bernard Boukamp⁴ and Rose-Noëlle Vannier^{2,1}; ¹Unite de Catalyse et Chimie du Solide, France; ²Centrale Lille Institut, France; ³Université de Lille, France; ⁴Universiteit Twente, Netherlands

The oxygen reduction reaction in a Solid Oxide Fuel Cell is a complex mechanism that strongly depends on the material used, its microstructure and the operating conditions.

Using Kröger and Vink's notation, the overall reaction can be written as $\frac{1}{2}\text{O}_2(\text{g})+2\text{e}^-+\text{V}_\text{o}\rightarrow\text{O}_\text{o}^\times$ [1], but there are several steps to consider: diffusion of

molecular oxygen into the reaction site, surface adsorption and dissociation of the oxygen molecule, charge transfer, incorporation and transfer of ions into the solid and at the electrode/electrolyte interfaces. Each step is associated with a characteristic time constant. For example, gas diffusion is a slow process; its frequency of about 1 Hz corresponds to relaxation times of about ten milliseconds. Conversely, the transfer of ionic species at interfaces is fast, with frequencies higher than 10^4 Hz corresponding to relaxation times of less than 10^{-5} seconds [2]. These reduction steps strongly vary with the oxygen partial pressure.

Here, $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$ material was studied as a model SOFC air electrode material [3-6]. A symmetrical cell composed of a (50%CGO+50% $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$) electrode screen-printed on a gadolinium-doped ceria electrolyte (CGO) was studied by electrochemical impedance spectroscopy (EIS). The measurements were performed at temperature ranging from 500°C to 800°C at different oxygen partial pressures (10^{-6} to 1 atm). The combination of CNLS-fit and the use of the distribution function of relaxation time (DRT) confirmed that in the case of a powder prepared by solid state route, the electrochemical response of the (50%CGO+50% $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$) composite is mainly limited by ionic diffusion and to a lesser extent by the oxygen exchange reaction at the surface of CGO and the redox reaction in $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$ [7]. The impact of grain size will be also discussed by comparison with powder prepared by Pechini route.

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DT09.16

Charge Transport and Acoustic Loss in Lithium Niobate-Lithium Tantalate Solid Solutions Holger Fritze¹, Yuriy Suhak¹, Steffen Ganschow², Dimitry Roshchupkin³, Claudia Kofahl¹, Bujar Jerliu¹ and Harald Schmidt¹; ¹Technische Universität Clausthal, Germany; ²Leibniz-Institut für Kristallzüchtung im Forschungsverbund Berlin eV, Germany; ³Institut problem tehnologii mikroelektroniki i osobocistyh materialov RAN, Russian Federation

Lithium niobate-lithium tantalate solid solutions (LNT) are polar dielectrics that represent an extraordinarily variable model system for the disclosure and application of new fundamental materials and physical phenomena due to its miscibility over the entire compositional range and the tunable size of ferroelectric domains. The impact of point defects and domain walls on macroscopic material properties, their interaction and high thermal stability provide a novel and broad range of emerging applications for piezoelectric structures such as actuators and acoustic crystals, but equally for nanoelectronic and optoelectronic applications up to high temperatures. The adjustment of stoichiometry and domain structure allows to tailor the crystal properties and, for example, to take advantage of the high piezoelectric coefficients and the expected high domain wall conductivity.

Initially, the distinctive properties of LNT in relation to other piezoelectric single crystals are introduced. Key features of the crystal growth processes and of the phase diagram are furthermore outlined. In this work the micro-pulling-down method and Czochralski growth are applied to growth LNT crystals of different Nb/Ta ratios. The latter method is also used to prepare periodically poled crystals.

The charge transport in bulk LNT at elevated temperatures is discussed which includes electronic and ionic contributions as function of temperature and oxygen partial pressure and related defect models. The electrical conductivity of LNT and LiNbO_3 show similar behavior in air at temperatures from 400 °C to 700 °C. It can be concluded that the dominant transport mechanism in LNT is the Li transport via Li vacancies. Further, the electrical conductivity of LiNbO_3 and LiTaO_3 is compared and found to differ above 600 °C. For example, the latter shows a gradually increasing activation energy with temperature which indicates a transition range with contributions of two or more conduction mechanisms.

Acoustic loss of single crystalline LNT is studied as a function of temperature by resonant piezoelectric spectroscopy. For this purpose, LNT bulk acoustic wave resonators with different Nb/Ta ratios, operated in the thickness-shear and thickness mode, are investigated. The results are compared to those previously reported for congruent LiNbO_3 . Contributions to the acoustic loss in piezoelectric LNT resonators and the underlying models are furthermore presented. It is shown that losses in LNT strongly increase above about 500 °C, which is attributed to a conductivity-induced piezoelectric/carrier relaxation mechanism. The high-temperature loss is determined by intrinsic material properties and therefore reflected correctly. At lower temperatures, however, the shape and relatively small size of the samples might impact the resonator quality factor. As the loss maximum depends on frequency, minimization of losses at a given anticipated application temperature could be achieved by an appropriate choice of operating frequency. Finally, it is shown that LNT thickness-shear and thickness mode acoustic resonators exhibit significantly lower loss with respect to LiNbO_3 resonators.

DT09.17

Defect Chemistry of p-Type Perovskite Oxide $\text{La}_{0.2}\text{Sr}_{0.8}\text{FeO}_{3-\delta}$ —A Combined Experimental and Computational Study Hohan Bae¹, Yonghun Shin², Donghwi Shin¹, Junghyun Park¹, Saron Park¹, Donghwa Lee² and Sun-Ju Song¹; ¹Chonnam National University, Korea (the Republic of); ²Department of Materials Science and Engineering, Pohang University Science and Technology, Korea (the Republic of)

Defect structure and mass and charge transport properties of LSF28 combined with experimental as well as computational study were presented. Defect chemical properties measured in a wide range of temperature and oxygen partial pressure can be clearly interpreted from delocalized electron model as well as commonly used localized electron model depending on the thermodynamic conditions. The experimentally measured electrical properties as a function of oxygen nonstoichiometry were understood not only through the defect structure but also through the first-principles DFT calculations. It was employed to identify the change in electronic structure during the hole-producing oxidation process in the Po_2 regime of 10^{-15} - 10^{-12} atm (750-900°C). In particular, the semiconductor-to-metal transition phenomenon was well explained by the fact that oxygen incorporation generates extra holes, which make the hybridized band empty and decrease the Fermi level. A simplified way to analyze the defect structure has been presented for LSF28, which is consistent with the conventional models. Hence, it is proved that the behavior of physical bulk properties could be expressed in a simpler form under thermodynamic conditions near “n-p transition regime”.

DT09.18

SCAN and SCAN+U Approximations to Investigate YBCO-Related Mixed Conductors Mariana Gómez-Toledo, López-Paz Sara, García-Martín Susana and Arroyo-de Dompablo Elena M.; Universidad Complutense de Madrid Facultad de Ciencias Químicas, Spain

Perovskite-type oxides are among the most important “energy materials” due to specific electrochemical, electrical or/and catalytic properties. To better understand these properties, and to optimize the applications of these oxides, a profound knowledge of crystal and electronic structure relationships can be achieved by means of computational calculations. Selecting an appropriate DFT methodology at the basic property level prediction –crystal, electronic and

magnetic structures- is a prerequisite prior to their utilization to investigate energy related properties as the point defect chemistry, redox thermodynamics and oxygen diffusion mechanisms. Recently, the strongly constrained and appropriately normed (SCAN) meta-GGA XC functional¹, has shown a superior performance (relative to the GGAs) to model the basic physical properties and phenomena associated to correlated oxides. Moreover, Carter and coworkers have demonstrated that the introduction of the Hubbard term (SCAN +*U* approach) improves the reproduction of the ground-state properties of binary 3d TM-oxides^{2,3}, being critical for the prediction of the right polymorph for Mn₂O₃ and Fe₃O₄². Assessing the performance of the SCAN and SCAN+*U* in the study of complex perovskite oxides consisting on various TM ions is an important step forward.

In this contribution we select the YSr₂Cu₂FeO_{7+δ} (0 < δ < 1) system to evaluate the appropriateness of the SCAN functional, and their more extended scheme SCAN+*U*. Their crystal structure, with an alternation of FeO_{1+δ}/SrO/CuO₂/Y/CuO₂/SrO layers along the c-axis can be referred to the YBaCuO-type structure, with the replacement of one layer of Cu cations. YSr₂Cu₂FeO_{7+δ} (0 < δ < 1) compounds shows a wide range of non-stoichiometry within the anion sub lattice resulting from the interplay between different oxidation states of the Fe and Cu atoms. The highly oxidized term YSr₂Cu₂FeO_{7.85}, is a metallic oxide with superconducting transition at T_c = 70 K⁴. YSr₂Cu₂FeO_{7.08}, is a typical insulator with antiferromagnetic (AF) long-range ordering⁵. In between those extremes, the air-synthesized YSr₂Cu₂FeO_{7.56} is a p-type semiconductor, mixed valence Fe³⁺/Fe⁴⁺ and Cu²⁺/Cu³⁺ oxide, which exhibits an interesting electrochemical behavior associated to catalytic activity in the oxygen reduction reaction (ORR), being a potential air-electrode for solid oxide fuel cells (SOFCs). We present in here DFT-calculations on the two end-members of the system, showing the impact of the introduction of *U* term in their electronic structure.

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DT09.19

Oxygen Exchange Kinetics on Tm-Stabilized Bi₂O₃-LSM Composites Linn Katinka Emhjellen¹, Wen Xing², Vincent Thoréon¹, Zuoan Li² and Reidar Haugsrud¹; ¹Universitetet i Oslo, Norway; ²SINTEF Industry, Norway

Composite materials showing oxygen transport by means of ambipolar oxide ion-electron conductivity find numerous technological applications, such as in electrodes for high temperature electrochemical interconversion of energy and oxygen transport membranes (OTMs). Bismuth oxide, stabilized in the high temperature cubic, d modification, exhibits superior oxide ion conduction, and when paired with an electronic conductor, the resulting composites show potential as OTMs [1, 2]. We have recently shown that Bi₂O₃ substituted with 20 atom% Tm (BTM) is chemically compatible with the well-studied electronic conductor Sr substituted LaMnO₃ (LSM). The composite exhibits among the highest reported oxygen flux for bismuth oxide based materials [3]. With high ionic and electronic conduction, surface kinetics limit oxygen permeation, and even with a membrane as thick as 1.5 mm, surface processes significantly influenced the oxygen flux in the BTM-LSM composites.

In the present contribution, we utilize gas-phase isotope based approaches to study the kinetics and determine the rate-determining step for the oxygen exchange on BTM-LSM composites. We have measured the rate of dissociative adsorption and incorporation of oxygen as a function of temperature and oxygen partial pressures for composites with different volume ratios of BTM and LSM, as well as for single-phase nominal BTM and BTM substituted with cations promoting electronic defects, Pr.

By comparing with estimated values for pure surface and bulk limitation, we confirm that the measured fluxes are in the mixed regime, approaching bulk limitation at the highest temperature (900 °C). Preliminary results indicate that the rate-determining step in the overall oxygen exchange varies with temperature and the volume ratio between LSM and BTM in the composite. The contribution aims to further elucidate details of the surface kinetics mechanism of oxygen exchange on BTM-LSM composites and compare it with single-phase and composite OTMs.

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DT09.20

Oxygen Nonstoichiometry Effect on Perovskite Oxygen Transport Ivan Kovalev, Rostislav Guskov, Mikhail Popov, Sergey Bychkov, Stanislav Chizhik and Alexander Nemudry; Institute of Solid State Chemistry and Mechanochemistry, SB RAS, Russian Federation

Complex oxides with mixed ionic-electronic conductivity (MIEC) are attractive because of their application possibility in the chemical, gas and energy industries. They can be used in different technologies, for example, producing pure oxygen, methane conversion, electrochemistry processes [1-3]. Despite the practical importance of these processes, there are no universally accepted concept today about the stages that determine the course of oxygen exchange on the nonstoichiometric MIEC oxides surface. As a result, there is a large scatter in the literature experimental data which prevents the development of a reliable oxygen permeability mechanism conception in the MIEC membranes and advance in technological aspects. Thus, understanding the factors that can ensure high oxygen permeability of perovskite oxides continues to be a challenging and actual problem. Earlier, we have developed new oxygen release techniques to obtain kinetic and equilibrium parameters in grossly nonstoichiometric oxides [4, 5]. The aim of this work is comprehensive analysis of the oxygen nonstoichiometry effect on the kinetic parameters in the processes of oxygen transport and chemical relaxation measurements. A theoretical model has been developed for comparing the results of three independent methods. The influence of

oxygen nonstoichiometry on the process of oxygen transport through gas-tight hollow fiber membranes was studied. Stable $\text{SrFe}_{0.98}\text{Mo}_{0.02}\text{O}_{3-\delta}$ (SFM2) perovskite was chosen as the object.

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DT09.21

On Unraveling the Ionic Conductivity of $\text{Bi}_{1-x}\text{P}_x\text{O}_{1.5}$ —An *Ab Initio* and Experimental Study Marcin Krynski¹, Jan Jamroz¹, Michal M. Struzik¹, Franciszek Krok¹, Isaac Abrahams² and Wojciech Wrobel¹; ¹Politechnika Warszawska, Poland; ²Queen Mary University of London, United Kingdom

Cubic bismuth oxide exhibit highest known oxide ion conductivity of around 1 S/cm at 800°C [1]. Below 730°C a phase transition is observed to the lower symmetry a-phase, leading to sudden drop of conductivity of around 4 orders of magnitude. The stability of the highly conductive phase can be improved by introducing rare earth ions [2]. However, doping with larger lanthanide ions leads to the formation of a very stable rhombohedral *b*-phase, that for some dopants, can exhibit exceptionally high ionic conductivity [3].

In this project we look at the rhombohedral $\text{Bi}_{1-x}\text{P}_x\text{O}_{1.5}$ system, characterized by a layered structure with fluorite-like blocks consisting of Bi/Pr layers within the block and two outer layers consisting exclusively of Bi atoms. Additionally, each block is separated from others by a van der Waals gap. To shed light on the dynamics within and between the said blocks we employ van der Waals corrected Density Functional Theory within a molecular dynamics setting. The study shows that the oxide ion dynamics of $\text{Bi}_{1-x}\text{P}_x\text{O}_{1.5}$ exhibits a tremendous level of dynamical heterogeneity, with centers of the diffusion processes migrating between the fluorite-like blocks and the van der Waals gap as the Bi/Pr ratio is changed. This is then associated with a change of the characteristic dynamical patterns observed in the vibrational density of states extracted from *ab initio* molecular dynamics as well as from Raman spectra. This allows for an understanding of the non-linear behaviour of the ionic conductivity of $\text{Bi}_{1-x}\text{P}_x\text{O}_{1.5}$ with respect to the praseodymium content.

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DT09.22

Investigation of Influence of Gas Atmosphere on Conductivity and Crystal Structure of $\text{Ce}_{1-x}\text{Pr}_x\text{O}_{2-\delta}$ ($x = 0.1, 0.2, 0.3$) Marzena Leszczynska-Redek¹, Kamil Kowalski¹, Marcin Malys¹, Aleksandra Dziegielewska¹, Stephen Hull², Wojciech Wrobel¹, Franciszek Krok¹ and Isaac Abrahams³; ¹Politechnika Warszawska, Poland; ²Rutherford Appleton Laboratory, United Kingdom; ³Queen Mary University of London, United Kingdom

Currently there is interest in praseodymium doped cerium oxide because of its properties including high oxygen ion conductivity, extensive deviation from stoichiometry and associated mixed ionic/electronic conduction depending on oxygen partial pressure ($p\text{O}_2$) and Pr content. These properties not only make the system suitable as an electrolyte but also, due to significant electronic conductivity, as an electrode in Solid Oxide Fuel Cells [1,2]. In this work we examine the dependence of crystal structure and conductivity behaviour on ceramic preparation method over a wide range of temperature and under different gas atmospheres.

Samples of $\text{Ce}_{1-x}\text{Pr}_x\text{O}_{2-\delta}$ ($x = 0.1, x = 0.2$ and $x = 0.3$) were prepared by three selected methods: solid state reaction, co-precipitation and the sol-gel based Pechini method. The crystal structure of all examined materials was characterised by X-ray powder diffraction at room temperature and as a function of temperature in air and nitrogen. Additionally, neutron diffraction measurements (Polaris diffractometer, ISIS Facility, United Kingdom) for samples prepared by standard solid state reaction were performed at room temperature and also for $x = 0.3$ in a specially designed gas flow rig under oxygen in variable temperatures up to 800 °C. The expansion of lattice parameter with temperature for all samples due to thermal and chemical expansion is observed. For samples prepared by co-precipitation, the chemical expansion of the unit cell due to oxygen loss ($\text{Pr}^{4+} \rightarrow \text{Pr}^{3+}$) is observed at lower temperature than for samples prepared by solid state reaction. The analysis of neutron diffraction data (for samples prepared by solid state reaction) reveal full occupancy of oxygen positions in this system which means that Pr has the 4+ oxidation state at room temperature. Refinement of the oxide ion content confirmed the complete reduction of praseodymium to the 3+ oxidation state at 800 °C ($d = 0.194(7)$). Electrical properties as a function of temperature under different gas atmospheres (air, oxygen and argon) were obtained by a.c. impedance spectroscopy. The highest total conductivity in air is obtained for samples prepared by the Pechini method. All prepared samples of the same composition were measured simultaneously using a multi-sample holder to ensure the same conditions (temperature and atmosphere). Ionic transference numbers were measured using a modified EMF method with an external adjustable voltage source in the concentration cell O_2 ($p\text{O}_2=1.01 \times 10^5$ Pa); Pt | oxide | Pt ; O_2 ($p\text{O}_2 = 0.2095 \times 10^5$ Pa). For samples prepared by solid state reaction the highest ionic transference numbers is ca. 0.7 at 800 °C for $x = 0.1$ and decreases with increasing Pr content.

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Acknowledgements

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DT09.23

Computational Study for Cr and S Poisoning Pathways on $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ Surfaces Bill Liu, Filip Grajkowski, Sophie C. Coppeters, t Wallant and Bilge Yildiz; Massachusetts Institute of Technology, United States

In order to advance our understanding of the role of surface modification and operational parameters on oxygen electrode performance, we will combine *ab initio* density functional theory (DFT) reaction energetics, defect chemistry, and microkinetic modeling to establish a quantitative model to provide more insights about Cr and S poisoning pathways on the surface-modified $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ (LSCF) with more oxidizable cations at the surface. LSCF

slabs terminated on different surfaces will be constructed and calculated to determine the most stable surface under operational conditions, which will be used as a reference to compare with surface-modified LSCF structures. To quantify Cr and S poisoning reaction pathways, the climbing image nudged elastic band (CI-NEB) method will be performed to calculate the energy barriers for each reaction step on 1) Sr-free LSCF, 2) Sr-segregated LSCF, and 3) surface-modified LSCF slabs. By obtaining the energy landscape of the entire reaction pathway, transition state theory will be applied to calculate the reaction rate constants and diffusivities. These values will be compared to quantify the impact of Sr segregation and surface modification on Cr and S poisoning, from the change in electronic structures as well as defects properties related to oxygen reduction reaction (ORR). These findings will guide the design of better performance and more durable oxygen electrodes for SOECs and SOFCs.

DT09.24

Kinetic Roughening of Boundaries Between Two Phases During Electrocoloration in an Oxide Thin Film Heung-Sik Park, Ji Soo Lim, Jeonghun Suh and Chan-Ho Yang; Korea Advanced Institute of Science and Technology, Korea (the Republic of)

Visualizing electrocoloration processes is a fast and direct method for investigating ionic dynamics in macroscopic scales. Our model material, a $\text{Bi}_{0.7}\text{Ca}_{0.3}\text{FeO}_{3-\delta}$ thin film is an ionic conductor having electrochromism, which show color changes according to its oxygen stoichiometry ($3-\delta$). [1] We induce topotactic transitions from as-grown phase ($\delta = 0.15$) to oxygen-vacancy-poor phase ($\delta = 0$) by applying voltage between coplanar electrodes. [2,3] Here, we observe kinetic roughening of boundaries between the two phases with optical microscopy. Width vs. position and width vs. time are plotted with different voltages and temperatures. Studies on unstable boundaries are quite active in various systems such as ferroic domain walls or fluid invasion in porous media. [4,5] However, those studies are lacking in the area about the topotactic transition or electrocoloration in spite of its importance in technological applications.

DT09.25

Effect of Molybdenum Concentration in $\text{SrFe}_{1-x}\text{Mo}_x\text{O}_{3-\delta}$ on Transport Properties and Kinetics of CO_2 Reduction Ahmad Shaur and Bernard Boukamp; Universiteit Twente Faculteit Technische Natuurwetenschappen, Netherlands

High-temperature solid oxide cells (SOCs) can electrochemically convert the greenhouse-gas CO_2 to CO and O_2 , which are valuable building blocks for chemical production and other related applications. In recent times, $\text{SrFe}_{0.75}\text{Mo}_{0.25}\text{O}_{6-\delta}$ has been identified as a most promising cathode material for the CO_2 reduction reaction. Partial substitution of molybdenum for iron in parent $\text{SrFeO}_{3-\delta}$ has been used to enhance its stability and CO_2 resistance. Herein, we investigate the effect of molybdenum concentration on transport properties and electrochemical performance of $\text{SrFe}_{1-x}\text{Mo}_x\text{O}_{3-\delta}$ ($x=0.05, 0.15, 0.25, 0.30$). Chemical diffusion coefficients and surface exchange coefficients of the materials are extracted from data of electrical conductivity relaxation. Data of electrochemical impedance on symmetrical cells is used to tailor the molybdenum concentration for efficient CO_2 electrolysis. Transformation of impedance data into a distribution function of relaxation times (DFRT) is used to gain insight into the elementary steps through which CO_2 reduction takes place.

DT09.26

Observation of Multi-Level Ionic Conductivity in Ca-Doped Bismuth Ferrite Thin Films Jeonghun Suh, Ji Soo Lim, Heung-Sik Park and Chan-Ho Yang; Korea Advanced Institute of Science and Technology, Korea (the Republic of)

Understanding oxygen vacancy transport is the cornerstone for a variety of future applications. Ca-doped bismuth ferrite is a promising material for studying collective ionic migration in solids¹⁻³. We conduct impedance analysis with different magnitudes of AC voltage to understand the ionic conduction mechanism of this material. To suppress the electronic contribution to the conductivity, we annealed the sample in a reducing condition at elevated temperatures before the measurement. By using the equivalent circuit model of a mixed conductor, we obtain ionic conductivity, which shows a multi-level feature. This result shows consistency with the observation from electroforming experiments with DC voltages. This work provides useful insight into the ionic conduction mechanism in solids.

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DT09.27

Thermodynamic and Electrochemical Stability of the $\text{Bi}_{1-x}\text{Pr}_x\text{O}_{1.5}$ Rhombohedral System Jan Jamroz¹, Wojciech Wrobel¹, Marcin Malys¹, Isaac Abrahams² and Franciszek Krok¹; ¹Politechnika Warszawska, Poland; ²Queen Mary University of London, United Kingdom

Bismuth oxide-based compounds exhibit excellent electrical properties and for many years have attracted the attention of many research groups [1]. Special attention was paid to the highly conductive fluorite $\delta\text{-Bi}_2\text{O}_3$ type phases, typically stabilized to room temperature by aliovalent metal cation doping. However, in the case of lanthanide dopants of large ionic radius, a rhombohedral β phase is observed rather than the cubic d-type phase. These rhombohedral phases exhibit high ionic conductivity, but additionally are more resilient to long-term annealing, compared to $\delta\text{-Bi}_2\text{O}_3$ based fluorites [2]. The exact nature of the ordering processes responsible for observed instabilities are not fully understood. In this work the stability of structural and electrical properties of the rhombohedral system $\text{Bi}_{1-x}\text{Pr}_x\text{O}_{1.5}$ over long-term annealing and in reducing atmospheres is investigated.

Compounds of general formula $\text{Bi}_{1-x}\text{Pr}_x\text{O}_{1.5}$ ($x = 0.200; 0.250; 0.325$) were synthesized by a solid-state reaction method. Prepared samples show high densities above 95% of theoretical values. XRD data and impedance spectroscopy data were collected over the temperature range 25 – 800 °C in various atmospheres – ambient air, Ar, N_2 and H_2 .

Studies of aging-resistance of structural and electrical properties of $\text{Bi}_{1-x}\text{Pr}_x\text{O}_{1.5}$ over long-term annealing were conducted. During annealing at 650 °C, total conductivity drops asymptotically reaching ca. 70 – 80 % of the initial value after 800 h, depending on composition. Structural data investigated by X-ray diffraction, collected during long term annealing revealed that while the basic rhombohedral structure is preserved, a minor change of a lattice size is observed. This structural change is correlated with changes in total conductivity. The character of these changes may imply an ordering of the oxide ion sublattice during annealing. Structural and electrical properties were also investigated in various atmospheres. No changes in total conductivity and in structure were observed during measurements in neutral atmospheres (Ar, N_2). Details of the oxide ion redistribution are presented in this work.

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DT09.28

Setting up a Multi-Analytical Tool for Pulsed Laser Deposition (i-PLD) Tobias M. Huber^{1,2}, Mathäus Siebenhofer^{1,3}, Christin Boehme¹, Alexander Schmid¹, Christoph Riedl¹, Andreas Nennung¹, Alexander K. Opitz¹, Markus Kubicek¹ and Juergen Fleig¹; ¹Technische Universität Wien, Austria; ²Huber Scientific, Austria; ³Center for Electrochemistry and Surface Science, Austria

In situ electrochemical impedance spectroscopy (EIS) during thin film growth by pulsed laser deposition process (i-PLD) is an advanced technique to investigate and electrochemically characterize ceramic thin films. This method allows the observation of dense thin films unaltered by degradation and provides information about the oxygen exchange kinetics as well as the defect chemistry of pristine thin films in its cleanest possible state.

PLD features:

As in a standard PLD deposition various parameters can be altered: Temperature, gas environment and pressure, laser fluence, target to sample distance, film material composition and thickness. Additionally the i-PLD setup allows to polarize illuminate, electrically characterize the growing thin film sample and determine the deposition rate in sub monolayer range online.

The investigated samples can be changed by additional layers and the surface can repeatedly be altered. Instead of chemical post-analysis of degraded thin films, the thin film electrode surface can be deliberately changed by depositing defined amounts of its constituents and multilayers can be deposited to stain the material, change the surface oxygen exchange kinetics or the oxygen transport properties. Degradation effects from gas phase impurities can be studied in defined environment.

Electrochemical characterization:

The heart piece of the setup is the electrochemical characterization with up to 10 electrodes that allows to monitor the growing thin film and manipulate it in real time. Many different techniques and sample geometries are used for different purposes: (i) **Classical cross plane two electrode EIS measurements** are the most used technique. The main challenge for this geometry is to find a suitable counter electrode with fitting capacitance and resistance values (ii) **Three-terminal EIS measurements** where we overcome the problem of properly positioning the reference electrode (RE). It is discussed that three potential error sources are particularly crucial: Asymmetric sample cells, short circuit currents across the RE, and capacitances between the three electrodes. The “wing geometry” is used which minimizes the measurement errors significantly. This geometry is applied to YSZ based electrochemical cells in the i-PLD (iii) **In plane EIS measurements** to characterize thin films in lateral direction (iv) Miniaturized electrodes (size variation and microelectrodes) (v) Polarization experiments and **Current-Voltage measurements** (vi) DC measurement methods such as **Van-der Pauw**.

Advanced tools:

Although i-PLD is a very useful in-situ tool to grow, tune and characterize thin film samples, knowing the exact amount of deposited material is key to i-PLD analysis. To measure deposition rates of PLD thin films are often time consuming and complicated. In many cases, the film is moved outside vacuum to measure its thickness, commonly by optical or cross-sectional electron microscopy, diffraction, profilometry, or Rutherford back scattering spectrometry. These approaches are most times destructive not suitable for fragile and hygroscopic materials and often time consuming and error-prone. To control the exact amount of material deposited down to sub atomic layer is crucial for nanoscale technologies based on thin-film heterostructures. A very accurate measurement solution is to use a **quartz crystal microbalance (QCM)** to measure the deposited amount of material directly in the PLD chamber. Sputter rates depend on many parameters such as pressure, fluence, and target to substrate distance additionally the plasma plume is directional. To ensure an accurate thickness characterization the QCM is placed at the exact same position as the substrate during PLD growth with the exact same deposition parameters.

This design enables **precise measurements of growth rates** and provides accurate quantification without breaking vacuum which can be used to quantitatively tune the surface composition of multicomponent oxide materials.

DT09.29

Application of Neutron Multi-Scale Structure Measurement to Structure Analysis of Cell Materials Haruyuki Takahashi, Hideaki Ichimura, Nana Fukaya, Takumi Inada, Yohei Noda and Satoshi Koizumi; Ibaraki Daigaku Kogakubu, Japan

Physical properties of ion-conducting composites and electrode materials are greatly affected not only by the crystal structure but also by the microstructure of the surface and interface. It is also important to measure the structures of multiple phases in the laminated cell simultaneously. Neutron diffraction is a powerful tool for the structure determination because of its high transmittance. Ibaraki Materials Design Diffractometer (iMATERIA) installed in J-PARC is a TOF type neutron diffractometer having four detectors: small-angle, low-angle, 90 degree and backward. The small angle scattering experiment for the micro-scale structure analysis and the high-resolution diffraction measurement for the crystal structure analysis can be made by iMATERIA. So, iMATERIA is useful for the multi-scale structure analysis of composites and electrode materials. The small-angle scattering, and the backward diffraction measurements are performed exclusively at present, because the backward detector is masked by the focusing slit equipped at the upper stream of neutron beam for the small-angle measurement. The simultaneous multi-scale measurement is important to shorten the measuring time and perform the operando-measurement. For that, it is necessary to set up the focusing slit at the vicinity of the sample position and to prepare the focusing slit from glassy materials to avoid the diffraction from the slit. In this study, high neutron absorbing glasses for the focusing slit were developed. Then the neutron multi-scale measurement system using glassy focusing slit was applied to the structure analysis for fuel cells and lithium-ion cells.

High neutron absorbing glasses were explored using elements possessing high neutron absorption cross-section. B₂O₃ as a glass-forming oxide, Li₂O and Gd₂O₃ as glass-modified oxides were chosen as neutron absorbing species. The neutron absorption cross-section of gadolinium is outstanding. Therefore, the gadolinium content in the glass is essential for the neutron absorption. SiO₂ was added to improve the chemical and mechanical stability of glasses. The glass-forming region in B₂O₃-SiO₂-Li₂O-Gd₂O₃ quaternary system was examined. Glasses including 30mol% Gd₂O₃ were successfully synthesized by press quenching method. On the other, samples including 10mol% Gd₂O₃ were vitrified as large-size board in air cooling. Then Glass with 10mol% Gd₂O₃ was formed to the focusing slit. Preliminary result shows that the neutron transmittance at 1 Å in 10mol% Gd₂O₃ glass is less than 0.1%. The transmittance in purchased borosilicate glass is around 20%. High neutron absorption in home-made Gd containing glass was verified. The neutron multi-scale measurement system using glassy focusing slit was applicable to the wide-q range structure measurement from 0.01 to 10 Å⁻¹.

The structure change of Ni-YSZ anode by repeated redox cycling at 850°C was investigated. Neutron diffraction profiles show the monoclinic phase appears at the first redox cycling. It is considered that a part of tetragonal phase of YSZ transforms to the monoclinic phase by the oxidation of Ni. The small angle scattering intensity increases with redox cycle. It corresponds to the increase of the grain boundary by the appearance of the monoclinic phase. Therefore, it is concluded that the small angle scattering data provides supplementary information on the diffraction data.

DT09.30

Thin-Film Oxide Electrodes with Varying Conductivity for High-Temperature Piezoelectric Resonators Hendrik Wulfmeier, Sebastian Schlack, René Feder and Holger Fritze; Technische Universität Clausthal, Germany

The availability of high-temperature and chemically stable devices for monitoring and controlling of high-temperature processes is a key requirement for efficient and environmentally friendly industrial production or energy conversion. Piezoelectric resonators based on oxide single crystals fulfil these requirements being mechanically and chemically stable in both oxidizing and reducing atmospheres even at temperatures of 1000 °C and above. However, the degradation of commonly used metal electrodes at elevated temperatures is often the primary failure mechanism as it may affect the performance of the piezoelectric resonators. Thin-film noble metal electrodes of Pt, Rh, Ir or their alloys are operational at temperatures up to e.g. 900 °C in case of Pt [1].

Typical degradation mechanisms include oxidization, agglomeration or evaporation of the metal films [2]. Oxide electrodes are expected to overcome these concerns. However, they suffer from low electrical conductivity in comparison to metal electrodes. A promising approach is to use doped oxide films resulting in increased electrode conductivities. Here, it is crucial to understand how resonator properties like effective resonator area and vibration characteristics are affected by the conductivity and thus defect and transport mechanisms in the electrodes.

Other problems may arise from differences in thermal expansion between oxide electrodes and piezoelectric resonators. Those could be minimized if the resonator and electrodes consist of identical or similar materials. Accordingly, the objective of this work is to create oxide electrodes, in particular, nearly monolithic resonators in which the electrodes also consist of the resonator material, but which is highly doped.

Resonator materials used in the present work are langasite family single crystals, in particular catangasite (CTGS, $\text{Ca}_3\text{TaGa}_2\text{Si}_2\text{O}_{14}$) and langasite (LGS, $\text{La}_3\text{Ga}_5\text{SiO}_{14}$). To form electrodes they are partially doped with Sr. Moreover, CTGS and LGS single crystals exhibit similar lattice constants. Therefore, doped LGS films are deposited on CTGS crystals to form nearly monolithic electrodes, as confirmed by XRD. The great advantage of CTGS resonators is their significant lower conductivity compared to LGS. This combination enhances the conductivity difference between doped LGS electrodes and the resonator material even more. Two major aspects are addressed: First, the growth of high-quality undoped and doped LGS thin-film electrodes by pulsed laser deposition (PLD) and, second, the characterization of the resulting nearly monolithic resonator devices. Homo- and hetero-epitaxial films are grown by PLD. High substrate temperatures (450–750 °C) are applied to obtain crystalline films. Ga evaporation during thin-film deposition as occurring here is a common phenomenon. It is compensated by an increased p_{O_2} (10^{-3} – 10 Pa) in the deposition chamber and by an increased Ga content in the PLD targets whose Ga content is three times as high in comparison to stoichiometric LGS. Crystallinity and stoichiometry of the films are confirmed by X-ray diffraction and secondary neutral mass spectrometry (SNMS).

Based on optimized growth parameters for the undoped films, Sr-doped LGS thin films are grown. Here, 33 % of La in the target composition is substituted by Sr. The film conductivity is increased by one order of magnitude compared to nominally undoped bulk LGS. Keyhole-shaped Sr-doped LGS electrodes are deposited on both sides of CTGS resonator blanks. The resonance behaviour of such nearly monolithic resonators is evaluated in the temperature range from 600 to 1000 °C and compared to that of CTGS resonator blanks. These resonators show stable operation and high resonator quality factors of 1200 even at 1000 °C.

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DT09.31

Investigating the Impact of the Microstructure on the Charge Transport in Microstructured Ceria Thin Films [Jan L. Dornseifer](#), Janis K. Eckhardt, Matthias T. Elm, Christian Heiliger and Peter J. Klar; Justus Liebig Universität Giessen, Germany

Polycrystalline thin films with electronic and/or ionic conductive properties have a wide range of applications ranging from energy applications to gas sensing. These devices and their applications require in addition to a careful materials selection an optimized microstructure. The microstructure has an enormous impact on electrical properties.

Impedance spectroscopy (IS) is one of the most powerful and frequently used experimental tools for the characterization and analysis of charge transport properties of novel mixed conducting materials. In IS measurements, the excitation signal consists of a sinusoidal AC-signal in form of a voltage or current. Thereby, the phase difference as well as the amplitude of the response signal is measured as a function of the frequency of the excitation signal. Individual transport processes within the material can be distinguished in the frequency domain if their characteristic frequencies differ. These transport mechanisms can also be resolved in the time domain by calculating the distribution of relaxation times (DRT) of the impedance.

In the standard analysis, so-called equivalent circuits are used for analyzing experimental impedance spectra. Thereby, the impedances of equivalent circuits with a few components are calculated and fitted to the measured data. This results in macroscopic transport quantities, i.e., resistances, capacitances and inductances. Theoretical models are inevitable in order to correlate these macroscopic properties to microscopic transport mechanisms. The currently established models lack of accuracy since the effects of the microstructure on the macroscopic transport properties are not precisely known yet.

Here, we show that the microstructure in polycrystalline cerium (IV)-oxide (ceria) thin films has a significant impact on the impedance spectra. An experimental approach is developed which enables to electrically contact single ceria microstructures/ agglomerates with an extension of 70 – 200 µm consisting of several grains. These ceria microstructures have defined transport pathways which can be easily identified by optical microscopy. Thus, the correlation of the measured impedance data with the underlying microscopic transport mechanisms is facilitated. A one-to-one correspondence between impedance spectra and structure can be established by computer-aided simulations based on an impedance network model. Thereby, the microstructure of the ceria agglomerates is accurately mapped and implemented. The results demonstrate that the arrangement of grains along individual transport paths cause additional signals in the DRT that are not related to any transport mechanisms as a local property, but arise from the global interplay of the transport paths of the network in the material.

DT09.32

Ionic Conductivity of a Thin Film YSZ Layer on a GDC Substrate [Isabel Fernandez Romero](#)^{1,2}, Stefanie Taibl² and Juergen Fleig²; ¹Robert Bosch GmbH, Germany; ²Technische Universität Wien, Austria

Solid oxide cells (SOFC and SOEC) have gained much interest over the last decades, leading to further research on suitable materials in order to reduce their operational temperature. Some of the most promising anode materials of solid oxide fuel cells are those with a mixed ionic/electronic conduction (MIEC), such as Ni/Gadolinia-Doped Ceria (GDC) composites. For the electrolyte material, 8 mol% Ytria-Stabilized Zirconia (YSZ) is typically used as it can block the electronic conduction present in the anode while maintaining good ionic conduction. It is of high interest to determine the properties of YSZ electrolyte layers in dependence of their thickness and preparation procedure in order to reduce the electrical resistance of the solid oxide cells.

However, depending on the substrate the determination of (across-plane) YSZ thin film properties is far from trivial. In principle, Electrochemical Impedance Spectroscopy (EIS) is a well-established technique which allows to differentiate the contribution of different migration mechanisms throughout a given structure. Still, it is often non-trivial to correlate individual impedance features with the ionic/electronic conductivities of individual processes or materials as the peak frequencies of migration mechanisms may have similar values. This is the case for a YSZ thin film electrolyte on a GDC substrate, as the grain and grain boundary ionic conduction of GDC and YSZ result in the superposition of their impedance features, which cannot be unambiguously separated by means of an equivalent circuit.

In this contribution, a non-destructive and reversible method will be presented for isolating the properties of YSZ thin films on GDC substrate by EIS. Our

approach makes use of the strongly increased electronic conductivity of GDC in hydrogen atmosphere. This method is employed to measure the conductivity and activation energy of different YSZ films with thicknesses between 200 nm and 2000 nm. Reactive High Impulse Power Magnetron Sputtering (rHiPIMS) was used to deposit the YSZ films on top of a polycrystal GDC substrate with a thickness of approximately 0,7 mm. The deposition method leads to high energies with which the target atoms reach the substrate, increasing the film density and favoring a columnar growth of the film. The measured conductivities are correlated with the microstructure of the resulting films.

SESSION DT10: Exsolution
Session Chair: Alexander Opitz
Tuesday Morning, July 19, 2022
Mezzanine Level, Second Floor, Georgian

9:10 AM **DT10.01

New Strategies to Overcome the Limitations of Nanoparticle Ex-Solution WooChul Jung; Korea Advanced Institute of Science and Technology, Korea (the Republic of)

The ex-solution phenomenon, a central platform for growing metal nanoparticles on the surface of host oxides in real time with high durability and a fine distribution, has recently been applied to various scientific and industrial fields, such as catalysis, sensing, and renewable energy. However, the high-temperature processing required for ex-solutions (>700 °C, especially with hydrogen gas) limits the applicable material compositions and has hindered advances in this technique.

This presentation introduces two novel material strategies to address this issue. The first is to promote the formation of metal nanoparticles by inducing a phase transition of the host oxide. As a case study, we selected WO₃ and Ir as parent oxide and active metal species, respectively, and demonstrated that Ir doping facilitates a phase transition in the WO₃ bulk lattice, which further promotes Ir ex-solution at the oxide surface and eventually enables the formation of Ir particles (< 3 nm) at temperatures as low as 300 °C. The second strategy is to generate exsolved particles in an oxygen atmosphere with only water vapor. The idea underlying this strategy is the hydrogenation reaction that occurs in triple-conducting oxides that simultaneously carry protons, oxygen ions, and electron holes and the subsequent reduction of transition metals. Here, Ag-substituted BaCo_{0.4}Fe_{0.4}Zr_{0.1}Y_{0.1}O_{3-δ} was chosen as a model system, and we succeeded in spontaneously forming Ag nanoparticles on the host oxide surface by supplying water vapor and achieving a high-performance electrode for protonic ceramic fuel cells. These material strategies open up new possibilities for further expanding the applications of the current ex-solution technique.

9:40 AM DT10.02

Metal Exsolution Dynamics at Complex Oxide Surfaces Moritz L. Weber^{1,2,3}, Bretislav Smid⁴, Sarah Fearn², Uwe Breuer¹, Marc-André Rose^{1,5,3}, Jia Guo², Andrea Cavallaro², Liam Yasin², Samuel J. Cooper², Norbert H. Menzler^{1,3}, Stephen J. Skinner², Regina Dittmann^{1,5}, Rainer Waser^{1,5,3}, Ainara Aguadero^{2,6}, Olivier Guillon^{1,3,7}, Felix Gunkel^{1,5} and Christian Lenser¹; ¹Forschungszentrum Julich GmbH, Germany; ²Imperial College London, United Kingdom; ³Rheinisch-Westfälische Technische Hochschule Aachen, Germany; ⁴Univerzita Karlova Matematicko-fyzikalni fakulta, Czechia; ⁵Juelich-Aachen Research Alliance (JARA-FIT), 52425 Juelich, Germany, Germany; ⁶Instituto de Ciencia de Materiales de Madrid, Spain; ⁷Juelich-Aachen Research Alliance (JARA-Energy), Germany

The concept of metal exsolution attracts much attention for the synthesis of nanostructured catalysts. Thermal reduction of doped perovskite parent oxides results in the migration of reducible cations from the oxide bulk to the surface, forming metallic nanoparticles that serve as catalytic centers. Ideal exsolution-type catalysts therefore dynamically adapt with respect to the oxygen chemical potential. The parameters that influence the kinetics of nanoparticle exsolution however, remain an open question in the scientific community.

We employ epitaxial thin films model systems with atomically defined surfaces to investigate the exsolution response of Ni in SrTi_{0.9}Nb_{0.05}Ni_{0.05}O_{3-δ}. While bulk properties of exsolution-active perovskites can be tuned to tailor the exsolution behavior (Weber, M. L. et al., ACS nano, 2021), our investigations show that most importantly the defect chemistry of the near-surface region determines the dynamics of the exsolution response.

In order to assess the dynamic changes in the surface chemistry during metal exsolution, we conduct *in-situ* near ambient pressure photoelectron spectroscopy. In addition, ¹⁸O oxygen labelling is used to investigate the oxygen exchange properties of exsolution-active perovskites of *n*-type and *p*-type doping by time-of-flight secondary ion mass spectrometry. In accordance with the nature of the dopants, strong differences in the oxygen exchange characteristics are detected in the perovskite bulk, while the oxygen exchange characteristics in the near-surface region are considerably influenced by the formation of space charge regions.

We conclude that the nanoparticle self-assembly at the perovskite surface is surface-controlled by interaction with the energy landscape of the complex oxide surface. Derived from our investigations, we propose a mechanistic model that describes how metal exsolution is mediated by the surface defect chemistry. Moreover, we demonstrate surface engineering of the topmost atomic layers can be utilized as a novel strategy for the active control of the exsolution behavior (Weber, M. L. et al., under review, 2021).

9:55 AM *DT10.03

Exsolution—Rethinking the Role of Nanoparticles in Materials Dragos Neagu; University of Strathclyde, United Kingdom

Nanoparticles have become an established component of catalyst and energy materials due to their role in speeding up chemical transformations. Conventionally, nanoparticles are produced by deposition methods, but over the last decade, a new method, redox exsolution has emerged, providing not only an alternative to their growth, but also numerous functional advantages. Exsolved particles are socketed and therefore much more resistant to coking under hydrocarbon environment and more resistant to sintering. They can be produced under reducing gas but also electrochemically, in situ, in a matter of seconds, resulting in highly active electrochemical cells for power generation or hydrogen production. Other applications include membranes, sensors, chemical looping and memristors. Overall, exsolution redefined what we should expect from nanoparticles in both role and functionality. Today exsolution is a rapidly growing field, with over 500 papers having been published across many areas of application.

This talk will introduce and discuss how nanoparticle exsolution may have led us to discover an entirely new role for nanoparticles – not only as catalytic centres but as strain centres within materials. Strain is an artificial distortion of a material's crystal structure induced by depositing it as a thin film on a

substrate in an epitaxial manner (crystallographically aligned). Strained materials often display order-of-magnitude enhancement in transport properties such as ion conduction. Within materials, exsolved nanoparticles seem to serve a similar role, straining the surrounding lattice and boosting its ion conduction, as evidenced by our experimental results and theoretical models. This opens an entirely new chapter in the role nanoparticles serve, as strain centres and acting as matrix-deforming conduits for ion transport within materials.

10:15 AM DT10.04

Quantitative Correlation of Surface Cation Segregation and Surface Activity of Sr(Ti,Fe)O_{3-δ} Through Microscopic Observation [Hyunseung Kim](#)¹, Kyuseon Jang¹, Bonjae Koo^{1,2}, Jun Kyu Kim¹, Jongsu Seo¹, Pyuck-Pa Choi¹ and WooChul Jung¹; ¹Korea Advanced Institute of Science and Technology, Korea (the Republic of); ²Sungshin Women's University, Korea (the Republic of)

Perovskite oxides, having the chemical formula of ABO₃, with mixed conductivity have attracted much attention as electrode materials for electrochemical conversion applications such as solid oxide fuel/electrolysis cells, oxygen permeation membranes, and metal-air batteries. They are featured for their high electronic/ionic conductivity and catalytic activity for oxygen reduction/evolution reactions. However, performance degradation due to structural and chemical instability at their surfaces remains a severe issue.

Although surface cation segregation, especially Sr segregation, is known as the representative reason for the degradation phenomenon of perovskite-based oxide electrodes, a clear understanding of the following questions is still lacking: how does Sr segregation occur, and how does it affect the electrode activity. One of the reasons for the ambiguity is that the perovskite oxide surfaces already experience Sr segregation during preparation due to the high-temperature processes. These already-segregated surfaces hinder the precise investigation of the intrinsic properties of perovskite oxide surfaces and the correlation of Sr segregation and surface activity.

In this study, an atomically-flat model thin-film system of SrTi_{0.5}Fe_{0.5}O_{3-δ} (STF), a representative air electrode material, was constructed and observed through angstrom-level-resolution surface analysis equipment such as AFM, APT, and HR-TEM, while the surface activity was characterized by electrical conductivity relaxation. Based on these efforts and supported by computational calculations, the initial processes of Sr segregation were studied, followed by the measurement of the intrinsic activity of STF and the quantitative relationship between Sr segregation and surface oxygen exchange kinetics.

SESSION DT11: Battery Materials, Anode

Session Chair: Don Siegel

Tuesday Morning, July 19, 2022

Mezzanine Level, Second Floor, Arlington

9:10 AM **DT11.01

Solid-State Batteries—An Electrode Challenge Dominic Spencer Jolly¹, Ziyang Ning¹, Xiangwen Gao^{1,2}, Guanchen Li^{1,2}, Dominic L. Melvin^{1,2}, T. James Marrow¹, Charles Monroe^{1,2} and [Peter G. Bruce](#)^{1,2,3}; ¹University of Oxford, United Kingdom; ²The Faraday Institution, United Kingdom; ³The Henry Royce Institute, United Kingdom

Despite the advent of solid electrolytes with significantly higher conductivities in recent years, a number of challenges still face the all-solid-state battery based on a Li metal anode, a ceramic electrolyte and an intercalation cathode. While such devices can be made to cycle at low rates, low capacities and high pressures, in practice current densities of several mA/cm² and stack pressures of 2 MPa or less are likely required for many applications. Many of the challenges lie at the electrodes.

We have shown that voids form in the Li metal on discharge (lithium anode stripping) when the rate of Li⁺ transport away from the Li/solid electrolyte interface exceeds the rate of Li transport in the Li metal to the interface. The voids grow in magnitude and number on cycling, leading to high local plating current densities on charging (lithium anode plating), Li dendrite (filament) penetration of the ceramic, cracking and short circuit. The Li metal transport is dominated by creep, therefore high temperatures even at low pressures can enable stable cycling at several mA/cm². Operando X-ray tomography has revealed how Li dendrites initiate then propagate through the ceramic and drive cracking from the rear of the crack, not the crack tip. Models for dendrite initiation and propagation will be described that explain the observations, and the implications for the rational design of solid electrolytes will be discussed. For the same reasons as in liquid electrolyte cells, the solid-state cathode is a composite of the solid electrolyte, the active material (e.g.

LiNi_{0.8}Co_{0.1}Mn_{0.1}O₂) and carbon. The performance of the composite cathode will be discussed, including the role of the composition, ion and electron transport and volume changes on the cathode performance.

9:40 AM DT11.02

Atomistic Simulations of Transition Metal Niobates as Next-Gen Battery Electrodes Benedict Saunders, Tanmoy Chakraborty, Wilgner L. da Silva, Alexandru Tanase, Richard I. Walton and [Bora Karasulu](#); University of Warwick, United Kingdom

High-rate electrode materials are needed to accelerate the adoption of electric vehicles by increasing power density and shortening charging times. Ternary niobium-based metal oxides, namely MNb₂O₇ (M: various transition metals) have attracted great attention due to their potential use as high-rate, high-capacity anodes and cathodes in lithium-ion battery (LIB) technology [1]. Lack of detailed knowledge on the disordered crystal structures of these chemically-doped niobate variants, however, currently limits their development [2], thus calling for conclusive in-depth investigations of structure–property relationships that combine computational and experimental efforts.

In this talk, I will discuss the density functional theory (DFT) simulations of various niobates containing a selection of transition metals (including V and Fe), and first-principles characterisation of their structural, electrochemical, and spectroscopic properties in connection with the in-lab measurements and testing. In addition, I will elaborate on our efforts in discovering novel niobate phases via high-throughput crystal structure predictions using the *ab initio* random structure searching (AIRSS) method [3], while introducing the new electrode materials that were consequently synthesised in the lab and demonstrated to have superior electrochemical performance.

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[2] Shen et al., *Mater. Horiz.*, 2021, 8, 1130–1152;

[3] C. J. Pickard, R. J. Needs, *PRL* 97, 045504 (2006);

9:55 AM *DT11.03

The Dynamic Local Chemistries at the Interfaces of All-Solid-State Batteries with Alkali Metal Anodes Edouard Querel¹, Rowena Brugge¹, Federico M. Pesci¹, Andrea Cavallaro¹, Nomaan Nabi¹, Ieuan D. Seymour¹ and [Ainara Aguadero](#)^{2,1}; ¹Imperial College London, United Kingdom; ²Consejo Superior

de Investigaciones Científicas, Spain

Solid-state batteries (SSBs) with alkali metal anodes hold great promise as energetically dense and safe alternatives to conventional alkali-ion cells. Form the different solid electrolytes, oxides present the advantage of displaying high alkali ion mobilities and good electrochemical stability window, allowing a priori, the use of alkali metal anodes and high voltage cathodes. Whilst bulk Li and Na ion dynamics have been optimised reaching values close to that of liquid electrolytes¹ the solid/solid (both grain boundaries and metal/solid electrolyte heterogenous) interfaces require much further understanding an optimisation². Local chemical and structural changes can lead to inhomogeneous current distribution affecting the electrochemical performance and promoting premature cell dead^{3,4}. An additional challenge is to accurately measure chemical inhomogeneities that can range in the nano to microscopic scale and that might be affected by processing history, cycling and measurement conditions. In the present work, we analyse intrinsic chemical inhomogeneities in solid electrolytes and evaluate the dynamic nature of the interfacial chemistry. We focus on the study of grain boundary composition and the formation of interphases at the Li(Na)/solid electrolyte interfaces using a combination of *ex situ* and *operando* surface analysis techniques. We probe that the complex nature of these systems requires a systematic analysis of different external factors that are contributing to electrochemical and chemical degradation of the interfaces and that the control of the interfacial composition is a powerful tool to optimise the life and performance of all-solid-state alkali-metal batteries.

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3. Quérel, E. *et al.* The role of NaSICON surface chemistry in stabilizing fast-charging Na metal solid-state batteries. *J. Phys. Energy* **3**, 044007 (2021).
4. Pesci, F. M. *et al.* Establishing Ultra-Low Activation Energies for Lithium Transport in Garnet Electrolytes. *ACS Appl. Mater. Interfaces* *acsami.0c08605* (2020) doi:10.1021/acsami.0c08605.

10:15 AM DT11.04

Highly-Conducting Alluaudite-Type Nanocrystallized Glass-Ceramics for Sodium-Ion Batteries [Maciej Nowagiel](#), Mateusz J. Samsel, Aldona Zalewska and Tomasz K. Pietrzak; Politechnika Warszawska, Poland

Application of renewable power sources (e.g. wind and solar power plants) carries new challenges concerning energy storage. One of the remedies to stabilize their output is the utilization of battery storage stations. In this field, sodium-ion batteries (NIBs) are expected to be a sustainable and cheap alternative to lithium ones [1]. Alluaudites, first described by Fisher in 1955 [2], are among prospective cathode materials for NIBs, with the theoretical gravimetric capacity close to 170 mAh/g [3]. Poor electrical conductivity is one of the main obstacles to their implementation.

Alluaudite structure can be adopted by various compounds. In our research, we studied materials with nominal composition of $\text{Na}_2\text{Fe}_3(\text{PO}_4)_3$, $\text{Na}_2\text{Fe}_2\text{V}(\text{PO}_4)_3$ and $\text{Na}_2\text{FeMnV}(\text{PO}_4)_3$. Some of these compositions have been synthesized for the first time. Thermal treatment of glassy samples led to nanocrystallization of alluaudite phase [4]. Previous studies on amorphous analogues of cathode materials for Li-ion batteries show a significant increase of electrical conductivity as a result of their thermal nanocrystallization, due to the occurrence of the preferable conditions for polaron hopping mechanism of conduction [5]. We have shown that a similar procedure can be successfully applied to sodium compounds as well. We observed a significant (5 orders of magnitude) and irreversible increase of conductivity, which resulted in nanomaterials with $\sigma(25^\circ\text{C}) \approx 1 \text{ mS/cm}$. We also elaborated optimal syntheses conditions to obtain alluaudite-like nanomaterials with maximum possible phase purity. The following parameters were taken into account: reagents used, presynthesis of the reagents, melting temperature, cooling rate, role of reducing atmosphere [6]. Optimization of nanocrystallization process allowed us to assemble and test our materials as cathodes in prototype sodium-ion cells.

Acknowledgements

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SESSION DT12: Solid/Liquid
 Session Chair: Till Frömling
 Tuesday Morning, July 19, 2022
 Mezzanine Level, Second Floor, Georgian

11:00 AM **DT12.01

Designing Novel Electroactive Materials by an Electrolyte Engineering Approach [Alexis Grimaud](#); Collège de France, CNRS, France

The design of electroactive materials for application such as Li-ion batteries or water electrolyzers has long thrived from the establishment of guiding principles relying on physical and chemical properties of bulk and/or surfaces of solids. Nevertheless, integrating redox active materials into practical devices require a perfect control over ions and electrons transfer at the liquid/liquid interface. Bearing in mind that this interface is dynamic in time, space and as function of applied potential, difficulties arise in characterizing solids under operation. Towards that goal, reactivity of solids with liquid electrolytes can be manipulating. For instance, we recently demonstrated that layered compounds known for their bulk intercalation properties in Li-ion batteries can be reacted with aqueous electrolytes to form novel hydrated phases. This reaction, occurring upon oxygen evolution reaction (OER), rely on the reversible intercalation of hydrated cations which enhance the OER kinetics while avoiding surface degradation, as visualize by post mortem characterization techniques as well as by fast Raman spectroscopy under operando conditions. Furthermore, we recently demonstrated that transition metal halides, vastly studied for their magnetic and electronic properties, can be used as Li^+ intercalation compounds despite their extreme solubility in classical carbonate solvents used in Li-ion batteries. For that, superconcentrated electrolytes were used, in which halides were shown to be stable. Owing to this stabilization, novel Li_xVX_3 ($\text{W} = \text{Cl, Br or I}$) compounds were thus prepared with tunable magnetic properties.

11:30 AM DT12.02

Impact of Molecular Water on the Defect Chemistry of LiSCN—A Pseudohalide with Nonspherical Anion Markus Joos¹, Maurice Conrad², Rotraut Merkle¹, Thomas Schleid² and Joachim Maier¹; ¹Max-Planck-Institut für Festkörperforschung, Germany; ²Universität Stuttgart, Germany

In the series of lithium halides, which are all Li⁺ cation conductors via lithium vacancies (Schottky defects), the conductivity increases systematically with increasing halide radius from LiF to LiI. Based on this, one might expect a high conductivity also for LiSCN, which can be regarded as a pseudohalide with large anion. However, it turns out that the anisotropic structure of the SCN⁻ anion and its asymmetric interaction strength with Li⁺ via S or N strongly affect the defect chemistry and transport properties.

Anhydrous LiSCN has a comparably low Schottky defect formation enthalpy (0.6 eV). Its DC ionic conductivity is low due to a remarkably high migration enthalpy of V_{Li} (0.9 eV), because a Li⁺ jump requires substantial structural relaxation of the environment, which slows down long-range transport.

LiSCN can reversibly incorporate and release water,^[1] which has significant effects on the V_{Li} transport. Water contents of $x \approx 1000$ ppm (LiSCN • x H₂O) suffice to raise the conductivity by ~3 orders of magnitude. In these substoichiometric amounts, water acts as a donor dopant (H₂O[•]_{SCN}) and strongly increases the concentration of lithium vacancies. In contrast to other dopants, the water incorporation also increases the mobility of lithium vacancies by lowering the migration enthalpy to 0.5 eV, even at very low water concentrations. At low temperatures, strong association of H₂O[•]_{SCN} with V_{Li} decreases the conductivity. A comprehensive and quantitative defect-chemistry model is derived, including defect formation enthalpies and migration barriers.

When the hydration level is increased to stoichiometric values, the mono- and dihydrate (LiSCN • n H₂O, n = 1 and 2) form. In case of the monohydrate, ion transport is determined by defect associates, causing an exceptionally high activation enthalpy (> 2 eV). Due to the low melting point of the dihydrate (38 °C) and the possibility of supercooling, the conductivity of two-phase mixtures of mono- and dihydrate is determined by percolating molten dihydrate within the solid matrix of the monohydrate, and reaches 7×10^{-4} S/cm at 25 °C.^[2]

This investigation on molecular water incorporation in LiSCN provides new insights into the properties of hydrated materials in the field of solid state ionics. A new concept for water uptake is discovered, i.e. water can act as a dopant on the anion site, which behaves differently compared to aliovalent cation dopants. Furthermore, the importance of specific chemical interactions of the small Li⁺ cation with O or N compared to softer, large atoms such as S on the transport behavior is demonstrated impressively.

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11:45 AM *DT12.03

Proton Conductivity and Thermal Stability of Anhydrous Silico- and Germano-Phosphoric Acid Glasses Takahisa Omata¹, Aman Sharma¹, Issei Suzuki¹, Tomohiro Ishiyama² and Junji Nishii³; ¹Tohoku University, Japan; ²National Institute of Advanced Industrial Science and Technology (AIST), Japan; ³Hokkaido University, Japan

Anhydrous and aqueous solution of phosphoric acid (H₃PO₄) exhibits extremely high proton conductivity and have long been studied as fuel cell electrolytes. High resistance against scum in hydrocarbon fuels and highly efficient cogeneration of heat and electricity are big advantages of the phosphoric acid fuel cells (PAFC); however, PAFCs have issues including vaporization loss of the electrolyte, because the electrolyte, because the electrolyte are liquid in the operating temperature range (150–200 °C). The methods to solidify H₃PO₄ without compromising its electrolyte properties are strongly required. To polymerize H₃PO₄ is one of the promising solidification methods of H₃PO₄ as well as the formation of H₃PO₄ salts, such as the cesium dihydrogen phosphate (CsH₂PO₄); however, even highly polymerized metaphosphoric acid ((HPO₃)_m) transforms into a liquid at >200 °C and is easily hydrolyzed to form H₃PO₄ [1]. This clearly indicates that the simple polymerization of H₃PO₄ is not sufficient to stabilize the solid phosphoric acid and cross-linking between phosphate ion chains is necessary to increase the melting temperature and achieve stability against hydrolysis. It is known that Si and Ge atoms in alkali phosphate glasses respectively form Si–O–P and Ge–O–P heteroatomic linkages and cross-link between phosphate ion chains, suggesting that copolymerization of H₃PO₄ with SiO₂ or GeO₂, i.e., formation of the silico- and germano-phosphoric acids, will stabilize the solid phosphoric acids. In the present study, we synthesized bulk solid anhydrous silico- and germano-phosphoric acid with an approximate composition of H₃Si₂P₉O₂₉ and H₄Ge₂P₁₀O₃₁, respectively [2,3], as transparent glasses by the electrochemical substitution [4] of precursor alkali silico- and germano-phosphate glasses (17at% of Ge was replaced with La to prevent crystallization the H₄Ge₂P₁₀O₃₁ glass). In the case of the H₃Si₂P₉O₂₉ glass, although its glass transition temperature (T_g) was 192 °C, it remained stable at higher temperatures at 200 °C and could be handled as a solid at ~280 °C because of its high viscosity. The H₃Si₂P₉O₂₉ glass exhibited proton conductivity (4×10^{-4} S cm⁻¹ at 276 °C) with a proton transport number (t_H) of 1 even under a dry atmosphere. In the case of the H₄Ge₂P₁₀O₃₁ glass, its T_g was 250 °C and could be handled as a solid at ~320 °C. Its proton conductivity was 3×10^{-4} S cm⁻¹ at 320 °C with t_H of 1. The similarities and differences between the roles of SiO₂ and GeO₂ will be discussed in terms of the glass structure and the nature of P–O bonding.

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12:05 PM DT12.04

Models for Surface Protonic Conductivity in Chemisorbed and Physisorbed Water Layers in Porous Nanoscopic CeO₂ Xinwei Sun and Truls Norby; Universitetet i Oslo Det Matematisk-naturvitenskapelige Fakultet, Norway

Electrical conductivity of porous CeO₂ samples with grain sizes in the nanometric range was investigated by impedance spectroscopy. The origins for the dual time constants over the entire temperature range is suggested to arise from conduction over the concave and convex part of surfaces, representing grain necks and grains, respectively. Surface protonic conduction in the temperature range 500–25°C is discussed in terms of a brick layer model that relates measured macroscopic conductivities to surface conductances predicted from different models for adsorption, dissociation, and migration. The activation enthalpies of surface protonic conductivity are merely 20–30 kJ mol⁻¹ above 300°C, and the preexponentials suggest weak molecular chemisorption with low coverage and migration of dissociated protons between surface oxide ions. The inverse temperature dependency below 200°C is typical of conduction in the first ice-like physisorbed water layer, which does not build well on surfaces dominated by weak molecular chemisorption. The preexponentials suggest that dissociated protons arise from and migrate within the same ice-like physisorbed layer. The above conclusions are supported by water vapour partial pressure dependencies of surface protonic conductivity in the chemisorbed and first physisorbed layer regimes of pH₂O^{1/2} and pH₂O², respectively. Water sorption measurement at room temperature confirmed the presence of multilayers of water. The long conductivity equilibration times at room temperature, which agree with previous study [1], may indicate a restructuring of the CeO₂ surface. The moderate increase in conductivity observed below 70°C is likely a result of an only weakly hydroxylated surface, which prohibits the coverage by liquid-like water layers, making CeO₂ appear as hydrophobic.

Reference:

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Acknowledgement: We acknowledge SUPROX project (# 280868) financed by the Research Council of Norway.

12:20 PM DT12.05

OH⁻ Conductivity and Water Uptake of Anion Exchange Thin Films Yuki Nagao, Fangfang Wang and Dongjin Wang; Japan Advanced Institute of Science and Technology, Japan

Anion exchange membrane fuel cells (AEMFCs) have attracted widespread attention because of the lower cost of using non-precious metal catalysts and high oxygen reduction reaction (ORR) kinetics in alkaline conditions.^[1] The previous research focused on the water uptake and OH⁻ conduction properties of anion exchange membranes (AEMs) as thick forms.^[2-5] The fuel cell reaction occurs at the triple-phase interface where the junction of ion-conductive ionomer, catalyst, and fuel/oxidant. The ionomer plays an important role to deliver OH⁻ ion between the thick membrane and electrochemical catalysts in fuel cells. However, the investigation of OH⁻ ion conduction and hydration properties of ionomers is important but not sufficient. This work demonstrated the relations between OH⁻ conductivity and water uptake of anion exchange thin films for the first time.^[6] The reported poly[(9,9-bis(6'-(N,N,N-trimethylammonium)-hexyl)-9H-fluorene)-*alt*-(1,4-benzene)] (PFB⁺)^[6] was synthesized as a model ionomer. We established in situ methods for measuring OH⁻ conductivity and water uptake of anion exchange thin films^[7] because OH⁻ ion easily exchanges for carbon dioxide in the air. The OH⁻ conductivity of 273 nm-thick PFB⁺ thin film form at 25 °C under 95 % relative humidity (RH) is comparable to the reported OH⁻ conductivity value of PFB⁺ bulk membrane. Reduced OH⁻ conductivity and water uptake were observed in 30 nm-thick PFB⁺ film compared to thicker 273 nm-thick PFB⁺ film. This reduced OH⁻ conductivity was caused by the decreased number of water molecules contained in thinner PFB⁺ films. Under the same number of water molecules contained, similar OH⁻ conductivity results can be obtained for both 273 and 30 nm-thick films. Results show a different trend compared to the case of the proton conductive thin films.^[8]

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SESSION DT13: Battery Electrolytes II
 Session Chair: Iwnetim Abate
 Tuesday Morning, July 19, 2022
 Mezzanine Level, Second Floor, Arlington

11:00 AM **DT13.01

Ion Dynamics in Solid Electrolytes as Probed by NMR—From Site Disorder to Interfacial Effects and Dimensionality Martin Wilkening; Technische Universität Graz, Austria

Ion dynamics in solid electrolytes is at the heart of modern all-solid-state batteries. In many cases, identifying the major origins that lead to facile long-range ion transport in solids needs a combination of many analytical tools exploring both local structures and ion exchange processes over a large dynamic range. Nuclear magnetic resonance (NMR), particularly if applied to lithium or fluorine containing materials, offers a range of time domain techniques to study both short-range and long-range hopping processes in condensed matter. Comparing results from NMR with those from broadband conductivity spectroscopy helps throwing some light on these origins. For instance, while (i) cation and anion site disorder, that is, the loss of site preferences, assists in increasing bulk ion dynamics in, e.g., Li-bearing thiophosphates or oxides, (ii) the interfacial effects in so-called two-phase ion conductors help establishing long-range ion transport in nanocrystalline ceramics. Finally, rapid diffusion (iii) is also expected for layered materials that are able to guide the ions along their buried interfaces having low-dimensional (2D, 1D) dimensions. We will give an overview of recently studied model substances for which NMR and conductivity spectroscopy helped us to experimentally identify the origins of fast ion transport on different length scales.

11:30 AM DT13.02

Kinetic Isotope Effect, Critical Phonon Occupation and Activation Barriers in Fast Lithium-Ion Conductors Matthias T. Agne¹, Joop Frerichs², Michael R. Hansen² and Wolfgang Zeier^{2,1}; ¹Forschungszentrum Julich Institut für Energie- und Klimaforschung, Germany; ²Westfälische Wilhelms-Universität Münster, Germany

The families of Li₁₀(Ge/Sn)P₂S₁₂ and Li₆(P/Sb)S₅X (X = Cl, Br, I) are, so far, the only Li⁺ compounds exceeding 10 mS cm⁻¹ at room temperature. The structure and transport of these materials has been widely investigated, and the ionic conductivities have been pushed continually higher, reaching values reasonable for solid state battery operation. From a structural perspective, however, they are markedly different, making them excellent model systems to compare in fundamental investigations. For example, if isotopic substitutions have any impact on ionic transport, known as kinetic isotope effects.

By using a combination of nuclear magnetic resonance spectroscopy and ab initio molecular dynamics to characterize temperature-dependent ion transport, it is demonstrated that the isotopic substitution of ⁶Li for ⁷Li increases the thermodynamic activation barrier for Li-ion transport in Li₁₀SnP₂S₁₂ and Li₆PS₅Cl. Although previous studies in Li⁺ conductors have indicated that lower vibrational frequencies generally result in lower activation barriers, we find that the lower average vibrational frequency of the ⁷Li⁺ ions results in a larger thermodynamic activation barrier. Unlike the case of proton conductors, the magnitude of the kinetic isotope effect cannot be explained by changes in the zero-point vibrational energy. We propose that the observed changes in activation barrier are related to the differences in critical phonon occupation needed to overcome the local barrier to transport. Our hypothesis is supported by an analytical model, based on the physics of quantum harmonic oscillators, that gives good agreement with experiment. Thus, the kinetic isotope effect provides unique insights into the vibrational perspective and frequency dependence of the activation barrier in these fast Li⁺ ionic conductors.

11:45 AM *DT13.03

Phase Control and Microstructure Engineering in Thiophosphate and Halide Solid Electrolytes [Bettina V. Lotsch](#)^{1,2}; ¹Max-Planck-Institut für Festkörperforschung, Germany; ²Ludwig-Maximilians-Universität München, Germany

Solid electrolytes (SEs) are a key component of all-solid-state batteries (ASSBs), which promise higher energy density along with safer operation compared to commercial Li ion batteries. As the ASSB technology matures, research in the field gravitates towards questions regarding stability, scalability, and integration of solid electrolytes into ASSBs with extended cycle life. As a consequence, new research areas have been emerging lately, including interfacial engineering and microstructure design, and questions such as the role of stack pressure on battery performance increasingly enter the focus of ASSB design.

In this talk, we will discuss the development and optimization of lithium^{1-3,6} and sodium^{4,5} thiophosphate and halide SEs and highlight the importance of synthetic control as a route to obtain phase-engineered solid electrolytes with enhanced ionic conductivities.

We will discuss the impact of controlling both crystalline and amorphous phase fractions on the ionic conductivity of the thiophosphate solid electrolytes $\text{Li}_7\text{SiPS}_8^3$ and $\text{Na}_4\text{P}_2\text{S}_6^{4,5}$ and highlight the influence of anion substitution and structural disorder on the Li transport mechanism in the layered solid solution series $\text{Li}_3\text{HoBr}_{6-x}\text{I}_x$.⁶ Besides controlling the bulk conductivities, we show that application of moderate pressure can be used as a tool to influence the microstructure of mechanically soft thiophosphates, revealing distinct pressure regimes which differently impact the Li ion conductivity of LGPS-type SEs.

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12:05 PM DT13.04

Decoupling Lithium and Host-Framework Stoichiometry Effects in $\text{Li}_{6+x}\text{PS}_{5-x}\text{I}_{1-x}$ Argyrodite Solid Electrolytes Lucy Morgan, Saiful Islam and [Benjamin Morgan](#); University of Bath, United Kingdom

The development of fast-ion-conducting solid electrolytes for use in all-solid-state batteries requires a detailed understanding of the key structural principles that give high ionic conductivities in specific materials. Lithium argyrodites based on $\text{Li}_6\text{PS}_5\text{X}$ (X= Cl, Br, or I) are promising lithium ion solid electrolytes with room temperature ionic conductivities of up to 10^{-2} S cm^{-1} . Recent experimental studies have shown that introducing subvalent cations into the host framework to give lithium stoichiometries $x(\text{Li}) > 6$ can give significant increases in lithium ion conductivities. The microscopic cause for this behaviour has previously been attributed to both the increase in lithium carrier concentration and to the changing host framework composition. Resolving the relative contributions from these two factors is challenging to do purely from experiments, where changes in host-framework stoichiometry and lithium stoichiometry are directly coupled.

To resolve the relationship between lithium stoichiometry, host-framework composition, and lithium conductivity in these lithium argyrodites we have performed a series of molecular dynamics studies on the series $\text{Li}_{6+x}\text{PS}_{5-x}\text{I}_{1-x}$ and on a series of non-stoichiometric “hypothetical” argyrodite compositions. These simulations allow us to decouple changes to the lithium stoichiometry from changes to the host-framework, and reveal how both factors affect lithium conductivity through two different mechanisms: increasing the lithium stoichiometry can be understood in terms of moving from a stoichiometric ordered to a non-stoichiometric ordered solid electrolyte, while the effect of the host-framework can be understood in the context of the degree of asymmetry within the anionic host substructure.

12:20 PM DT13.05

Polycationic Substituted Lithium Superionic Argyrodite Solid Electrolytes [Jing Lin](#)¹, Jürgen Janek^{1,2}, Aleksandr Kondrakov^{1,3}, Torsten Brezesinski¹ and Florian Strauss¹; ¹Karlsruhe Institute of Technology (KIT), Germany; ²Justus Liebig Universität Giessen, Germany; ³BASF SE, Germany

In recent years, solid-state batteries are attracting great attention because of potentially higher energy and power densities than conventional Li-ion batteries. Yet, they are plagued by the development of high performing solid electrolytes, mainly lacking in high Li-ion conductivity and electrochemical stability; thus, the ongoing quest for exploration of new materials and compositions. One promising class of materials are the so-called lithium argyrodites with the general formula $\text{Li}_6\text{PS}_5\text{X}$ (X = Cl, Br, I). Past studies have shown significant improvements of Li-ion conductivity via substitution, mainly on the phosphorous site, due to increasing the shared site occupancy between S^{2-} and X⁻ and/or the occurrence of additional Li positions. However, the possibility of polycationic substitution and resulting structural effects have not been studied yet.

Within this context, we present a systematic study of the influence of polycationic substitutions on Li-ion conductivity in argyrodite-based superionic conductors. The as-synthesized materials were characterized by synchrotron and neutron powder diffraction techniques in combination with nuclear magnetic resonance and electrochemical impedance spectroscopy. It is found that polycationic element mixing induces a high anion site disorder (up to ~10%) and leads to short Li interlayer jump distances and very low activation energies of <0.2 eV for Li-ion conduction, resulting in high r.t. ionic conductivities up to 13 mS/cm. Finally, as a proof of concept, such materials were tested as solid electrolyte in solid-state batteries. Overall, our results show the possibility to achieve polycationic substitution in lithium argyrodites, thereby opening up large compositional space for the development of novel Li-ion conductors with improved properties.

SESSION DT14: Surface Reaction
Session Chair: Alexis Grimaud
Tuesday Afternoon, July 19, 2022
Mezzanine Level, Second Floor, Georgian

2:00 PM **DT14.01

Electrochemical Characterization of Thin Films During Pulsed Laser Deposition [Markus Kubicek](#); Technische Universität Wien, Austria

Electrochemical Characterization of Thin Films During Pulsed Laser Deposition

Mixed conducting oxides are important materials owing to their excellent performance as solid oxide fuel and electrolysis cell electrodes, for sensors, permeation membranes or iono-electronic devices. Due to their typically rather complex stoichiometry, thin films are often grown by pulsed laser deposition. Over the last years, we developed and optimized a technique for in-situ electrochemical characterization directly in the deposition chamber (i-PLD). This technique allows gaining deeper insight into several aspects that are relevant for enhancing the performance of materials and surfaces. Largest advantages of i-PLD vs conventional ex-situ measurements are the outstanding sample to sample reproducibility, the possibility to characterize a film layer-by-layer over its whole thickness, and the higher purity of surfaces and interfaces showing the true potential of certain materials. This enables detailed investigations of the oxygen incorporation and evolution reactions and also of the defect chemical situation inside a mixed conducting oxide thin film and at surfaces and interfaces. In addition to several other application examples of the method, sub-nanometer decoration layers deposited intentionally at the surface of mixed conductors will be discussed in more detail.

The surface of a mixed ionic electronic conductor is often the bottleneck for oxygen exchange, as several materials exist that combine high electronic with high ionic conductivity and therefore exhibit fast conduction and diffusion. The surface reaction on the other side is much more complex and requires among others: adsorption, breaking the O₂-bond, interaction with an oxygen vacancy, and electron transfer reactions. Additionally, the defect chemical situation at the surface may be further complicated by space charges, adsorbates, strain (release) or other effects. Experimentally it can be shown that tiny amounts of impurities may either activate or inactivate a surface with respect to the oxygen exchange reaction [1, 2]. While the latter is generally undesired and often described as degradation or poisoning, activation of surfaces offers great potential for improving existing materials. Measurements using (La,Sr)CoO_{3-δ} and (Pr,Ce)O_{2-δ} as mixed conducting oxides will be used as basis to discuss the effects of surface decoration layers from few % of a monolayer up to a full monolayer thickness. Different models in literature (space charge vs. surface acidity [3]) and their capabilities and limitations to explain the experimental results are discussed.

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2:30 PM DT14.02

Bulk and Surface Oxygen Transport Properties of Mixed Oxide-Ion and Electron Conductors Obtained by Combined Oxygen Permeation Cell and Oxygen Probe Method Kevin Huang; University of South Carolina System, United States

Surface exchange kinetics and bulk diffusion of oxygen are of paramount importance to the activity of oxygen electrocatalysis and performance of electrochemical devices such as fuel cell, metal-air batteries, and oxygen separation membranes. Conventional approaches to obtaining these transport properties are often limited to single property under a specific non-operational condition. Here we use a combined oxygen permeation cell and oxygen probe method to simultaneously attain rates of oxygen surface exchange and bulk conductivity/chemical diffusivity of three representative mixed oxide-ion and electron conductors, namely SrCo_{0.9}Ta_{0.1}O_{3-δ} (SCT), La_{0.6}Sr_{0.4}CoO_{3-δ} (LSC) and La_{0.6}Sr_{0.4}FeO_{3-δ} (LSF), operated under a gradient of oxygen chemical potential. The results explicitly show that SCT exhibit the highest oxide-ion conductivity/chemical diffusivity, fastest rates of surface oxygen exchange kinetics, thus promising to be the best oxygen electrocatalyst. We have also mapped out the distribution of oxygen chemical potential gradient across the membranes and applied B-transport number concept to illustrate the rate-limiting steps in the overall oxygen permeation process.

2:45 PM *DT14.03

Relationship Between Acidity and Oxygen Exchange Kinetics in Mixed Conducting Oxides Clement Nicollet; Institut des Materiaux Jean Rouxel, France

In Solid Oxide Fuel Cells, oxygen electrode polarization related to electrochemical reactions at the gas/solid interface is often the dominant flux limiting mechanism. Accumulating surface impurities is known to lead to a reduction in long term durability. On the contrary, surface modification with selected metal oxides can also have a positive effect on the oxygen surface exchange rate¹. As there is no clear understanding as to why some elements poison oxide surfaces while others enhance their oxygen exchange kinetics, defining a general descriptor is highly desirable, and is the goal of this work.

In a previous study we used Pr-doped ceria as a model mixed ionic and electronic conductor and infiltrated it with binary oxides of various acidities². By comparing the evolution of the surface exchange kinetics with different infiltrated oxides, it was possible to define the acidity of the infiltrated oxide as a descriptor that allows one, on the one hand, to predict what will be the effect of a given oxide on the surface exchange kinetics, and on the other hand to tune the surface exchange coefficient over 7 orders of magnitude with great precision. In this presentation, we will explore the implications of these finding in terms of reactions mechanisms, and how can the acidity/surface exchange relationship be extended to other mixed conductors.

First, the protocol of infiltrating binary oxides to a mixed conductors is applied to perovskites oxides such as (La,Sr)CoO₃ and (LaSr)FeO₃, and characterized in terms of oxygen exchange kinetics, by conductivity relaxation and impedance spectroscopy. The influence of the infiltrated oxides is then discussed with respect to their acidity, and compared to our previous work on Pr doped Ceria.

Second, the Smith acidity factor³ is calculated for a variety of perovskite oxides, and data collected from the available literature for surface exchange kinetics is analyzed with respect to this new acidity factor. An attempt to use this factor as a complementary tool to describe oxygen surface exchange kinetics is discussed.

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3:05 PM DT14.04

Characterization of LaNiO₃-PrNiO₃ Solid Solutions as Oxygen Electrode Materials for SOEC Aleksey Yaremchenko¹, Dzyana Boiba¹, Mikhail Patrakeev², Kiryl Zakharchuk¹ and Blanca I. Arias-Serrano^{1,3}; ¹University of Aveiro, Portugal; ²Institute of Solid State Chemistry UB RAS, Russian Federation; ³Leibniz Institute for Plasma Science and Technology, Germany

Ln₂NiO_{4+δ} (Ln = La, Pr, Nd) and its derivatives with Ruddlesden-Popper structure demonstrate high mixed ionic-electronic conductivity, moderate thermal and negligible chemical expansion, and, therefore, attract significant attention as prospective cathode materials for intermediate-temperature solid oxide fuel cells (IT-SOFC). However, Ln₂NiO_{4+δ} are thermodynamically unstable at SOFC operation temperatures and slowly decompose to a mixture of higher-order Ln_{1+n}Ni_nO_{3n+1} (n = 2, 3) phases, perovskite-like LnNiO₃, and LnO_y. On the contrary, LnNiO₃ perovskites have limited stability at elevated temperatures under oxidizing conditions. In particular, LaNiO₃ decomposes on heating in air above ~1000°C. Cathodic polarization can also be expected to

induce the decomposition of the LnNiO_3 perovskite phase at lower temperatures characteristic for IT-SOFC operation. At the same time, redox changes imposed by anodic polarization (in solid oxide electrolysis cell mode) under oxidizing conditions should not be of risk for the phase stability of LnNiO_3 . Thus, the goal of the present work was the evaluation of LaNiO_3 - PrNiO_3 solid solutions as prospective oxygen electrode materials for solid oxide electrolysis cells.

$\text{La}_{1-x}\text{Pr}_x\text{NiO}_{3-\delta}$ ($x = 0, 0.2, 0.5$ and 1.0) solid solutions with perovskite-like structure were prepared by combustion synthesis with calcinations in oxygen at 800 - 1000°C . Porous ceramic samples were sintered in oxygen at 950 - 1050°C . The materials were synthesized and characterized by XRD, SEM/EDS, dilatometry, TGA, coulometric titration, and electrical measurements. All prepared $\text{La}_{1-x}\text{Pr}_x\text{NiO}_{3-\delta}$ perovskites were found to be oxygen-deficient with oxygen nonstoichiometry δ slightly increasing with Pr content. The cation composition was found to have a negligible impact on the low- $p(\text{O}_2)$ stability limits: all materials decompose at $\log p(\text{O}_2) \sim -3.5$ atm at 800°C . Increasing Pr content results in a decrease in p -type electronic conductivity: from ~ 460 S/cm for $x = 0$ - 0.2 to 220 S/cm for $x = 0.5$ and 115 S/cm for $x = 1.0$ at 800°C in air, but also reduces thermal expansion coefficient from 13.7 ppm/K for $x = 0$ to 11.8 ppm/K for $x = 1.0$ at 30 - 950°C in air. Comparative assessment of the electrochemical performance of $\text{La}_{1-x}\text{Pr}_x\text{NiO}_{3-\delta}$ -based electrodes in contact with $(\text{ZrO}_2)_{0.92}(\text{Y}_2\text{O}_3)_{0.08}$ (8YSZ) and $(\text{La}_{0.8}\text{Sr}_{0.2})_{0.98}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{3-\delta}$ (LSGM) solid electrolytes was performed in air at 600 - 800°C using symmetrical cell configuration.

3:20 PM DT14.05

Investigating the Oxygen Exchange Properties of Multilayered $\text{SrTi}_{0.3}\text{Fe}_{0.7}\text{O}_{3-\delta}$ | $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_{3-\delta}$ Thin-Film Electrodes via *In Situ* Impedance Spectroscopy During Pulsed Laser Deposition [Christin Boehme](#)¹, [Matthäus Siebenhofer](#)¹, [Sergej Raznjevic](#)², [Christoph Riedl](#)¹, [Zaoli Zhang](#)², [Juergen Fleig](#)¹ and [Markus Kubicek](#)¹; ¹Technische Universität Wien, Austria; ²Austrian Academy of Sciences, Austria

In-situ impedance spectroscopy during pulsed laser deposition (i-PLD) allows for electrochemical characterization of thin films during growth. To date the i-PLD technique has been utilized, for example, to investigate the electrochemical properties of pristine $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_{3-\delta}$ (LSC) thin films [1, 2] as well as the oxygen reduction pathways of several mixed ionic and electronic conducting materials [3].

In this work, we expand the i-PLD method to analyze the oxygen exchange properties of multilayered $\text{SrTi}_{0.3}\text{Fe}_{0.7}\text{O}_{3-\delta}$ (STF) | LSC thin film electrodes grown epitaxially on single crystalline yttria-stabilized zirconia (YSZ). A particular focus is laid on elucidating if and how lattice strain between the single layers may influence the chemical capacitance (C_{chem}) and thus, the defect chemistry of the multilayered system. To achieve a dense and homogeneous multilayer morphology a $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{2-\delta}$ interlayer is deposited on top of the YSZ single crystal at the beginning of the i-PLD process, which enables epitaxial growth of the perovskite multilayer system. Individual layers of STF and LSC are grown in steps at 600°C and an oxygen partial pressure of 0.04 mbar to obtain thickness dependent values of the polarization resistance and C_{chem} . In addition to the i-PLD measurements, the structure and morphology of the STF | LSC multilayer system are characterized by X-ray diffraction (XRD), atomic force microscopy (AFM) and high-resolution transmission electron microscopy (HR-TEM).

XRD reciprocal space mapping confirms epitaxial growth of the multilayer system. Additionally, HR-TEM measurements show that the cubic structure of STF is generally maintained throughout the multilayer system whereas for LSC changes of in-plane and out-of-plane lattice parameters are observable. Our i-PLD measurements furthermore show a fine structure in the chemical capacitance over the layer sequence. Most notably, an abrupt increase in the absolute values of C_{chem} within the first 2 nm for the STF layers can be observed. C_{chem} slopes evaluated in this range reveal that C_{chem} increases with a rate of ~ 9000 F/cm³, which is far above the expected values for STF and also by a factor of ~ 2 higher than explainable by a point defect model. Our model assumes a twofold impact of the stiffer STF lattice on the more elastic LSC: i) imposing strain on a growing LSC layer and ii) an impact of STF on LSC underneath while growing STF. Quantification of these two effects is discussed together with vacancy ordering, for which at least two different types were found in HR-TEM measurements.

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SESSION DT15: Polymer Electrolytes; Ca, Mg Conductors

Session Chair: Montse Casas Cabanas

Tuesday Afternoon, July 19, 2022

Mezzanine Level, Second Floor, Arlington

2:00 PM **DT15.01

Effect of Yield Stress on Stability of Solid Block Copolymer Electrolytes Against Lithium Metal Electrodes [Nitash Balsara](#); Lawrence Berkeley National Laboratory, United States

In the field of lithium-ion batteries, two critical factors that drive the research are energy density and safety.¹ Formation of irregular lithium protrusions during battery cycling has limited the development of new battery technologies.^{2,3} Understanding the factors that affect the growth of protrusions could enable successful implication of lithium metal anodes. In this context, solid polymer-based electrolytes, with high storage modulus, have been shown to significantly reduce the nucleation and growth of protrusions during cycling.⁴

We have studied the electrochemical properties of organic-inorganic hybrid diblock and triblock copolymers mixed with lithium bis(trifluoromethanesulfonyl)imide salt. Both the copolymers have similar molecular weights and conducting phase volume fractions. Although the ionic conductivity of the diblock copolymer was a factor of five higher than that of the triblock copolymer, the cycle life of Li/polymer/Li cells containing the triblock copolymer is almost a factor of 50 higher. The rigidity of polymer electrolytes was determined by studying shear modulus and yield stress. Although, both the copolymers exhibit similar storage shear modulus, the yield stress of the triblock copolymer is three times higher than the diblock copolymer. This was attributed to the presence of bridging polymer chains between the adjacent lamellae in the triblock copolymers. Such small difference in the yield stress resulted in difference in cell life time as well as the morphology of the lithium protrusions.

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2:30 PM DT15.02

Calcium Electrolytes—Conduction Mechanism Investigation Tanguy Picard¹, Nicolas Sergent¹, Cristina Iojoiu^{1,2}, Fannie Alloin^{1,2}, Jean-Sébastien Filhol^{3,2} and Marie-Liesse Doublet^{3,2}; ¹Laboratoire d'Electrochimie et de Physico-chimie des Materiaux et des Interfaces, France; ²RS2E, France; ³Institut Charles Gerhardt de Montpellier, France

Calcium batteries are considered one of the most suitable candidates for post-lithium batteries due to their high charge density, a theoretical specific capacity for Ca⁰ of 1,340 mAh/g and a high volumetric capacity of 3,833 mAh/mL similar to that of Li. Additionally, calcium metal technology seems to be safer than lithium considering i) the reactivity and metal properties, Ca is less prone to burst in flame in contact with air, and ii) Ca plating-stripping, reported so far, did not show any dendrites growth. On the other hand, calcium plating is impaired by sloppy surface reactivity due to high resistive passivation layer. Therefore, the development of a stable electrolyte, especially polymer-based electrolyte, is still the weak point to build a high-performance Ca battery. Fundamental understanding of the earth alkaline ions transport mechanisms is of prior importance to develop new conducting materials. Several experimental and modelling approaches are ongoing to find the most suitable candidate in terms of stability windows, reactivity vs Ca⁰ and ionic conductivity.

This work is focused on polyether-based electrolytes and DFT and MD are used to both i) go deeper in the understanding of unexpected experimental behaviour of electrolytes in term of evolution of the ionic conductivity vs temperature, ii) study mass transport in the investigated divalent based electrolytes. Such work would allow us to compare Li⁺ and Ca²⁺ transport mechanisms in liquid, solid polymer and single conducting polymer electrolytes and guide experimental work towards promising polymer structures.

The first outstanding result for a divalent-based liquid electrolyte being a non-monotonic conductivity *i.e.* a conductivity that starts decreasing at a given temperature. We were able to explain this decrease using periodic DFT calculations, taking into account long range electrostatic interaction to account for the low dielectric property. Indeed, high DN polyether-based electrolytes with divalent cation (Ca²⁺, Mg²⁺...) suffer from a lower salt dissociation compared to alkaline-based ones, being a low-dielectric media, decreasing their ionic conductivity.

In parallel, work has been done to rationalize the commonly used VTF model, based on weak electrolyte and free volume theories. The aim is to develop a new model that is not parametric, meaning that all values have physical meaning and can be measured and/or computed and its formalism depends on transport mechanism (perfect gas, gas kinetics, Brownian motion...).

2:45 PM *DT15.03

Ion Transport in Electrolytes with Salt Aggregates Lei Cheng; Argonne National Laboratory, United States

Fast ion transport is essential for the high performance of the electrolyte. The solvation environment of the ion in liquid electrolyte determines the ion mobility and transport mechanism. In electrolytes with high salt concentrations or weakly solvating solvents, ionic aggregates form, and the unique inhomogeneous ion distribution profoundly influence ion transport mechanism and rate. Using molecular dynamics simulations, we studied ion dynamics in various electrolyte systems to reveal the favorable or adverse role of the salt aggregates on the transport properties of the electrolytes.

3:05 PM DT15.04

Post-Treatment Study on Blended Polymer for Solid-State Lithium Batteries Rozita Sadeghzadeh¹, David Lepage¹, Arnaud Prébé¹, Gabrielle Foran¹, David Ayme-Perrot² and Mickaël Dollé¹; ¹Université de Montréal, Canada; ²TotalEnergies SE, France

The widely used Li-ion battery (LIB) is the most established rechargeable energy storage device. Therefore, the development of new electrode and electrolyte materials is essential for improving battery performance. To this end, this work focuses on the development of electrolytes with both high ionic conductivity and good chemical and mechanical stability.¹

Solid polymer electrolytes (SPEs) have been presented as safer alternatives for liquid electrolytes as they tend to be non-flammable, have enough mechanical strength to resist dendrite growth, and do not leak. However, these materials tend to be less conductive than liquid electrolytes. Gel polymer electrolytes (GPE), which have been studied since decades and have recently garnered significant attention, present a possible solution to this dilemma as they combine the ionic conductivity of liquid electrolytes with the increased safety of SPE.² GPE, with polar functional groups that are able to dissolve salts, are of particular interest. Moreover, if they have low glass transition temperature and weak coordination to lithium salts are a good option for electrolyte.³

This work presents a post-treatment procedure to convert an SPE to a GPE in order to take advantage of the easy processability of SPE and the higher ionic conductivity of GPE. The initial SPE was prepared by combining two polymers with LiTFSI (bis(trifluoromethanesulfonyl)imide) via extrusion mixing. This method of GPE processing was also found to improve other aspects of the electrolyte such as thermal and electrochemical properties which were characterized using cycling voltammetry, electrochemical impedance spectroscopy, and thermal gravimetric analysis. Additionally, the salt-polymer interaction in the GPE was characterized using FTIR, NMR, and SEM-EDX. The half-cell LFP/electrolyte/ Li metal showed a high capacity near to the theoretical one at C/20 at temperature 60 C. Additionally, the ionic conductivity of the electrolyte is around 10-4 S/cm. These first results confirmed that this blend of the polymers is a good electrolyte candidate for lithium-ion batteries.

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3:20 PM DT15.05

Investigation of MgZ₂Se₄ (Z = Sc, Er, Tm, Y) Spinel as Mg-Ion Conductors for All-Solid-State Mg Batteries Clarissa Glaser¹, Marcus Rohnke^{1,2} and Jürgen Janek^{1,2}; ¹Justus Liebig University Giessen, Germany; ²Center for Materials Research, Germany

Over the last decades, there has been an increasing interest in developing next-generation solid-state battery cells relying on multivalent ions that offer higher volumetric energy densities than monovalent ion cells including Li-ion and Na-ion batteries. Among them, Mg batteries appear to be an attractive choice as alternative to the alkali-ion technology due to the outstanding characteristics of the Mg anode such as the low redox potential, superior safety and

high magnesium abundance. However, in the development of solid-state Mg batteries, the identification of an appropriate electrolyte with high Mg-ion mobility is the most challenging and limiting factor.^[1] Recently, computational investigations of the magnesium selenide spinels MgZ_2Se_4 ($Z = \text{Sc, Er, Tm, Y}$) predict low Mg^{2+} migration barriers (< 380 meV) along the tetrahedra-octahedra-tetrahedra diffusion path in their crystal structure. This makes these materials potential candidates as good Mg-ion conductors. However, with the exception of MgSc_2Se_4 ($\sigma_{\text{ion}} = 10^{-4}$ S/cm as reported), no experimental conductivity study exists. Considering that the shared trigonal face between tetrahedra and octahedra along the migration path is widened in those spinels with larger Z ions (Er, Tm, Y) compared with Sc, higher ionic conductivities can be expected.^[2-4] In this context, we present the successful synthesis of the MgZ_2Se_4 spinels *via* one- and two-step solid-state reaction methods, as well as their characterization, respectively. Phase-purity of the prepared samples was examined by X-ray powder diffraction combined with Rietveld refinements. UV absorption and photoluminescence measurements were carried out to investigate the electronic properties. Moreover, DC polarization measurements and electrochemical impedance spectroscopy have been performed for the four different ternary selenides. The initial evaluation of the impedance data according to the reported equivalent circuit^[3-4] indicates a high ionic conductivity of the new spinels. More effort is being devoted to precisely analysing the ionic conductivity of these materials due to their mixed-conducting behaviour. Conclusively, further strategies to prove the Mg-ion mobility of the MgZ_2Se_4 spinels will be demonstrated.

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SESSION DT16: Proton Uptake and Transport II

Session Chair: Hitoshi Takamura

Tuesday Afternoon, July 19, 2022

Mezzanine Level, Second Floor, Georgian

4:00 PM *DT16.01

Proton Conductivity and Mobility in Triple-Conducting Perovskites $\text{Ba}_{0.95}\text{La}_{0.05}\text{Fe}_{1-x}(\text{Y,Zn})_x\text{O}_{3-\delta}$ Christian Berger¹, Rotraut Merkle¹, Jörg Exner², Ralf Moos² and Joachim Maier¹; ¹Max-Planck-Institut für Festkörperforschung, Germany; ²University of Bayreuth, Germany

Barium ferrates from the series $\text{Ba}_{0.95}\text{La}_{0.05}\text{Fe}_{1-x}\text{M}_x\text{O}_{3-\delta}$ (BLFM with $\text{M}=\text{Y, Zn}$; $x=0, 0.2$) are mixed proton-, oxide ion-, and electronic conductors and therefore of interest for various applications such as protonic ceramic fuel and electrolyser cells (PCFC and PCEC), or hydrogen separation membranes. Proton concentrations have been measured for a larger range of triple conducting perovskites [1][2], and the degree of hydration is significantly lower in such mixed conducting perovskites compared to $\text{Ba}(\text{Zr,Ce,Y})\text{O}_{3-\delta}$ electrolytes. However, the measurement of proton mobility or conductivity is challenging, as it is superimposed by a high electronic and a non-negligible oxygen vacancy ionic conductivity. Nevertheless, its value is important to judge whether it suffices to make the whole surface of a PCFC cathode active for the oxygen reduction reaction.

In the current work, Wagner-Hebb DC polarisation measurements with a proton-selective electrode were carried out to obtain the proton conductivity. A pore-free $\text{BaCe}_{0.8}\text{Y}_{0.2}\text{O}_{3-\delta}$ layer of approximately 20 micrometer thickness was applied with powder aerosol deposition on dense BLFM pellet samples as an electrode with high proton selectivity. Oxygen vacancies are blocked by operating under conditions of complete hydration of the $\text{BaCe}_{0.8}\text{Y}_{0.2}\text{O}_{3-\delta}$ layer (25 mbar H_2O , $T \leq 450^\circ\text{C}$). The application of reducing conditions ($9 \times 10^{-27} \leq p\text{O}_2/\text{bar} \leq 9 \times 10^{-22}$) furthermore suppresses the hole conductivity in the $\text{BaCe}_{0.8}\text{Y}_{0.2}\text{O}_{3-\delta}$ layer.

The proton conductivity of BLFM obtained from DC polarisation provides values in the range of $4 \times 10^{-6} \leq \sigma_{\text{OH}^+} / \text{Scm}^{-1} \leq 2 \times 10^{-5}$ at 400°C , with the highest conductivity for $\text{Ba}_{0.95}\text{La}_{0.05}\text{Fe}_{0.8}\text{Zn}_{0.2}\text{O}_{3-\delta}$. In addition to the proton conductivity, the water chemical diffusion coefficient $D_{\text{H}_2\text{O}}^{\text{H}}$ can be extracted from the transient behavior of the DC polarization experiment. Within the moderate degree of hydration of BLFM in these experiments, $D_{\text{H}_2\text{O}}^{\text{H}}$ can be assumed close to the proton diffusion coefficient D_{OH^+} . Values in the order of $4 \times 10^{-7} \leq D_{\text{OH}^+} / \text{cm}^2\text{s}^{-1} \leq 5 \times 10^{-6}$ are obtained at 400°C .

The results show that the proton mobility in the investigated barium ferrates is comparable to that in proton conducting electrolytes. The activation energy of ≈ 0.5 eV for all BLFM samples is in the typical range for proton migration barriers in $\text{Ba}(\text{Zr,Ce,Y})\text{O}_{3-\delta}$ perovskites. The variation of proton mobility with dopants on the iron site will be discussed in this contribution.

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4:20 PM DT16.02

Understanding the Origin of Enhanced Catalytic Activity in $\text{LnCo}_{0.5}\text{Ni}_{0.5}\text{O}_{3-\delta}$ ($\text{Ln} = \text{Pr, La}$) Perovskites Type Oxides on Protonic Electrochemical Devices Leonard Kwati, Aleksandar Staykov and Hiroshige Matsumoto; Kyushu Daigaku, Japan

Proton-conducting solid-oxide electrolyzer and fuel cells (PCECs/PCFCs) are promising viable, intermediate-temperature technologies for H_2 production and energy conversion. Although, to date, significant progress has been made on developing suitable electrolytes for these devices. The development of corresponding single-phase electrodes tailored explicitly for protonic electrolytes has been hindered by difficulties finding highly efficient mixed proton-electron conductors (MPECs) with effective catalytic activity toward oxygen reduction and evolution reactions (ORR/OER). Also, the basic principles required to achieve high electronic conductivity accompanied by proton and oxygen-ion conduction are not well understood. This paper investigates the origin of catalytic activity in $\text{LnCo}_{0.5}\text{Ni}_{0.5}\text{O}_{3-\delta}$ ($\text{Ln}=\text{Pr}$ and La) perovskites “positrodes” for PCFC by experiment and computation. Our strategy is to understand the fundamental properties that make an excellent MPEC electrode, some of which including hydration, sufficient electronic conductivity, proton migration, and good catalytic activity. First principle calculations of $\text{LnCo}_{0.5}\text{Ni}_{0.5}\text{O}_{3-\delta}$ ($\text{Ln}=\text{Pr}$ and La) were performed using plane wave DFT method and hybrid HSE06 functional for accurate band gaps estimations, implemented in the Vienna Ab-initio Software Package. Geometry optimization is performed, and all forces were relaxed to 0.01 eV/Å². Our results show that the catalytic activity, ionic transport, and electronic properties of these class of materials are direct consequences of the valence shell structure of the A-site cation.

Acknowledgments

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4:35 PM *DT16.03

Surface Exchange Study of Proton Ceramic Electrochemical Cell's Positrode by Gas Phase Analysis [Vincent Thoréton](#) and Reidar Haugsrud; Universitetet i Oslo, Norway

Positrode materials for Proton Ceramic Electrochemical Cells (PCECs) require sufficiently high proton transport kinetics both in the bulk and at its interface with the gas phase. In that sense, fundamental understanding of the proton and oxygen transfer at the surface of Mixed Proton and Electron conducting Ceramics (MPECs) positrode materials for Proton Ceramic Electrochemical Cells (PCECs) is desirable, aiming to improve the performance of PCECs.

Isotopic Exchange Gas Phase Analysis techniques (Pulse Isotopic Exchange (PIE) or Gas Phase Equilibration (IE-GPE)) have been successfully applied for measuring the surface exchange kinetics of oxygen on Solid Oxide Electrochemical Cells (SOECs) revealing the rate limiting steps. Extending the methodology to study species containing protons and oxide ions is a challenging but exciting task, allowing to study the interaction of different species at the surface and their effect on the overall surface exchange kinetics.

In the present contribution, we report on the surface exchange kinetics for a PCFCs cathode material ($\text{BaGd}_{0.3}\text{La}_{0.7}\text{Co}_2\text{O}_{6-\delta}$), electrolyte ($\text{BaZr}_{0.7}\text{Ce}_{0.2}\text{Y}_{0.1}\text{O}_3$) and composites of both in dry and humid conditions. The surface reaction mechanisms are interpreted in term of defect chemistry.

Acknowledgements

The authors acknowledge support of the FRINATEK project 262393 "Fundamentals of Surface Kinetics in High Temperature Electrochemistry" (FUSKE) of the Research Council of Norway.

Cathode materials for protonic ceramic fuel cells (PCFCs)

4:55 PM DT16.04

Direct Measurements of Hydrogen Exchange and Diffusion Kinetics at Elevated Temperatures in Proton-Conducting Solid Oxide Materials [Mudasir A. Yattoo](#) and Stephen J. Skinner; Imperial College London, United Kingdom

Storage of purified hydrogen is one of the central challenges in addressing climate change and reducing our reliance on fossil fuels for energy conversion and storage, and therefore there is a global surge in research and development concerning hydrogen purification and storage. In this regard, we are studying proton conduction in solid oxide materials at elevated temperatures for applications in hydrogen separation and compression membranes. Hydrogen compression is the most recommended method to store hydrogen for automotive applications as it allows an increase in the hydrogen volumetric energy density.

Traditionally the protonic conductivity in these materials is measured by indirect methods. For example, conductivity measurements in mixed gas atmospheres, comparing for example dry N_2 with humidified N_2 , thereby allowing the contribution of protons to be evaluated. In this study, we for the first time report the evaluation of protonic conductivity in $\text{BaZr}_{1-x}\text{Ce}_x\text{Y}_{0.2}\text{O}_{3-\delta}$ (BZCY) and $\text{BaZr}_{0.1}\text{Ce}_{0.7}\text{Y}_{0.2-x}\text{Yb}_x\text{O}_{3-\delta}$ (BZCYYb) by direct measurements afforded by the Isotope Exchange Depth Profiling (IEDP) technique with deuterium labelling. We also report the kinetics of H/D transport through the bulk materials and across metal-ceramic interfaces with particular interest in the behaviour of the interface between the key Pd/Pd alloy catalyst component and the hydrogen transporting oxide ceramic material. The transport and interface behaviour information will be of significance in designing hydrogen separation and compression membranes.

5:10 PM DT16.05

Thermodynamics of Proton Transport in Doped Barium Cerate-Zirconate Triple Conducting Oxides [Jagoda E. Budnik](#), Tadeusz Miruszewski, Aleksandra Mielewczyk-Gryn and Maria Gazda; Politechnika Gdanska, Poland

Triple conducting oxides (TCOs) are a class of ceramics that, under specific conditions, conduct three different types of charge carriers: oxygen ions, electrons or holes, and protons. TCO materials have attracted the interest of the scientific community thanks to their prospective applicability in a wide range of electrochemical devices [1,2]. In general, acceptor-doped perovskite oxides exhibit mixed ionic-electronic conductivity (MIEC). Moreover, they also undergo water uptake in the presence of water vapor. Protons are incorporated into the structure via hydration or hydrogenation reaction, depending on the predominant charge carrier concentration (oxygen ions or electron holes) in the material.

$\text{BaCe}_{0.6}\text{Zr}_{0.2}\text{Y}_{0.2-x}\text{M}_x\text{O}_{3-\delta}$ ($\text{M} = \text{Fe}, \text{Tb}$) oxides are compounds related to the acceptor-doped barium cerate-zirconate solid solution - $\text{BaCe}_{0.6}\text{Zr}_{0.2}\text{Y}_{0.2}\text{O}_{3-\delta}$ (BCZY622). BCZY622 exhibits proton and oxygen ion conductivity, which makes it applicable as an electrolyte material for protonic ceramic fuel cells (PCFC) [3]. Moreover, doping with transition metal elements might enhance the electronic partial conductivity of this material, making it a triple conducting oxide. Given the complexity of the diffusion and electrical transport mechanisms involved in proton conduction in TCOs, a thorough understanding of those phenomena is required to appropriately develop novel materials with desirable features including improved proton uptake and mobility of introduced proton defects.

In this work, single-phase polycrystalline samples of $\text{BaCe}_{0.6}\text{Zr}_{0.2}\text{Y}_{0.2-x}\text{M}_x\text{O}_{3-\delta}$ ($\text{M} = \text{Fe}, \text{Tb}, x = 0.1, 0.05, 0.02$) were synthesized using the solid state reaction method. X-ray diffraction (XRD) was used to examine the crystal structure and phase composition of the samples, while thermogravimetric analysis (TGA) was performed to determine the proton concentration. Electrochemical impedance spectroscopy (EIS) was used to conduct preliminary measurements of electrical conductivity of materials in dry and humidified air. The thermodynamics of proton transport was investigated using the electrical conductivity relaxation (ECR) method. The influence of water in the atmosphere on the diffusion and surface exchange processes for oxygen during oxidation and reduction was also examined. The diffusion and surface exchange coefficients were estimated by fitting the measurement data using the ECRTTOOLS Matlab toolbox [4].

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5:25 PM DT16.06

High Entropy Rare-Earth Ortho-Niobates - Structural, Thermal and Electrical Properties [Arkadiusz Dawczak](#), Aleksandra Mielewczyk-Gryn, Wojciech Skubida and Maria Gazda; Politechnika Gdanska, Poland

High entropy oxides (HEOs) are one of the most interesting new groups of ceramic materials. Their complex properties, which can be easily modified by changes of elements in their composition, are interesting both from the basic research and application point of view. The general concept of entropy stabilization is based on the possibility to stabilize a single-phase crystal structure by increasing the configurational entropy of the system. To achieve a

high value of the configuration entropy, at least five different elements in one sublattice need to be mixed. This means that the configurational entropy, may at finite temperatures achieve the value large enough to dominate and become a driving force for forming a single-phase solid solution instead of multiphase compounds [1]. Lanthanum niobate is a well-recognized proton conductor and has been used in various electrochemical devices, for example, Protonic Ceramic Fuel Cells (PCFC) [2]. Depending on the temperature lanthanum niobate can be stable in two polymorphs, low-temperature which is monoclinic and corresponds to Fergusonite-type structure, and high-temperature phase which is tetragonal and corresponds to Scheelite-type structure [3,4]. In this work, we focus on a novel type of HEOs, based on the lanthanum ortho-niobate. The chosen compositions (with formula ABO_4) are the exemplary oxides with five different cations at the A-site of the Fergusonite structure. The stoichiometries have been chosen to ensure both the entropic stabilization of the Fergusonite or Scheelite phase and elevation of the electrical conductivity. In this work, we examine the structural, thermal and electrical properties of the $(La_{0.2}Nd_{0.2}Sm_{0.2}Gd_{0.2}RE_{0.2})NbO_4$ series of the high entropy rare-earth ortho-niobates (where RE are rare-earth elements, like Y, Pr, Eu, Tb and Ho). The choice of the constituent elements has been undertaken based on their preferred valence state and ionic radius. The samples of the materials were synthesized via solid-state synthesis method. We determined the structure and phase composition of materials by using X-ray powder diffraction at room and high temperatures (HT-XRD). Additionally, the structure and phase composition of materials were investigated with the use of synchrotron radiation. The diffraction (MCX) and spectroscopic X-ray absorption spectroscopy (XAS) studies at room temperatures were performed. Thermochemical properties were carried out with thermogravimetry (for hydration and oxidation studies). The measurements of the temperature dependence of electrical conductivity were carried out using electrochemical impedance spectroscopy under dry and wet air.

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Acknowledgements

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5:40 PM DT16.07

Exploration of Off-Stoichiometric CsH_2PO_4 —A Novel Superprotonic Compound and Non-Stoichiometry in Cubic $[Cs_{1-x}H_x]H_2PO_4$ Louis S. Wang¹, Sawankumar V. Patel², Erica Truong², Yan-Yan Hu² and Sossina Haile¹; ¹Northwestern University, United States; ²Florida State University, United States

CsH_2PO_4 or CDP is an exceptional proton conducting electrolyte due to its impressive conductivity at intermediate temperatures (228 - 300 °C) in which it exists as a highly disordered superprotonic cubic phase. Exploration into off-stoichiometry in CDP, through mixture of the compound with $CsH_3(PO_4)_2$ to produce sample compositions $(1-x)CsH_2PO_4 - xH_3PO_4$, resulted in the discovery of a new superprotonic compound and also revealed that the cubic phase of CDP can accommodate high amounts of non-stoichiometric Cs deficiency. The new superprotonic compound $Cs_7(H_4PO_4)(H_2PO_4)_8$, or CPP, of composition $x = 2/9$ was discovered to form at 90 °C through reaction of the precursor compounds. The structure of CPP was revealed through single crystal diffraction to bear extraordinary $H_4PO_4^+$ cations on select Cs sites of a structure that otherwise resembles cubic CDP [1]. Notably, CPP is stable in nominally dry argon up to 151 °C at which temperature the material displays a proton conductivity of $9.3 \times 10^{-4} \text{ S cm}^{-1}$. At temperatures above 155 °C, samples throughout the composition range $0 \leq x \leq 2/9$ in $(1-x)CsH_2PO_4 - xH_3PO_4$ were discovered to adopt the cubic crystal structure of superprotonic CDP, but with stoichiometry $[Cs_{1-x}H_x]H_2PO_4$. Structural studies imply that Cs deficiency in this phase, termed α -CDP(ss), manifests as Cs vacancies, charge balanced by excess protons [2]. α -CDP(ss) displays eutectoid phase behavior with a eutectoid composition of $x = 0.18$, which was established through thermal analysis, high-temperature in situ x-ray diffraction, and variable-temperature NMR spectroscopy. The proton conductivity of the α -CDP(ss) phase was found to be relatively insensitive to composition, and when coupled with the eutectoid phase behavior, this result presents the opportunity to extend the lower operating temperature limit of CDP-based devices. More generally, the non-stoichiometry demonstrated here in CDP presents a powerful new approach to the modification of solid acids.

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SESSION DT17: Battery Electrolytes III Including F-Conductors

Session Chair: Lei Cheng

Tuesday Afternoon, July 19, 2022

Mezzanine Level, Second Floor, Arlington

4:00 PM *DT17.01

Stacking Faults Assist Lithium-Ion Conduction in a Halide Based Superionic Conductor, Li_3YCl_6 Hayden Evans¹, Elias Sebt², Hengning Chen³, Craig Brown¹, Pieremanuele Canepa³ and Raphaela Clement²; ¹National Institute of Standards and Technology, United States; ²University of California Santa Barbara, United States; ³National University of Singapore, Singapore

In the pursuit of urgently-needed, energy dense solid-state batteries for electric vehicle and portable electronics applications, halide solid electrolytes offer a promising path forward with exceptional compatibility against high-voltage oxide electrodes, tunable ionic conductivities, and facile processing. For this family of compounds, synthesis protocols strongly affect cation site disorder and modulate Li^+ mobility. In this work, we reveal the presence of a high concentration of stacking faults in the superionic conductor Li_3YCl_6 and demonstrate a method of controlling its Li^+ conductivity by tuning the defect concentration with synthesis and heat treatments at select temperatures. Leveraging complementary insights from variable temperature synchrotron X-ray diffraction, neutron diffraction, solid-state nuclear magnetic resonance, density functional theory, and electrochemical impedance spectroscopy, we identify the nature of planar defects and the role of nonstoichiometry in lowering Li^+ migration barriers and increasing Li site connectivity in mechanochemically-synthesized Li_3YCl_6 . With heat treatments at temperatures as low as 333 K (60 °C), we decrease the concentration of planar defects, and offer insight to how this change affects conductivity. Findings from this work are expected to be generalizable to other halide solid electrolyte candidates and provide an improved understanding of defect-enabled Li^+ conduction in this class of Li-ion conductors.

4:20 PM DT17.02

Identifying Driving Forces for Activation Barrier Changes, Using a Two-Dimensional Substitution Approach in the Solid Solution $\text{Na}_3\text{P}_{1-x}\text{Sb}_x\text{S}_{4-y}\text{Se}_y$

Paul S. Till and Wolfgang Zeier; Westfälische Wilhelms-Universität Münster, Germany

The need for highly conductive solid electrolytes to build well performing All Solid-State batteries with high energy densities has fueled research efforts in the field of ionics over the recent years.^{1,2} To further optimize current electrolyte families a fundamental understanding of the connection between the crystal structure, the lattice dynamics and the diffusion process are necessary.³ These connections are often investigated in solid solution type substitution experiments in which the chemical composition of the electrolyte is systematically varied and the effects of structure and lattice dynamical changes on the transport are monitored.⁴⁻⁶ The simultaneous alterations of the crystal structure and the lattice dynamics in these substitution series however, make it extremely challenging to discern different influences on the transport properties. To overcome the limitations of such simple one-dimensional substitution series we herein present a two-dimensional solid solution approach in the $\text{Na}_3\text{P}_{1-x}\text{Sb}_x\text{S}_{4-y}\text{Se}_y$ system, comprised of the four substitution series $\text{Na}_3\text{P}_{1-x}\text{Sb}_x\text{S}_4$, $\text{Na}_3\text{P}_{1-x}\text{Sb}_x\text{Se}_4$, $\text{Na}_3\text{PS}_{4-y}\text{Se}_y$ and $\text{Na}_3\text{SbS}_{4-y}\text{Se}_y$. By a direct comparison of the different substitution series, the influences of static and dynamic changes on the activation barriers are evaluated, enabling the identification of main driving forces for activation barrier changes.

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4:35 PM DT17.03

Ionic Conductivity Increase in Sodium Antiperovskites Due to Octahedral Tilt Disorder Yiliang Li¹, Yin Liang², Ping-Chun Tsai¹, Duhan Zhang¹, Sunil Mair¹, Matthew Ko¹, Lapidus Saul² and Yet-Ming Chiang¹; ¹Massachusetts Institute of Technology, United States; ²Argonne National Laboratory, United States

Na_3OCl is a well-studied prototypical fast ion conducting compound representative of the antiperovskite family, which is of interest for solid-state electrolytes.^[1-3] Here, we surprisingly observed a 100x increase in its ionic conductivity (from 10^{-1} to 10 mS/cm) with increasing temperature at $\sim 305^\circ\text{C}$. Carrying out temperature-dependent synchrotron X-ray diffraction (SXRD), differential scanning calorimetry (DSC) and impedance spectroscopy, we show that this conductivity transition is correlated with a transition from tetragonal to cubic symmetry antiperovskite. Careful Rietveld refinement of the SXRD data shows that the high temperature cubic phase has sodium displacements consistent with octahedral tilt disorder within the cubic phase. While previous work on this compound has shown that the differences in formation energy between different stable noncubic tilt systems are small (< 50 meV)^[4], this is the first evidence that octahedral tilt fluctuations within a high symmetry phase can give rise to increased ionic conductivity.

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4:50 PM *DT17.04

Evaluation of Ion Transport Properties in Solid Solutions of PbSnF_4 Using ^{19}F NMR Arunkumar Dorai, Takahisa Omata and Junichi Kawamura; Tohoku Daigaku, Japan

Batteries based on the fluoride shuttle are promising for the development of high energy density batteries suitable for the electric vehicles and grids. Fluorite structured systems based on PbF_2 structure deliver high ionic conductivity with the introduction of aliovalent compounds due to the presence of inequivalent lattice sites. Especially in Sn doped system shows the maximum conductivity at ambient temperature ($\sim 10^{-3}$ Scm^{-1}) among all fluoride ion conductors. Further increase in conductivity has been achieved in solid solutions of $\text{Pb}_{1-x}\text{Sn}_x\text{F}_4$ ($x=0.4-0.6$) prepared by mechanical milling. In the present work, we have investigated the effect of Pb to Sn ratio on the structural and ion transport properties (diffusion coefficient) using ac impedance and ^{19}F NMR spectroscopy. Solid solutions of $\text{Pb}_{1-x}\text{Sn}_x\text{F}_4$ were prepared by mechanical milling. Irrespective of the composition the prepared solid solutions were observed to be formed in the gamma phase, which is generally formed at higher temperatures. A maximum ionic conductivity of 9.4×10^{-4} Scm^{-1} is observed for the solid solution with $x = 0.45$ as confirmed by ac impedance analysis. The fluoride ion dynamics is studied using ^{19}F NMR relaxation time and PFG-NMR measurements. The ^{19}F NMR relaxation time measurements exhibits a characteristic T_1 minima signifying the ^{19}F homonuclear dipole-dipole interaction due to the fast exchange of fluoride ions.

5:10 PM DT17.05

Structural Features and Diffusion Mechanisms in a Disordered Fluoride-Ion Conductor Briséis Mercadier^{1,2,3}, Samuel Coles⁴, Mathieu Duttine⁵, Christophe Legein⁶, Monique Body⁶, Olaf Borkiewicz⁷, Christian Masquelier^{2,1}, Benjamin J. Morgan⁴ and Damien Dambournet^{3,1,8}; ¹RS2E - Réseau sur le stockage électrochimique de l'énergie, France; ²Laboratoire Reactivité et Chimie des Solides, France; ³Physicochimie des Electrolytes et Nanosystemes Interfaciaux, France; ⁴University of Bath Faculty of Science, United Kingdom; ⁵Institut de Chimie de la Matière Condensée de Bordeaux, France; ⁶Institut des Molécules et Matériaux du Mans, France; ⁷Argonne National Laboratory Advanced Photon Source, United States; ⁸Sorbonne Université, France

As the share of renewable energy in energy mixes increases everywhere, so does the demand for energy storage. Fluoride-ion batteries are a recent type of all-solid-state batteries (ASSB) developed as a complement of Lithium-ion, using an abundant element, F⁻, as the charge carrier¹. For such a device, a solid electrolyte with high fluoride ion conductivity is needed besides the presently known PbSnF_4 ($\sigma_{\text{RT}} = 2.10^{-3}$ S.cm^{-1}). It is possible to substitute lead for Ba and Sr, which gives us a unique opportunity to probe possible alternative mechanisms of F-ion conduction in this family of materials. The MSnF_4 (M = Pb,

Ba, Sr) family has two polymorphic structures, one of which being a disordered cubic phase, obtained via mechanochemical synthesis². It is only scarcely studied so far, as disordered phases are difficult to describe using conventional characterizations³. Its ionic conductivity is orders of magnitude higher than that of its precursors and it would be therefore interesting to understand what structural / chemical changes impact the ionic mobility.

Cubic BaSnF₄ was chosen, here, as a case study. The local environments of the various atoms were probed using a range of local-scale characterization techniques. ¹¹⁹Sn Mössbauer spectroscopy highlights the disordered nature of the material by showing that the 5s² lone electron pair of Sn is stereoactive, creating numerous new environments for the fluoride ion, with various coordination numbers and bond lengths, which are described using Pair distribution function. By coupling these experimental results with computational calculations, a structural model was obtained for this phase. Through generating a high number of random structures via Density Functional Theory, relaxing them and comparing the energies of the various resulting configurations, we show that the lone pairs of tin do not induce any local ordering, making this structure truly disordered.

Afterwards, this model was used to understand the fluoride-ion mobility through Ab Initio Molecular Dynamics simulations, once again coupled with experimental techniques (notably ¹⁹F Magic Angle Spinning Nuclear Magnetic Resonance). Two behaviours are highlighted, depending on the environment of the fluoride ion. Barium-surrounded fluorides are mainly immobile, owing to the strong Ba-F bond. On the other hand, tin-surrounded fluorides are extremely mobile, which can be linked back to the stereoactive electron lone pair of Sn(II). This lone pair is also shown to be dynamic and to be moving on an extremely rapid time-scale, possibly inducing a paddlewheel-like mechanism similar to that of a sulphide electrolyte.

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5:25 PM DT17.06

Nano-Scale Two-Phase Separation in Ba_{0.6}La_{0.4}F_{2.4} Solid-State Electrolyte [Shun Sasano](#)¹, Ryo Ishikawa¹, Kazuaki Kawahara¹, Atsushi Mineshige², Naoya Shibata^{1,3} and Yuichi Ikuhara^{1,3}; ¹Tokyo Daigaku, Japan; ²Hyogo Kenritsu Daigaku, Japan; ³Ippan Zaidan Hojin Fine Ceramics Center, Japan

There is an increasing demand of electrochemical energy storage with high energy density for the application in electric vehicles. A fluoride-ion battery is one of good candidates for the next-generation batteries owing to the high theoretical energy density, compared with a lithium-ion battery [1]. However, the ionic conductivity of the solid-state electrolytes in fluoride-ion batteries is significantly lower at room temperature (10⁻⁶ S cm⁻¹), and it is therefore an urgent task to explore the faster fluoride-ion conductors [2]. Since grain boundaries in polycrystals strongly affect the ionic conductivity of solid-state electrolytes, it is important to analyze and control microstructures in the electrolytes [3]. Ba_{0.6}La_{0.4}F_{2.4} (BLF) is widely used as a solid-state electrolyte in fluoride-ion batteries owing to the wide electrochemical potential window and the relatively high fluoride-ion conductivity at 420 K (10⁻⁴ S cm⁻¹) [4]. Although the ionic conductivity of BLF can be improved by mechanochemical synthesis [5], it is still unclear the origin of such improvement in ionic conductivity. Here, we investigate the atomic structure of mechanochemically synthesized BLF polycrystal by using atomic-resolution scanning transmission electron microscopy (STEM) combined with electron energy-loss spectroscopy (EELS), where we would clarify the relationship between the fluoride-ion conductivity and microstructure of BLF.

The BLF polycrystal was synthesized by mechanochemical milling using the high purity powders of BaF₂ and LaF₃. The raw material powders were well mixed and placed in a tungsten carbide pot containing 140 tungsten carbide balls under an Ar atmosphere at room temperature. The mechanochemical milling was performed at 600 rpm for 3 h. The ball-milled sample was then pressed as a disc and subsequently heated at 1073 K for 5 h under an Ar atmosphere. The chemical composition of the BLF sample was evaluated by the energy-dispersive X-ray spectrometry (EDX), and the ratio of BaF₂/LaF₃ was determined to be 59.9:40.1. The atomic structure of BLF sample was observed by STEM, which shows that nano-scale domain structures are distributed in the bulk of the BLF polycrystal. The chemical analysis by EELS further revealed that the nano-scale La-rich tysonite-type domain is formed in Ba-rich fluorite-type matrix. Such two-phase separation in mechanochemically synthesized BLF polycrystal could be related to the improvement of fluoride-ion conductivity of BLF. Details will be discussed in this presentation.

Acknowledgement

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5:40 PM DT17.07

Fluoride-Ion Solid Electrolyte of La-Sr-F-S Multiple-Anion Compounds [Shintaro Tachibana](#)¹, Kazuto Ide², Hisatsugu Yamasaki², Takeshi Tojigamori², Hidenori Miki², Takashi Saito³, Takashi Kamiyama³ and Yuki Orihara¹; ¹Ritsumeikan University, Japan; ²Toyota Motor Corporation, Japan; ³High Energy Accelerator Research Organization(KEK), Japan

All-solid-state fluoride-ion batteries (FIBs) are highly attracted attention due to high theoretical energy density and high safety compared with those of conventional lithium-ion batteries (LIBs)[1]. However, it is far from practical use because there is no solid electrolyte which exhibits high ionic conductivity and offers wide electrochemical potential window like lithium-ion conductor. The previously reported fluoride-ion conductors are mostly single-anion compounds[2]. To our best knowledge, there is few reports on the fluoride-ion conductor materials containing mixed-anion compounds. In the field of material sciences, multiple-anion compounds have recently attracted attention, and novel structures with multiple anions have been reported. Compared with existing materials such as oxides and fluorides, mixed-anion compounds have the possibility to exhibit innovative functions due to their specific crystal and coordination structure[3]. Therefore, using mixed-anion compounds could realize much higher physical properties than ever before. We have already proposed the material design of fluoride ion conductor using fluorosulfide compounds, where Yb₃F₄S₂ exhibits mixed ionic and electrical conduction[4]. Although Yb₃F₄S₂ is not suitable as a solid electrolyte due to the electrical conductivity, appropriate substitution to Yb site may find fluoride ion conductors in the same crystal structure.

In this study, we synthesized La₂SrF₄S₂ compounds by solid-state reaction. In the synthesis, F⁻-deficient and F⁻-excess type of La-Sr-F-S compounds

were synthesized by controlling the weight ratio of the LaF_3 and SrF_2 precursors. The crystal structure of the synthesized compounds was characterized by X-ray diffraction. Neutron diffraction and ^{19}F MAS NMR reveal fluoride-ion conduction mechanism of the $\text{La}_2\text{SrF}_4\text{S}_2$ compounds. Electrochemical Impedance Spectroscopy indicate that the prepared $\text{La}_2\text{SrF}_4\text{S}_2$ compounds shows $2.95 \times 10^{-5} \text{ S cm}^{-1}$ at 423 K. The electrochemical potential window of $\text{La}_2\text{SrF}_4\text{S}_2$ compounds is more than 4 V. Since Fluoride-sulfide $\text{La}_2\text{SrF}_4\text{S}_2$ has already secured a fluoride ion conduction path without introducing lattice defects, its conduction mechanism differs from those of $\text{La}_{1-x}\text{Ba}_x\text{F}_{3-x}$ fluoride ion conductor originating from F^- vacancy.

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SESSION DT18: Poster Session II: Protons
 Tuesday Afternoon, July 19, 2022
 6:00 PM - 8:00 PM
 Mezzanine Level, Second Floor, Stadler

DT18.01

Impact of Na Concentration on the Phase Transition Behavior and H^- Conductivities of $\text{Ba}_2(\text{Li}_{1-x}\text{Na}_x)\text{H}_3\text{O}$ Solid Solution Kei Okamoto^{1,2}, Fumitaka Takeiri^{1,2,3}, Masao Yonemura⁴, Takashi Saito^{2,4}, Kazutaka Ikeda^{2,4}, Toshiya Otomo^{2,4}, Takashi Kamiyama^{2,4} and Genki Kobayashi^{1,2}; ¹Bunshi Kagaku Kenkyujo, Japan; ²Sogo Kenkyu Daigakuin Daigaku, Japan; ³Kagaku Gijutsu Shinko Kiko, Japan; ⁴Daigaku Kyodo Riyo Kikan Hojin Ko Energy Kasokuki Kenkyu Kiko, Japan

A hydride ion (H^-) has promising features for fast ionic conduction in solids, such as monovalence, a suitable ionic size comparable to O^{2-} , and high polarizability. We recently have developed a new K_2NiF_4 -type oxyhydride $\text{Ba}_{1.75}\text{LiH}_{2.7}\text{O}_{0.9}$ (BLHO), which exhibits H^- superionic conductivity ($\sigma \geq 10^{-2} \text{ S/cm}$, $E_a \leq 30 \text{ kJ/mol}$) above 315°C via the order-disorder phase transition [1]. In this work, we synthesized solid solutions $\text{Ba}_2(\text{Li}_{1-x}\text{Na}_x)\text{H}_3\text{O}$ to stabilize the H^- superionic phase in BLHO, and investigate the impact of Na concentration on the phase transition behavior and conductivities [2].

Powder samples of nominal composition $\text{Ba}_2(\text{Li}_{1-x}\text{Na}_x)\text{H}_3\text{O}$ ($x = 0.2, 0.4, 0.6, 0.8$) were synthesized by high pressure methods. The sintering conditions is $600 - 700^\circ\text{C}$ for 1hr under $2 - 3 \text{ GPa}$. The crystal structure and composition were determined by Rietveld analyses for X-ray diffraction (XRD) and neutron diffraction (ND) data. The phase transition behavior for each composition was investigated by temperature controlled XRD and differential scanning calorimetry (DSC). Ionic conductivities were measured by electrochemical impedance spectroscopy with an applied voltage of $10 - 50 \text{ mV}$ in the frequency range $35 \text{ MHz} - 0.1 \text{ Hz}$.

$\text{Ba}_2(\text{Li}_{1-x}\text{Na}_x)\text{H}_3\text{O}$ maintained the K_2NiF_4 -type structure with BLHO up to the composition of $x \leq 0.6$. The change in lattice constants with increasing Na contents was in accordance with Vegard's law, indicating that the solubility range in the sample is $0 \leq x \leq 0.6$. The temperature controlled XRD and DSC measurements confirmed that the transition temperature to the superionic conduction phase tends to decrease with increasing Na contents. The temperature at which the conductivity drastically enhances toward the superionic conduction state also lowers with the change in phase transition behavior, suggesting that the Na-doping effectively stabilizes the superionic phase of BLHO.

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DT18.02

Effect of H^- Concentration on Electrode Properties for Perovskite-Type Oxyhydride $\text{BaTiO}_{3-x}\text{H}_x$ Tasuku Uchimura^{1,2}, Fumitaka Takeiri^{1,2,3}, Kei Okamoto^{1,2}, Takashi Saito^{4,5}, Takashi Kamiyama^{4,5} and Genki Kobayashi^{1,2}; ¹Bunshi Kagaku Kenkyujo, Japan; ²The Graduate University for Advanced Studies (SOKENDAI), Japan; ³Kagaku Gijutsu Shinko Kiko, Japan; ⁴Daigaku Kyodo Riyo Kikan Hojin Ko Energy Kasokuki Kenkyu Kiko, Japan; ⁵Sogo Kenkyu Daigakuin Daigaku, Japan

A perovskite-type oxyhydride $\text{BaTiO}_{3-x}\text{H}_x$ is a unique compound exhibiting H^-/e^- mixed conductivity [1,2]. Recently, we have demonstrated that $\text{BaTiO}_{3-x}\text{H}_x$ can act as a hydrogen-permeable electrode for H^- conductors [3]. However, to apply $\text{BaTiO}_{3-x}\text{H}_x$ to electrodes for electrochemical devices such as fuel cells, it is necessary to improve both conductivities of e^- and H^- . In this study, we focused on the relationship between H^- concentration x in $\text{BaTiO}_{3-x}\text{H}_x$ and the electrode properties. The samples with various compositions in $0 < x \leq 2$ were synthesized by the mechanochemical method and the effect of H^- contents on crystal structures and electrochemical properties including H^- and e^- conductivities, and hydrogen permeability were investigated.

In preparation of $\text{BaTiO}_{3-x}\text{H}_x$, starting materials BaH_2 , BaO , TiO_2 , and TiH_2 were mixed with the nominal composition $0 \leq x_{\text{nom}} \leq 2$ in Ar-filled glovebox. The mixtures from starting materials were dry-milled in a ZrO_2 container with ZrO_2 balls under Ar atmosphere at room temperature. Obtained powder was characterized by X-ray diffraction (XRD), neutron diffraction (ND), and thermogravimetry/differential thermal analysis (TG-DTA), which determined the composition and crystal structure.

After mechanical activation, laboratory-XRD patterns derived from cubic-perovskite phase with the space group of $\text{Pm}\bar{3}\text{m}$ were detected.

As x_{nom} increased from 0.1 to 1.25, calculated lattice constant linearly expanded up to 4.043 \AA ($x_{\text{nom}} = 1.25$). In $x_{\text{nom}} = 1.25$ and 2, the lattice constant was constant, and the impurities was detected. Therefore, the maximum solubility limit of $\text{BaTiO}_{3-x}\text{H}_x$ might be approximately 1. Moreover, we estimated oxygen deficiencies ($\approx \text{H}^-$) of single-phase $\text{BaTiO}_{3-x}\text{H}_x$ by TG measurement under O_2 flow, assuming the following equation $\text{BaTiO}_{3-x}\text{H}_x + 0.5x\text{O}_2 \rightarrow \text{BaTiO}_3 + 0.5x\text{H}_2$. From the weight gain rate, the calculated oxygen deficiency of $x_{\text{nom}} = 1$ is 0.84, which indicated that $\text{BaTiO}_{3-x}\text{H}_x$ synthesized by mechanochemical method contains higher H^- concentration than that by O^{2-}/H^- exchange reaction. The results of XRD and TG-DTA indicated that $\text{BaTiO}_{3-x}\text{H}_x$ ($x > 0.60$) might be synthesized by mechanochemical method. In the presentation of the day, we will discuss the detailed characterization including neutron diffraction, and the correlation between H^- concentration and the electrode property for $\text{BaTiO}_{3-x}\text{H}_x$.

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DT18.03

Structure and Proton Conduction in $\text{CsHSO}_4\text{-H}_3\text{PW}_{12}\text{O}_{40}$ Composites Nana Fukaya, Ryuya Nakaomoya, Takumi Inada, Yohei Noda, Satoshi

Koizumi and Haruyuki Takahashi; Ibaraki Daigaku, Japan

The development of solid electrolytes for the intermediate-temperature fuel cells is expected. One of the candidates for solid electrolytes are inorganic solid acids, such as CsHSO_4 (CHS). The CHS transforms to superprotonic phase at 141 °C. It has been tried that high proton conduction is maintained in a wide temperature range by composites of CHS and another compound. $\text{H}_3\text{PW}_{12}\text{O}_{40}$ (WPA) has been known as one of another compounds for CHS-composites. In the previous research, it was shown that the composite of CHS and WPA at 90:10 (mol%) by mechanical milling (MM) method indicates high proton conductivity of 10^{-4} – 10^{-2} S/cm from 30 to 150 °C. In the present investigation, composites were prepared by the solution method. The advantages of the solution method are the uniformity of solution and the clear distinguishment of matrix element in the composite.

CHS and WPA aqueous solutions were appropriately mixed. CHS/WPA molar ratio of $x/(100-x)$ was abbreviated to Csx. A coprecipitation was formed in the solution. Two kinds of samples were prepared; one is dried sample A of coprecipitation, another is dried sample B from aqueous solution including coprecipitation. The sample A of Cs90 was calcined at 800 °C for 3 hours: Cs90H.

It was verified that the proton conductivity for sample B of Cs90 is similar to that for CHS-WPA composite by MM method. In contrast, the proton conductivity for sample A was about 10^{-6} S/cm. Therefore, the sample A is a matrix element of composite. All the sample A: Cs60, Cs90 and Cs90H was identified as $\text{Cs}_x\text{H}_{(3-x)}\text{PW}_{12}\text{O}_{40}$ (CsWPA) based on the XRD patterns. CsWPA is obtained from the replacement of H with Cs in WPA. The XRD peaks of Cs60 and Cs90 were broader than that of Cs90H. The crystallite size of Cs60 and Cs90 was evaluated as 40 nm and 35 nm according to the Scherrer equation, respectively. The sharp diffraction peaks of Cs90H result from the crystal growth by calcination at 800 °C. Although the XRD profiles of Cs60 and Cs90 was almost the same, it was found that the amount of Cs for both samples was different by the XRF measurement. The composition of Cs60 and Cs90 was estimated to be $\text{Cs}_2\text{HPW}_{12}\text{O}_{40}$ and $\text{Cs}_3\text{PW}_{12}\text{O}_{40}$, respectively.

The sample A of Cs90 and Cs90H are powdery. On the other, Cs60 is transparent and glass-like outer shape. So, all the sample A were observed under an optical microscope and the SEM. The SEM images show that the average particle size of both Cs90 and Cs90H are 100 nm, while Cs60 was like a broken section of glasses same as macroscopic view. The surface areas of Cs60, Cs90 and Cs90H are 60 m²/g, 100 m²/g and 3 m²/g by the BET method, respectively. It was found that the microstructure of the CsWPA is different depending on the composition.

The effect of microstructure of CsWPA as a matrix element of composites on the proton conduction was investigated. Composites of CHS and CsWPA: Cs60, Cs90 and Cs90H was prepared. The phase transition of CHS was observed in the Cs90H-composite. The Cs90H-composite behaves just a mechanical mixture rather than a composite. In contrast, the phase transition of CHS did not detect in the Cs60- and Cs90-composites. The proton conductivity for the Cs60-composite is 2×10^{-3} S/cm at 130 °C, that is higher than that for the Cs90-composite of 1×10^{-5} S/cm. It is concluded that the interfacial areas of matrix element play an important role on the proton conduction of CHS-CsWPA composites.

DT18.04

Structure, Microstructure and Electrical Transport Properties of High-Entropy $\text{BaZr}_{0.2}\text{Hf}_{0.2}\text{Sn}_{0.2}\text{Ti}_{0.2}\text{M}_{0.2}\text{O}_3$ (M = TM, RE) Perovskite Oxide Group Daniel Jaworski, Wojciech Skubida, Aleksandra Mielewczyk-Gryn, Sebastian Wachowski, Tadeusz Miruszewski and Maria Gazda; Politechnika Gdanska, Poland

The discovery of high-entropy alloys at the start of the XXI century established a new path in materials engineering. A few years later Rost et al. proved that the high entropy concept can be applied in oxides, creating high-entropy oxides (HEO) family [1]. High-entropy perovskite oxides (HEP) is a subgroup of HEO, firstly reported by Jiang et al. in 2018 [2]. They form ABO_3 structures and contain minimum 5 different metal cations in A or B sublattice in equimolar amounts. The high configurational entropy as a design concept allows stabilization of single oxide phase and induces severe lattice distortions that influence not only mechanical but also transport properties. Thanks to large possible metal combinations and synergistic effects, with each discovered oxide there are always new relations to examine of oxide's structural, microstructural, and transport properties.

In our previous work, we determined the proton conductivity in two high-entropy perovskite oxides containing 5 and 7 different elements in B-site [3]. However, in this study we present a much broader examination of a group denoted as $\text{BaZr}_{0.2}\text{Hf}_{0.2}\text{Sn}_{0.2}\text{Ti}_{0.2}\text{M}_{0.2}\text{O}_3$, where M is another transition or rare-earth metal cation. All samples were synthesized using the solid-state reaction method in a two-step synthesis. The characterization of materials was performed using X-ray diffraction, scanning electron microscopy, thermogravimetric analysis and electrochemical impedance spectroscopy.

It was found that the type of added cation influenced greatly the size of lattice constant, sinterability of the pellets and thermal expansion coefficients. In the terms of electrical transport properties, the conductivity range from 0.1 to 10^{-6} S/cm at 800 °C and activation energies indicates the ionic or electronic type of conductivity. Moreover, in humidified conditions the hydration, hydrogenation and isotopic effect are visible.

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DT18.06

Hydration Entropy of Triple Conducting Perovskites—Correlations Derived from DFT Calculations and Experimental Data Petter Rosander¹, Maximilian F. Hoedl², Rotraut Merkle², Göran Wahnström¹, Eugene Kotomin² and Joachim Maier²; ¹Chalmers University, Sweden; ²Max Planck Institute for Solid State Research, Germany

Oxides with protonic, electronic, and oxygen vacancy conductivity ("triple conductors") are key functional materials as electrode in protonic ceramic fuel and electrolyzer cells, or for hydrogen permeation membranes. While $(\text{Ba,Sr,La})(\text{Fe,Co,Zn,Y})\text{O}_{3-d}$ perovskites exhibit a high concentration of oxygen vacancies, the degree of hydration by dissociative water incorporation $\text{H}_2\text{O} + \text{V}_\text{O}^{\bullet\bullet} + \text{O}_\text{O}^{\text{s}} \rightarrow 2 \text{OH}_\text{O}^{\bullet}$ remains significantly smaller than in $\text{Ba}(\text{Zr,Y})\text{O}_{3-z}$ electrolyte materials.[1] This is a consequence of standard hydration enthalpy as well as entropy being less favorable than for $\text{Ba}(\text{Zr,Y})\text{O}_{3-z}$. The less negative hydration enthalpy of $(\text{Ba,Sr})\text{FeO}_{3-d}$ can be related to a large degree of covalency of the Fe-O bonds, including partial hole transfer from Fe to O,[2] which decreases the basicity of the oxide ions.

The present investigation is focused on elucidating the origin of the more negative standard hydration entropy in $(\text{Ba,Sr})\text{FeO}_{3-d}$. [3] Extended phonon calculations of supercells with protonic defects and/or oxygen vacancies are performed using a highly efficient algorithm for the extraction of force constants.[4] The changes in the phonon spectra upon introducing defects are analyzed in detail. Correlations of calculated and experimental hydration entropies with other materials parameters will be discussed.

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DT18.07

Proton Conductivity in BaZrO₃-Based Thin Film Prepared by Pulsed Laser Deposition Eiki Niwa, Taiki Kawashita, Hyo Y. Kim, Niki Nakagawa, Jun T. Song, Atsushi Takagaki and Tatsumi Ishihara; Kyushu Daigaku, Japan

Recently, protonic ceramics-based fuel cell (PCFC) is attracting as the clean and highly efficient energy conversion device without the emission of CO₂, NO_x and so on because global warming has been more serious. Solid oxide fuel cell (SOFC) has been expected as one of such promising devices. SOFC can generate high power density due to high-temperature operation. However, the present SOFC whose electrolyte is oxide-ion conductor cannot be operated under high fuel utilization condition. PCFC is high energy conversion device at intermediate temperature. In this study, we investigated the preparation of the thin film of the BaZrO₃ based electrolyte for PCFC electrolyte such as BaZr_{1-x}Yb_xO_{3-δ} (BZYb) and BaCe_{1-x}Zr_xY₃O_{3-δ} (BZCY) by pulsed laser deposition (PLD) method and the electrical conductivity of these thin films was measured by Van der Pauw method. The fabrication of NiFe anode-supported PCFC with these thin-film electrolyte was also tried. Thin film was prepared by PLD with 2 kinds of BZYb target, which were prepared by solids state reaction and Pechini method. 2 kinds of the sample of thin film of BZYb were analyzed by X-ray diffraction method in order to compare the formed phases and crystalline orientation. Both thin-film samples have the single phase of the cubic perovskite-type structure. The X-ray diffraction pattern of thin film with the target material by solid state reaction method was close to that of powdery state. On the other hand, the thin film with the target material by Pechini method is high crystalline orientation because only the diffraction peak with certain Mirror index in XRD pattern was extremely high. It was suggested that the thin film with the target by Pechini method is low grain boundary content. It was confirmed from SEM observation that 2 kinds of BZYb target materials have the different of sintering density. The target material by solid state reaction method is low density in spite of the sintering at 1700 °C and can be confirmed many pinholes on the surface. In contrast, the surface morphology of the target material by Pechini method was dense. The electrical conductivities of high-orientation thin films are higher than that of sintered-body sample with same composition. In this study, increased proton conductivity in thin film is reported.

DT18.08

Water Uptake Kinetics in High Entropy Oxides Wojciech Skubida, Daniel Jaworski, Tadeusz Miruszewski and Maria Gazda; Politechnika Gdanska, Poland

High entropy oxides (HEO) can be described as multicomponent oxides stabilized by configurational entropy [1]. These materials can exhibit novel and unexpected properties which have not been sufficiently studied so far. Considering possibility of utilization of HEOs in electrochemical devices it is crucial to know their electrical properties.

Electrical conductivity relaxation (ECR) is one of the methods which allows to observe and measure the diffusion of ionic species in materials. A chemical diffusion that proceeds via ambipolar transport is caused by a gradient of the chemical potential of neutral species. Diffusion of water in solids can be described by a single-fold process (a single diffusion coefficient) [2,3] and in some cases by the two-fold relaxation process (multiple diffusion coefficients) [4-7].

In this work we present comprehensive studies of electrical transport properties of selected materials as a function of temperature during isothermal change from dry to humidified atmosphere. The properties were investigated via ECR measurements utilizing impedance spectroscopy. Impedance spectroscopy method, allows in some cases, to separate bulk- and grain boundaries-related influence on the transport properties which may clarify which diffusion path of water and charge carriers (protons, oxygen ions) limits the process kinetics. What is more, the difference between diffusion paths of water molecule (as a whole) and correlated proton and oxygen ions can be observed. The path of proton migration through an oxides can be defined precisely as the description of proton-related transport properties such as bulk diffusion and surface exchange reaction are possible. Collected data allowed to calculate diffusion and surface exchange coefficients of water molecule (D_{H₂O}, k_{H₂O}), protons (D_H, k_H) and oxygen ions (D_O, k_O).

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DT18.09

Hydrogenation Transformation of BaZr_{0.5}In_{0.5}O_{2.75} Cubic Perovskite Hajime Toriumi, Sho Kitano, Hiroki Habazaki and Yoshitaka Aoki; Hokkaido University, Japan

Cubic perovskite type barium zirconate, BaZr_{1-x}In_xO_{3-δ} (0 < x < 0.7), have been intensively studied for their excellent proton conductivity and tolerance to high p_{H₂O} atmosphere. Despite the fact that In(III) oxides are readily reduced at elevated temperature under reduced atmosphere, the thermochemical behavior of BaZr_{1-x}In_xO_{3-δ} under reduced conditions is still unclear. Herein, we demonstrated that BaZr_{0.5}In_{0.5}O_{2.75} (BZI55) is converted to highly-oxygen-deficient perovskite phase with metallic conductivity by reduction in H₂ gas at elevated temperature. BZI55 was synthesized by solid state reaction method. Pale white BZI55 was changed to black-colored phase by heating at 800°C for 24h in dry H₂. Hereafter, the black phase after the H₂ reduction was denoted as H-BZI55. The XRD measurements confirmed that H-BZI55 still retained cubic perovskite structure and the change of lattice constants by the H₂ reduction was only -0.07%. TG measurements revealed that BZI55 loose the weight by 2.7% by H₂ reduction at 800°C, and thus the composition of H-BZI55 was estimated to BaZr_{0.5}In_{0.5}O_{2.27} by assuming that mass loss was caused only by the loss of lattice oxygen. Electrical conductivity of H-BZI55 were measured by 4-probe DC method in dry H₂ atmosphere. H-BZI55 exhibits metallic conduction behavior with less-pronounced temperature dependence and the conductivity was significantly high in the range of 10⁻¹-10⁻² S cm⁻¹ at temperature above 300°C. The concentration and mobility of the hydrogen impurity were under investigation.

DT18.10

Effects of Sintering Additives on the Proton Uptake of BaZr_{0.4}Ce_{0.4}Y_{0.1}Yb_{0.1}O_{2.9} Amir Masoud Dayaghi¹, Laura Almar², Sonia Escolástico Rozalén², Einar Vøllestad³, Jose M. Serra² and Truls Norby¹; ¹Universitetet i Oslo, Norway; ²Instituto de Tecnologia Quimica, Spain; ³SINTEF Community, Norway

We examined the effect of NiO, ZnO, and CuO sintering additives in small (0.5 wt%), moderate (1 wt%), and large (2 wt%) amounts, on the hydration thermodynamics and sintering behaviour of proton conducting BaZr_{0.4}Ce_{0.4}Y_{0.1}Yb_{0.1}O_{2.9}. Adding a small amount of NiO, and a moderate amount of ZnO or

CuO has an insignificant effect on effective acceptor concentration, and thus proton concentration. Increasing the amounts to moderate for NiO and high for ZnO and CuO decreased the effective acceptor concentration. NiO sintering additive has the most detrimental effect on hydration while has the highest positive impact on grain growth and densification. Consequently, a small amount of NiO is found to be the preferable sintering aid with respect to optimising both hydration and sintering. Moreover, different strategies for controlling the BaO activity in the environment during pellets sintering were applied, highlighting the importance of the sintering processes on proton uptake and suggesting a partial explanation for the wide diversity in conductivity values reported in literature.

DT18.11

Biomaterial “HAp-Collagen Complex” of Non-Humidified Proton Conductivity Tomoki Furuseki and Yasumitsu Matsuo; Setsunan Daigaku, Japan

In recent years, biomaterials, such as polysaccharides and proteins, have been attracting attention as novel environmentally friendly materials because biomaterials exist abundantly in nature and have biodegradable. In addition, those have a variety of excellent functions such as enzymatic reactions and ion transport etc. In the previous studies, we reported that the biomaterials such as DNA, collagen, and the squid axon with ion channels exhibit proton conductivity under humidified conditions. In addition, the fuel cell using these biomaterials as the electrolyte becomes a power source to drive electric devices such as the LED light. It is also known that hydroxyapatite (HAp), which is one of the inorganic biomaterials, shows proton conductivity from a high temperature of $\sim 700^\circ\text{C}$. The HAp exists as a complex with collagen in nature, such as bones and fish scales in nature. However, the proton conductivity of the HAp-collagen complex has not yet been investigated, despite the fact that both HAp and collagen show proton conductivity. In this study, the proton conductivity of the HAp-collagen complex was investigated with fish scales as the natural HAp-collagen complex specimen. In order to investigate the electrical conductivity in the HAp-collagen complex, we have measured the temperature dependence of electrical conductivity of the collagen, HAp and HAp-collagen complex under the non-humidified condition in the temperature range from 100 to 200°C . As a result, the electrical conductivities of the HAp and HAp-collagen complex increased with increasing temperature, while the non-humidified collagen didn't show the remarkable temperature dependence of electrical conductivity. These results indicate that HAp-collagen complex and HAp have the potential of proton conductor. To ensure that this electrical conductivity in the HAp-collagen complex is proton conductivity, we prepared the deuterium specimen (D-HAp collagen) and measured proton conductivity. It was found that the electrical conductivity of the D-HAp collagen becomes lower than that of the HAp-collagen complex. This result indicates that electrical conductivity observed in the HAp-collagen complex is caused by the migration of protons. Further, it was also found that the values of proton conductivity in HAp and HAp-collagen complex at 190°C become $3.73 \times 10^{-6} \text{ S/m}$ and $8.20 \times 10^{-5} \text{ S/m}$, respectively. These results indicate that the HAp-collagen complex exhibits higher conductivity than HAp. In addition, from the temperature dependence of proton conductivity in these materials, we have obtained the activation energies of the HAp and HAp-collagen complex. The activation energies of proton migration in HAp and HAp-collagen complex were 0.42 eV and 0.11 eV, respectively. In this way, the activation energy becomes lower due to the formation of the complex of HAp and collagen. These results indicate that the proton conduction pathway changes by forming the complex of HAp and collagen. Furthermore, to investigate the role of the HAp molecule in the HAp-collagen complex, we have prepared specimens with several concentrations of the HAp molecule and measured the proton conductivity of these materials. As a result, the proton conduction pathway in the HAp-collagen complex is formed above 25% HAp concentration. These results indicate that, in the HAp-collagen complex, the new proton conduction pathway is formed by doping of HAp, and high-proton conduction in the HAp-collagen complex is realized under the non-humidified condition.

DT18.12

Study on Proton Conductivity via Hydrated Water in Chitosan Yuki Hirota¹, Taiki Tominaga², Yukinobu Kawakita³ and Yasumitsu Matsuo¹; ¹Setsunan Daigaku, Japan; ²CROSS, Ippan Zaidan Hojin Sogo Kagaku Kenkyu Kiko, Tsuchiura, Ibaraki, JP, other/research, Japan; ³J-Parc Center, Japan

Bio-materials with proton conductivity are essential for applying to the next-generation energy “fuel cells”. Recently, we demonstrated that the biofuel cell using biopolymer “chitosan” drives electrical devices such as the LED light and indicated that the hydration of chitosan yields high-proton conductivity. From these results, it is deduced that the hydration of the side chain causes higher proton conductivity in biopolymers in chitosan. As well-known, there are various types of hydrated water, such as tightly bound, loosely bound, and free waters in biomaterials.

In this work, we have investigated the relationship between proton conductivity and the loosely bonded water in the side chain of chitosan using relative permittivity and neutron quasi-elastic scattering (QENS).

The chitosan sheet using this work was 0.08 mm in thickness and 4.5 cm \times 4.5 cm in area. Furthermore, the number of water molecules was adjusted to 12 per chitosan-monomer unit.

In order to separate the types of water molecules in the hydrated chitosan, we measured the temperature dependence of relative permittivity ϵ_r . As a result, ϵ_r in the hydrated chitosan begins to increase with the change of slope around 245 K and shows small peaks at around 261 K and 273 K.

These results indicate that these peaks are caused by the water molecule included in the hydrated chitosan because there are no peaks at about 261 K and 273 K in dry chitosan. This result means that two types of water at least exist in the hydrated chitosan. Considering that the melting point of free water is at 273 K, it is deduced that the peak at around 273 K is caused by the melting of free water in the hydrated chitosan. The peak at around 261 K means that waters are melting even below 273 K, at which free waters melt. It is well known that the bonded water melts even below 273 K by freezing point depression. Considering these facts, the peak at around 261 K is caused by the melting of the bonding water with the side chain of chitosan, and the beginning of the increase in ϵ_r at around 245 K results from the local melting of loosely bonded waters observed as the precursor effect of the melting of the water bonded with the side chain of chitosan.

In addition, we have investigated proton dynamics of the loosely bonded water in chitosan from a microscopic point of view using QENS. From this result, the activation energy associated with the melting of the loosely bound waters can be calculated to be 0.32 eV. This value is in good agreement with that of 0.35 eV obtained from the Arrhenius plot of proton conductivity in the hydrated chitosan.

These results suggest that proton conduction in chitosan was caused by the rearrangement of hydrated waters between the side-chain in chitosan and water molecules.

DT18.13

Proton Conductivity in Hydrated Dipeptides Crystal Gly-Ser and Gly-Pro Hitoki Semizo, Haruka Kai, Hitoshi Nishimura and Yasumitsu Matsuo; Setsunan University, Japan

As well known, the fabrication of a low-cost fuel cell without the environmental load in the manufacturing and waste processes is required. Biofuel cells using biomaterials are environmentally friendly and inexpensive. For example, collagen, chitin and DNA are abundant in nature and exhibit proton conductivity in humidified conditions. Therefore, these biomaterials can be used as electrolytes of fuel cells. The biopolymer “collagen” is a protein composed of amino acids such as “glycine”, “proline”, and “hydroxyproline”, and these amino acids are bonded with water molecules. In the previous works, we have indicated that proton exchange between water and the side chain of these amino acids plays an important role in proton conductivity. In this study, we have investigated the relationship between hydration of the side chain in amino acids and the proton conductivity of glycylproline (Gly-Pro) composed of glycine and proline. In addition, the proton conductivity of glycylserine (Gly-Ser), in which the side chain is different from Gly-Pro, has been measured, and the key factors required for the appearance of proton conductivity have been investigated.

Gly-Pro and Gly-Ser crystals were grown from these solutions by a slow evaporation method. The proton conductivity of Gly-Pro and Gly-Ser crystals was measured using a precision LCR meter by changing the hydration number n , which is of water molecules per Gly-Pro monomer (or Gly-Ser monomer) at room temperature.

It was found that proton conductivity of Gly-Pro crystals started to increase at $n \sim 0.04$, saturated once at $n \sim 0.2$, increased again with increasing n , and became almost constant around $n > 0.5$. This result indicates that the hydration of Gly-Pro peptide is in two stages, $n \sim 0.2$ and $n \sim 0.5$. These results indicate that in Gly-Pro crystals, the saturation of proton conductivity at $n \sim 0.2$ is achieved by the breaking and rearrangement of hydrogen bonds in the first hydration cell, which is the hydration of water molecules with the N-H group of glycine and the C=O group of proline. In addition, it is deduced that the proton conductivity increases above $n \sim 0.5$ due to further hydration of water molecules to the first hydration cell.

On the other hand, in the Gly-Ser crystal, proton conductivity begins to increase at $n \sim 0.2$, then increases linearly with increasing n until $n \sim 2$, and thereafter the Gly-Ser crystal begins to melt. The structure at $n = 2$ in Gly-Ser suggests that the N-H group of glycine and the O-H group of serine are hydrated. These results indicate that the proton conductivity of Gly-Ser crystals is caused by the breaking and rearrangement of hydrogen bonds between the N-H group of glycine, the abundant O-H groups of serine and water molecules. From these results, it is deduced that the high-proton conductivity of Gly-Ser crystal is realized by the abundant O-H groups that are absent in Gly-Pro crystal.

DT18.14

Molecular Water Incorporation—From Doping to Confined Quasi-Liquid Transport Markus Joos¹, Maurice Conrad², Christian Schneider³, Rotraut Merkle¹, Thomas Schleid², Bettina V. Lotsch^{3,4} and Joachim Maier¹; ¹Max-Planck-Institut für Festkörperforschung, Germany; ²Universität Stuttgart, Germany; ³Max-Planck-Institut für Festkörperforschung Abteilung für Nanochemie, Germany; ⁴Ludwig-Maximilians-Universität München, Germany

Molecular water incorporation encompasses a broad range of interactions in solid state ionics, extending from substitutional mechanisms over chemical reactions and additive incorporation up to solid-liquid phase transitions. It is important for both fundamental science as well as technological applications. One can distinguish irreversible hydrolysis, and reversible incorporation. The latter can occur in molecular form, or dissociatively. The dissociative hydration of oxygen vacancies is the basis for protonic ceramic proton conductors operating at 300–600 °C. Molecular incorporation is important for proton conducting polymer electrolytes. Furthermore, it occurs in various inorganic materials and affects their ionic transport properties also with respect to ions other than H⁺/OH⁻.

We discuss similarities and differences of molecular water incorporation and its effect on Li⁺ cation conductivity for two prototypical compounds Li₂Sn₂S₅ and LiSCN, which are representative for two-dimensional layered materials and three-dimensional structures, respectively. The amounts of water incorporation observed for these materials range from trace amounts to stoichiometrically hydrated and up to water-excess compounds.

In LiSCN, molecularly incorporated water traces (~0.1%) act as dopant on the anion site (H₂O[•]_{SCN}) which is compensated by mobile V_{Li} defects^[1]. This does not only increase the concentration of mobile defects, but interestingly also their mobility. This substitutional mechanism of water doping is probably highly material specific. A more common molecular incorporation mechanism is the formation of stoichiometric hydrates, which occurs for many inorganic salts (e.g. lithium halides, LiSCN)^[2]. They are distinguishable by an altered crystal structure, modified physical properties (e.g. lower melting point), and often by a lower activation enthalpy of ion transport. However, in some special cases the activation enthalpy is severely increased (e.g. in LiI × 2 H₂O and LiSCN × 1 H₂O), which is possibly related to a strong trapping of the mobile defect by H₂O.

For materials composed of two-dimensional insoluble structural units (e.g. (Al,Si)-oxide layers or negatively charged SnS₂ sheets) and weakly bound cations, water can intercalate between the layers and coordinate to the interlayer cations (e.g. in vermiculite minerals or lithium tin sulfide, Li₂Sn₂S₅). In a limiting case, the addition of water results in a complete hydration shell for the mobile cation, which leads to liquid-like ion transport in a confined solid matrix, reaching conductivities as high as 2 × 10⁻² S/cm at 25 °C.^[3]

Extensive hydration can eventually lead to a dispersion or full liquefaction for both layered and three-dimensional materials, finally approaching conductivities typical for concentrated aqueous solutions. The transition depends on the composition of the host material, and can be entropically driven (lowering of the melting point) or due to structural collapse (complete solvation of at least one sublattice, e.g. exfoliation). This complex solid-liquid transition region is so far poorly understood and deserves further investigation.

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DT18.15

Electrochemical and Thermochemical Characterization of Mixed-Conducting High-Entropy Oxides Tadeusz Miruszewski, Daniel Jaworski, Wojciech Skubida and Maria Gazda; Politechnika Gdanska, Poland

The idea of entropy stabilization of inorganic materials triggered out the intensive research activity. High entropy oxides (HEOs) are a new class of multicomponent oxides stabilized by configurational entropy [1]. When various elements form one crystal structure, the neighbourhood of each cation is different. The differences between the constituents include valence difference, different bonding energy, atomic radii etc. This leads to a strong lattice strain that distorts the atom positions. The lattice distortions influence not only mechanical but also transport properties of HEO materials. In consequence, the transport properties, including both electrical and thermal properties, strongly depend on the structural properties [2-3].

Mixed ionic and electronic conductors conduct both mobile ions (oxygen ions or protonic defects) and electrons/holes. Triple conducting oxides (TCOs) belong to mixed ion-electron conductors however they are characterized by three mobile charge carriers - electrons, protons, and oxygen ions. Cubic perovskites containing both acceptor-type constituents as well as transition metals were showed to be promising triple conducting oxides [4-5]. What is very interesting, the protonic conductivity in triple conducting oxides may play a major role in TCO-based thermoelectrical devices.

Most of the properties of high entropy oxides which may exhibit mixed ionic-electronic conductivity, especially their thermoelectrical and electrochemical properties, have not been studied so far. We propose that, the combination of the high configurational entropy and mixed oxygen ionic, protonic and electronic conductivity (HEOs-TCOs) of selected high-entropy perovskites may render them interesting thermoelectrical and electrochemical materials.

This work is related to systematic description and understanding the thermoelectrical and electrochemical properties of different Ba(Ce,Zr,Y,Ti,Sn,Fe,Co,Mn)O₃ oxides with compositions and structures based on the oxides being protonic, oxygen ionic and electronic conductors. A structure and microstructure data of these materials will be analyzed with the use of X-ray Diffractometry (XRD) as well as by Scanning Electron Microscopy (SEM). Electrical conductivity measurements will be performed both by DC four-wire technique and Electrochemical Impedance Spectroscopy (EIS) as a function of temperature and water vapour or oxygen partial pressures. The temperature dependence of Seebeck coefficient and total thermal conductivity will be also measure and analyze.

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DT18.17

Manufacturing of Mixed Proton-Electron Conducting Ceramics—3D-Printing and Laser Post-Processing [Joanna Pospiech](#), Malgorzata Nadolska, Mateusz Cieslik, Aleksandra Mielewczyk-Gryn, Maria Gazda and Sebastian Wachowski; Politechnika Gdanska, Poland

Advanced manufacturing processes, such as 3D printing technologies, are attracting attention and are widely used in the energy conversion sector, as they allow the fabrication of the desired microstructures and shapes for specific electrochemical devices. Furthermore, the short prototyping time and low production costs make 3D printing appealing for industrial applications. Additive manufacturing of protonic conductive fuel cells elements is quite a novel approach. As recently, Mu et al. proposed the laser 3D-printing method that allows obtaining protonic ceramics with the desired crystal structures, microstructures, and geometries [1]. The designed method showed successful results which made laser post-processing a promising substitution for conventional solid-state synthesis carried in furnaces.

In this study, we present the results of technology development of 3D printing of the $\text{Ba}_{0.5}\text{La}_{0.5}\text{Co}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$ ceramics as positrodes for protonic ceramic fuel cells. The main focus of this work was integrating the micro-extrusion process with precise IR laser post-processing of deposited layers. The influence of the laser power, scanning speed and other parameters were investigated. Prepared printable inks consisted of ceramic powders dispersed in the polyvinyl alcohol (PVA) matrix, which was later removed in the post-processing stage. They were deposited on the dense BZCY442 electrolyte in order to examine the interface adhesion for the future proton conducting fuel cell elements. The characterization of the printed materials phase composition and microstructure before and after laser post-processing was carried out using X-ray diffraction technique and Scanning Electron Microscopy. Various compositions and conditions were tested and the most appropriate parameters of the laser post-processing were chosen.

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DT18.18

Tailoring the $\text{Ba}_{0.5}\text{La}_{0.5}\text{CoO}_{3-\delta}$ Properties by Iron Substitution [Iga Szpunar](#)¹, Aleksandra Mielewczyk-Gryn¹, Daria D. Balcerzak¹, Ragnar Strandbakke², Einar Vollestad³, Maria Balaguer⁴, Alfonso J. Carrillo⁴, Jose M. Serra⁴, Maria Gazda¹ and Sebastian Wachowski¹; ¹Politechnika Gdanska, Poland; ²Universitetet i Oslo, Norway; ³SINTEF Industri, Norway; ⁴Instituto de Tecnologia Quimica, Spain

Lanthanum barium cobaltite $\text{Ba}_{0.5}\text{La}_{0.5}\text{CoO}_{3-\delta}$ with perovskite structure is an extensively studied material. Interest in this compound results mainly from its potential application in electrochemical cells¹. It exhibits high electrical conductivity and good catalytic properties. However, its thermomechanical properties limit the applications. The thermal expansion coefficient of $\text{Ba}_{0.5}\text{La}_{0.5}\text{CoO}_{3-\delta}$ (BLC) is significantly higher than that of most of the used electrolytes, e.g., $\text{BaZr}_{1-x}\text{Ce}_x\text{Y}_y\text{O}_{3-\delta}$ (BZCY)². What is more, the proton concentration – and thus proton conductivity – is reported to be low. Iron substitution in cobalt sublattice gives the opportunity to gradually tailor the properties of this compound. Fe substitution can lower the TEC and it may also affect the concentration of proton defects³. With lowered TEC and higher proton conductivity $\text{Ba}_{0.5}\text{La}_{0.5}\text{Co}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$ may be successfully applied as a positrode in protonic ceramic fuel cells (PCFC).

In this study, we present the effect of iron substitution on the functional properties of $\text{Ba}_{0.5}\text{La}_{0.5}\text{Co}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$. The series of materials with a wide range of Fe content ($0 \leq x \leq 1$) were synthesized by solid-state reaction. The structure was investigated by the means of powder X-ray diffraction. The thermogravimetry was used for hydration and oxidation studies under air and nitrogen atmospheres. TEC was determined by the means of dilatometry, and electrical conductivity was investigated with a 4-point DC method.

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DT18.19

Electrical Conductivity and Transport Properties of $\text{La}_{0.9}\text{Sr}_{0.1}\text{MO}_{3-\delta}$ (M=Al, Ga, In, Er, Y) Perovskites Under Various Oxygen Partial Pressures [Cai Yen He](#) and Yi Hsuan Lee; National Taipei University of Technology College of Mechanical and Electrical Engineering, Taiwan

In this study, $\text{La}_{0.9}\text{Sr}_{0.1}\text{MO}_{3-\delta}$ (M=Al, Ga, In, Er, Y) were studied by measuring the electrical conductivity in wet and dehydration (dry oxygen at 1173k for 2h) conditions under wide range of oxygen partial pressures ($p_{\text{O}_2} = 10^{-28} \sim 0$ atm at 873 and 1073 K). Sr doped La-based perovskite materials have different ion transport properties, including oxide ion, proton and mixed proton and oxide ion conductors. $\text{La}_{0.9}\text{Sr}_{0.1}\text{GaO}_{3-\delta}$ and $\text{La}_{0.9}\text{Sr}_{0.1}\text{AlO}_{3-\delta}$ are considered as oxide ion conductors, $\text{La}_{0.9}\text{Sr}_{0.1}\text{YO}_{3-\delta}$ and $\text{La}_{0.9}\text{Sr}_{0.1}\text{ErO}_{3-\delta}$ are regarded as proton conductors. In addition, and $\text{La}_{0.9}\text{Sr}_{0.1}\text{InO}_{3-\delta}$ is a mixed proton and oxide ion conductor. According to our results, the conductivities of $\text{La}_{0.9}\text{Sr}_{0.1}\text{GaO}_{3-\delta}$ and $\text{La}_{0.9}\text{Sr}_{0.1}\text{AlO}_{3-\delta}$ showed approximately the same values in wet and dehydration conditions. Since $\text{La}_{0.9}\text{Sr}_{0.1}\text{GaO}_{3-\delta}$ and $\text{La}_{0.9}\text{Sr}_{0.1}\text{AlO}_{3-\delta}$ are considered as oxide ion conductors, conductivities did not change before and after the dehydration operation. In the case of proton conductors such as $\text{La}_{0.9}\text{Sr}_{0.1}\text{YO}_{3-\delta}$ and $\text{La}_{0.9}\text{Sr}_{0.1}\text{ErO}_{3-\delta}$, conductivity reduction could be observed significantly after the dehydration treatment under low oxygen partial pressures. On the other hands, dehydrated samples have higher conductivity than undehydrated ones under high oxygen partial pressures. It is suggested that more oxide-ion vacancies could react with oxygen to form holes to increase total conductivities after the dehydration operation. Furthermore, the conductivity of $\text{La}_{0.9}\text{Sr}_{0.1}\text{YO}_{3-\delta}$ and $\text{La}_{0.9}\text{Sr}_{0.1}\text{ErO}_{3-\delta}$ after the dehydration treatment decreased with the increase of CO concentration in CO–CO₂ atmosphere. It is indicated that oxide-ion vacancies near the surface could react with CO to increase polarization resistances. Finally, $\text{La}_{0.9}\text{Sr}_{0.1}\text{InO}_{3-\delta}$ is considered as a composite conductor. The conductivity in wet atmosphere is higher than after dehydration condition especially at lower temperature.

DT18.20

Microwave-Assisted Sintering of a Disordered Hexagonal Perovskite $\text{Ba}_7\text{Nb}_4\text{MoO}_{20}$ Electrolyte for Protonic Ceramic Electrochemical Cells Yoonseok Choi, Tae-Woo Kim, Sun-Dong Kim, Hye-Sung Kim and Ji Haeng Yu; Korea Institute of Energy Research, Korea (the Republic of)

The development of proton-conducting electrolyte materials with high conductivity and stability are essential for the practical application of solid oxide fuel/electrolyzer cells by lowering their operating temperature below 600°C. Hexagonal perovskite $\text{Ba}_7\text{Nb}_4\text{MoO}_{20}$ and its derivatives recently open up new directions in the design of protonic conductors besides the doped barium cerates/zirconates as they feature high conductivity in the absence of hole contributions in the temperature range between 400 to 600°C and show excellent chemical stability. However, such unique structures are formed at temperatures below 1100°C, otherwise, it easily contains secondary phases with poor conductivity. For this reason, it requires multiple calcination steps and delicate sintering processes to obtain the high-density electrolyte with high purity. To address this issue, we adopt microwave-assisted sintering, which comprises a short-term densification step using a microwave followed by an annealing step. The effects of some important process parameters such as temperature and annealing time were investigated in terms of phases, microstructures, density, and conduction properties of $\text{Ba}_7\text{Nb}_4\text{MoO}_{20}$ electrolytes. Our research shows that high purity and highly dense electrolytes can be fabricated with substantially reduced time and energy compared to the conventional sintering process.

DT18.21

Compositional and Structural Control in LLZO Solid Electrolytes Kade Parascos¹, Joshua L. Watts¹, Jose A. Alarco¹, Yan Chen² and Peter C. Talbot¹; ¹Queensland University of Technology, Australia; ²Oak Ridge National Laboratory, United States

Garnet-based solid-state electrolytes (SSEs) represent a promising class of materials for next generation batteries with improved safety and performance. However, lack of control over the composition and crystal structure of the well-known $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZO) garnet material has led to poor reproducibility with a wide range of ionic conductivities reported in the literature. Several recent studies have suggested that the homogeneity of the precursor mixture plays a critical role in obtaining targeted chemical and structural properties in the product. In this study, the role of precursor homogeneity in controlling the compositional and structural evolution of Al-doped LLZO is explored. In-situ X-ray and neutron powder diffraction (XRD and NPD) investigations coupled with scanning electron microscopy/energy dispersive spectroscopy (SEM/EDS) observations reveal a strong correlation between the spatial distribution of the doping element and the stability of the high-conductivity cubic-LLZO phase. Here, a solution-based synthesis technique is employed to introduce atomic-level mixing and enhance dopant homogeneity to mitigate the formation of the low-conductivity tetragonal phase. Further, the observed increase in cubic-LLZO obtained through the solution-based approach persisted without phase transformation upon cooling, which is an essential requirement for the application of this material as an SSE. Comparatively, conventional solid-state processing showed significant formation of the unwanted tetragonal LLZO modification. Impurity phases were also eliminated by improving elemental homogeneity along with a reduction in the onset of the formation of the cubic-LLZO phase to 700°C. It is expected that the experimental techniques presented here can be applied to other solid electrolyte systems to enable the reproducible synthesis of high-performance materials for future solid-state batteries.

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SESSION DT19: Simulation Techniques
 Session Chair: Rotraut Merkle
 Wednesday Morning, July 20, 2022
 Mezzanine Level, Second Floor, Georgian

9:10 AM **DT19.01

Accelerated Computations of Ionic Transport in Complex and Correlated Materials Boris Kozinsky; Harvard University, United States

Atomistic computation of ionic transport is a powerful tool for understanding and designing complex electrolytes, but progress is limited by two obstacles. The first is the lack of methods to perform molecular dynamics (MD) at sufficient time scales and system sizes to capture transport dynamics and disorder / interfaces that often control the material's performance. To address this issue we develop machine learning models for interatomic forces that achieve near-quantum accuracy and order of magnitude higher speed than DFT calculations. The Neural equivariant interatomic potential model (NequIP) is based on tensor-valued symmetry-preserving network architectures and achieves state-of-the-art accuracy and training efficiency for ionic conductors [1]. In order to enable autonomous selection of the training set for reactive systems, we developed the FLARE code that automatically constructs accurate non-parametric interatomic force fields on-the-fly from a molecular dynamics simulation [2]. We demonstrate the performance of accelerated MD simulations on dynamics of disordered ionic motion, superionic phase transitions, and transport across interfaces.

The second difficulty is that of accurately computing ionic conductivity in the presence of correlations. We have introduced a method for rigorously capturing correlations with molecular dynamics, that is orders of magnitude faster than the existing approach [3]. We use spectral decomposition of the short-time ionic displacement covariance to learn a set of diffusion eigenmodes that encode the correlation structure and form a basis for analyzing the ionic trajectories. This allows for significant acceleration and reduction of the uncertainty in computations of ionic conductivity in large electrolyte systems with a steady-state correlation structure.

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 Y. Xie et al, npj Comput Mater 7, 40 (2021)
 [3] N. Molinari et al, Phys Rev Lett 127, 025901 (2021)

9:40 AM DT19.02

Probing Ion Migration in ABX_3 Perovskite Compounds—Five Fallacies of Simulations Roger A. De Souza; Rheinisch-Westfälische Technische Hochschule Aachen, Germany

The migration of the constituent ions of the ABX_3 perovskite structure is attracting ever increasing attention because of its relevance for a variety of applications. In some cases, the rate of ion migration should be increased, for example, in materials based on LaGaO_3 or $(\text{Na,Bi})\text{TiO}_3$ for fuel cell electrolytes, while in other cases, BaTiO_3 for capacitors or $\text{CH}_3\text{NH}_3\text{PbI}_3$ for photovoltaic devices, it should be minimised. Simulation studies have a central role to play in interpreting and explaining experimental transport data and providing insights at the atomic scale. A variety of simulation techniques have been employed to examine ion migration in perovskites to date. These techniques involve molecular static or molecular dynamic calculations, and employ classical pair potentials, reactive force-fields or quantum-mechanical calculations. Regardless of the technique, the results of simulations are often regarded as “scientific truth”. In this contribution, taking ion migration in BaTiO_3 [1], CaTiO_3 [2], LaMnO_3 [3] and MAPbI_3 [4] as examples, we draw attention to problems that may arise when using static calculations to obtain reliable activation barriers and to issues with molecular dynamics simulations of ion diffusion. We demonstrate that a far more critical approach to simulation results in the literature is required.

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 [3] J. M. Börgers and R. A. De Souza, *Phys. Chem. Chem. Phys.* **22** (2020) 14329.
 [4] D. Barboni and R. A. De Souza, *Energy Environ. Sci.* **11** (2018) 3266.

9:55 AM *DT19.03

Kinetic Monte Carlo Simulations of Ionic Conductivity in Electrolyte Materials Steffen Grieshammer; Rheinisch-Westfälische Technische Hochschule Aachen, Germany

Solid electrolytes, as found in solid state batteries or fuel cells, represent complex solid solutions with high concentrations of defects. In these materials, the interactions between the charge carriers and interactions with other defects can no longer be neglected when estimating the ionic mobility and conductivity. In fact, the transport properties result from the motion of the ions through various local environments with individual migration barriers and an analytical solution is generally not available.

Kinetic Monte Carlo methods enable the simulation of the transport in strongly doped materials with interacting defects by sampling the various migration environments allowing fast simulation of ionic conductivity for varying temperatures and compositions.

We designed the software MOCASSIN to provide easily accessible Monte Carlo simulations in crystalline electrolytes and simulate a wide range of systems. Parameterized with energies from density functional theory calculations, a better understanding of transport behavior as well as prediction of ionic conductivity is possible.

In this talk, I present our recent applications of Kinetic Monte Carlo simulations to solid electrolytes including cationic and anionic conductors for batteries and fuel cells. Combining first principles calculations with the KMC simulations, the link between the microscopic energy landscape and the macroscopic transport is established. Here, I demonstrate the strength of this method and discuss possible limitations.

- [1] S. Grieshammer, S. Eisele, *Diff. Foundation*, 2021, 29, 117-142.

10:15 AM DT19.04

Computation Material Design via Defect Optimizations of Li-Ion Conductors for Solid-State Li-Ion Batteries Sokseiha Muy and Nicola Marzari; Ecole Polytechnique Federale de Lausanne, Switzerland

Solid-state Li-ion batteries are strong contenders to replace current Li-ion batteries using liquid electrolytes, promising superior safety due to reduced flammability, larger range of operating temperatures as well as a higher energy density. The success of this technology hinges on the discovery of new Li-ion conducting materials such Li-containing argyrodite or garnet families with comparable ionic conductivity to that of liquid electrolytes and ideally be stable against high-voltage cathodes and Li anodes. In this talk, I will present a case study of computational material design and optimization of Li-ion conductors involving the selection of optimal dopants in terms of defect thermodynamics, and assessing their influence on Li-ion mobility. The comprehensive defect chemistry of the materials is obtained using a newly developed python package (“AiiDA-Defects”), which utilizes the AiiDA framework, a robust open-source high-throughput infrastructure that provides workflow automation while simultaneously preserving and storing the full data provenance in a relational database, thus making it queryable and traversable, and enabling high-performance data analytics. Detailed molecular dynamics simulations using machine-learned neural-network potentials trained on ab-initio data are used to estimate the ionic conductivity of Li. The reliability of the trained neural network potentials with respect to the size and diversity of the training data is also discussed. Finally, the extensive molecular dynamics trajectories are analyzed to reveal the mechanistic origins of the high mobility of Li-ion in this family of compounds.

SESSION DT20: Fundamentals of Hybrid Perovskites

Session Chair: Clare Grey

Wednesday Morning, July 20, 2022

Mezzanine Level, Second Floor, Arlington

9:10 AM **DT20.01

Solid State Ionics of the “Photo-Perovskites” Joachim Maier; Max-Planck-Institut für Festkörperforschung, Germany

Joachim Maier
 Max Planck Institute for Solid State Research, Physical Chemistry of Solids,
 70569 Stuttgart, Germany, e-mail: office-maier@kf.mpg.de

Organic-inorganic halide perovskites such as methyl-ammonium lead iodide are in the focus on photoelectrochemistry and presently belong to the most heavily investigated materials. From a solid state ionics point of view they show familiar properties to mixed conductors such as sensitivity to stoichiometry, stoichiometric polarization under load, chemical diffusion characterized by chemical resistance and chemical capacitance. Various reported “anomalies” resolve themselves when viewed in this way.

Also nano-ionic phenomena characterized by ion-redistribution at interfaces (e.g. $\text{TiO}_2/\text{MAPbI}_3$) can be demonstrated which – owing to the hitherto sole concentration on electronic redistribution – means a paradigm change for the photovoltaic community. A practical problem is provided by the low intrinsic and extrinsic chemical stabilities in particular under illumination. The contribution reports on the progress in this respect and discusses also the behavior of substitutions of ABC_3 on the A, B and C sites. Surprisingly, light also “affects” Solid State Ionics. The iodide conductivity was found to be enhanced along with e^- formation on illumination. This amazing finding fuels hopes for speculations about a new field “optoionics” and the possibility of novel light triggered electrochemical devices. Directly related with this phenomenon are enhanced chemical transport and permeation rate under illumination as well as reversible photo-demixing of I-Br mixtures.

9:40 AM *DT20.02

Understanding the Effect of Cation and Anion Substitution on Vacancy Migration in Perovskite Solar Cells Matt Pilot¹, Sam Pering², Peter Baker³, Dibyajyoti Ghosh⁴, Saiful Islam⁵ and Petra Cameron¹; ¹University of Bath, United Kingdom; ²Loughborough University, United Kingdom; ³Rutherford Appleton Laboratory, United Kingdom; ⁴Indian Institute of Technology Delhi, India; ⁵University of Oxford, United Kingdom

The highest efficiency Perovskite Solar Cells (PSC) often contain two [1], three [2] or even four [3] A site cations in the ABX_3 crystal structure. As well as a higher efficiency, mixed cation devices show higher reproducibility and stability [2]. Anion vacancies are highly mobile in lead halide perovskites and in our own work we have demonstrated that mixing both cations and anions strongly influences vacancy migration [4, 5]. In our first study we systematically changed the cation size, from rubidium (ionic radius 152 pm) to guanidinium (ionic radius 278 pm). In the second study we added increasing amounts of bromide into methyl ammonium lead iodide (MAPI). We use a combination of muon spectroscopy ($\mu\text{-SR}$), impedance spectroscopy and computational modelling to study the effect of mixing and our results showed that even small amounts of cation or anion substitution increases the activation energy for the motion of what we believe to be iodide vacancies.

In our more recent work, we have looked at the effect of the simultaneous substitution of cations and anions. We show that the results are much more complex in highly mixed materials, but that clear trends can still be observed. We have also investigated the effect that regions of 2-D perovskite (created by adding small amounts of the very large molecule, 5-aminovaleric acid to the perovskite) have on ion migration. In particular I will discuss our latest results from $\mu\text{-SR}$ studies of powders and impedance studies of complete cells.

- [1] Nature Energy, 2017, 2, 972–979
- [2] Energy Environ. Sci., 2016, 9, 1989–1997
- [3] Energy Environ. Sci., 2017, 10, 2509–2515
- [4] Energy & Environmental Science 12 (7), 2264–2272
- [5] Journal of Materials Chemistry A 7 (39), 22604–22614

10:00 AM DT20.03

Nonlinear Ion Mobility at High Electric Field Strengths in the Perovskites SrTiO_3 and $\text{CH}_3\text{NH}_3\text{PbI}_3$ Dennis Kemp and Roger A. De Souza; Rheinisch-Westfälische Technische Hochschule Aachen, Germany

Materials with the ABX_3 perovskite structure find application in ceramic capacitors, solid oxide fuel cells, photovoltaic cells or resistive switching devices. In all cases, ionic defects are present, and under an applied bias, these charge carriers will move. With the ongoing trend towards nanoscale device dimensions, the application of a few volts automatically translates into high electric field strengths and hence, to a non-linear increase in the ion mobility. In this study^[1], we investigated the mobility of anions $X(u_x)$ along $\langle 100 \rangle$ as a function of temperature T and field strength E using molecular dynamics (MD) simulations. Two different systems were examined: cubic SrTiO_3 as a representative inorganic perovskite and cubic $\text{CH}_3\text{NH}_3\text{PbI}_3$ (MAPbI_3) as a representative hybrid inorganic-organic perovskite. Both systems show field-independent mobilities at low field strengths ($E < 10^9 \text{ MV cm}^{-1}$) as expected. In the case of SrTiO_3 the field-dependent oxide-ion mobility u_0 can be described very well with an analytical treatment^[2] and a modified Haven ratio. In contrast, the field-dependent mobility of iodide ions u_1 in the hybrid perovskite MAPbI_3 revealed some unusual features. At high field strengths, the iodide ion mobility was underestimated by the analytical treatment, while in the field-independent regime u_1 was lower than expected, implying that moderate electric fields can decrease the anion mobility in MAPbI_3 . The role of the methylammonium (MA) cations in producing this behaviour is discussed. With the results of our study we are now able to quantitatively predict $u_x(T, E)$ for cubic, inorganic ABX_3 perovskites along $\langle 100 \rangle$. For the hybrid perovskites, more complex models need to be developed.

Literature:

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10:15 AM DT20.04

The Thermodynamics of Photo De-Mixing in Two-Dimensional Dion-Jacobson Mixed Halide Perovskites Yaru Wang¹, Alessandro Senocrate¹, Marko Mladenović², Algirdas Dučinskas³, Gee Yeong Kim¹, Ursula Rothlisberger², Jovana Milić³, Davide Moia¹, Michael Grätzel³ and Joachim Maier¹; ¹Max-Planck-Institut für Festkörperforschung, Germany; ²Institute of Chemical Sciences and Engineering, École Polytechnique Fédérale de Lausanne (EPFL), Switzerland; ³École polytechnique Fédérale de Lausanne (EPFL), Switzerland

Mixed halide perovskites are promising candidates for solar cells, light-emitting diodes and other opto-electronic devices owing to their tunable bandgaps. Interestingly, under light, these materials undergo segregation into two phases with different halide compositions (photo de-mixing). These two phases remix back in the dark to the pristine state (dark re-mixing)^{1, 2}. This phase instability is undesirable when aiming to solar cells with a stable output, while it creates possibilities for new device architectures.³ The observed light-induced evolution of different phases involves significant ion transport. However, the understanding of the thermodynamic factors and the underlying defect chemical mechanisms involved in this process is still missing. The improved stability of two-dimensional (2D) perovskites⁴ makes them suitable model systems for investigating photo de-mixing compared with classic three-dimensional (3D) mixed halide perovskites.

Here, we investigate the phase behavior of 2D Dion-Jacobson mixtures based on $(\text{PDMA})\text{Pb}(\text{Br}_{0.5}\text{I}_{0.5})_4$ (PDMA: 1,4-phenylenedimethan ammonium spacer) under light. We demonstrate that 2D mixed halide perovskites undergo reversible photo de-mixing both optically and structurally with direct transformation from the pristine phase to the de-mixed phases. We investigate the temperature dependent photo de-mixed compositions to extract the phase diagram under light (photo-miscibility-gap) with multiple methods in a temperature range that is relevant for optoelectronic applications. Lastly, we propose a model that discusses possible opto-ionic effects, which can contribute to the driving force of de-mixing^{2, 5, 6} and should therefore be considered in

the overall energy balance of the process, together with the electronic effects discussed in the literature.^{7,8} Our work sheds light on fundamental questions related to the phase behavior and the role of defects on the driving force of de-mixing. These findings will also aid compositional engineering of halide mixtures to enable optimization of optoelectronic devices as well as the development of other emerging systems exploiting opto-ionic effects.

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SESSION DT21: Defects and Transport Mechanisms

Session Chair: Steffen Grieshammer

Wednesday Morning, July 20, 2022

Mezzanine Level, Second Floor, Georgian

11:00 AM **DT21.01

Defects and Transport in Inherently Disordered Oxide Structures Truls Norby; Universitetet i Oslo Det Matematisk-naturvitenskapelige Fakultet, Norway

It is more than 20 years since the defect notation for inherently disordered crystals was mentioned and 10 years since it was properly presented, see Ref. [1] and references therein. It defines a lattice site with statistically disordered partial occupancy as “perfect” if the disorder is an inherent and necessary part of the description of the structure in its ground state. Simple examples comprise the 3/4 occupancy of the oxide ion site in $\delta\text{-Bi}_2\text{O}_3$ and the 5/6 occupancy of the oxide ion site in perovskite $\text{Ba}_2\text{In}_2\text{O}_5$. Other examples mentioned in Ref. [1] are disordered, high-symmetry polymorphs of $\text{Sr}_6\text{Nb}_2\text{O}_{11}$, $\text{Ca}_{12}\text{Al}_4\text{O}_{33}$, and CsHSO_4 . The notation allows the various occupants, such as oxide ions and vacancies to be assigned effective charges in a consistent manner. In turn, one gets a consistent treatment of effects (or lack of effects) of heating, non-stoichiometry, and doping. The definition and use of the notation met mixed receptions, but has been used later to describe and understand structure, defects, and transport in e.g. “ $\text{La}_6\text{WO}_{12}$ ” which turned out to be a nonstoichiometric composition based on a structure $\text{La}_{28}\text{W}_4\text{O}_{54}$ with 54/56 occupancy of the oxide ion site [2]. In this presentation, I will review the basis and definition of the nomenclature, its recent uses to understand new oxide ion conductors such as $\text{Ba}_7\text{Nb}_4\text{MoO}_{20}$, and discuss its applicability to Li-ion conducting oxides.

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11:30 AM DT21.02

Role of the Anion Sublattice Defects in the Mixed Conducting Properties of Layered-Perovskites Susana Garcia-Martin; Universidad Complutense de Madrid, Spain

Layered perovskites $\text{LnBaTM}_2\text{O}_{5+\delta}$ (Ln= Lanthanide; TM= Transition Metal) have proven to have excellent properties as air-electrodes for solid oxide fuel cells (SOFCs) [1]. Their catalytic properties for oxygen reduction reaction (ORR) are associated in part with their mixed-conduction properties. The ionic conductivity in these layered-perovskites seems to depend on the location of the anion vacancies within the $(\text{LnO})_x$ planes creating high conducting layers for the oxygen-anion diffusion. Location of anion vacancies within the crystal structure of oxides needs the use of advanced characterization techniques. We have solved the crystal structure of several $\text{GdA}'\text{B}_2\text{O}_{5+\delta}$ (A =lanthanide element A' = Ba, Ca and B = Co, Mn, Fe) perovskites by means of scanning transmission electron microscopy (STEM) and electron energy loss spectroscopy (EELS) mapping [2-5]. The combination of these two techniques enable to view the crystal structure with atomic resolution. The high angle annular dark field mode of STEM (HAADF-STEM) provides information of the location of the heaviest atoms of the structure and, with the assistance of the EELS-mapping, of the cation ordering within the A and B cation sublattices. On the contrary, the bright field mode (BF-STEM) gives information of the light elements of the compound, i.e. oxygen atoms in the case of these perovskites. A thorough analysis of the BF-STEM images allows location of the anion vacancies within the crystal structure. We present in here some examples of determination of the crystal structure of $\text{GdA}'\text{B}_2\text{O}_{5+\delta}$ layered-perovskites by STEM (HAAADF and BF modes) and EELS mapping. We have also studied the ORR activity of these oxides by means of impedance spectroscopy and found interesting crystal structure-properties relationships that allow us to conclude that particular locations of the anion vacancies might favor the oxygen diffusion and promote the ORR activity.

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11:45 AM *DT21.03

Mixed Conductors Beyond Simple Perovskites Konrad Swierczek; Akademia Gorniczko-Hutnicza imienia Stanisława Staszica w Krakowie Wydział Energetyki i Paliw, Poland

For $\text{ABO}_{3-\delta}$ (A: rare-earth elements, alkaline earth metals; B: 3d metals) perovskite-type oxides the electronic structure of BO_6 octahedra governs the charge transport properties in the bulk, while deviation from the oxygen stoichiometry, realized through the oxygen vacancies, lowers the coordination number of the B-site cations and enables ionic conduction. At the same time, surface-exposed BO_5 (as well sites with lower oxygen coordination) are responsible for the electrocatalytic activity of the material. B-site metal-oxygen bonds in such perovskites possess intermediate properties between ionic

and covalent character, with the energy difference of the $3d$ metal and $2p$ oxygen states being one of the most important factors governing physicochemical characteristics. Compositional flexibility observed in the perovskite-type oxides through an appropriate doping strategy at the A-, B- and even O-sites enables modification of the crystal structure, including formation of different superstructures. This is generally governed by the so called tolerance and other derived structural factors. This in turn is linked with the equilibrium oxygen content at room temperature, formation of the additional (ordered or disordered) oxygen vacancies at elevated temperatures, and mixed ionic-electronic charge transport, affected strongly by the introduction of elements with varying charge state. Also, one of the fundamental parameters, e_g states filling, may be adjusted, which is known to greatly influence electrocatalytic activity of a particular material in various redox processes. Regarding formation of different superstructures, e.g. for the 1:1 occupancy at the A- or/and B-site of different cations, formation of the rock salt, columnar or layered-type of structural arrangement may be present.

In this work, several groups of mixed ionic-electronic conductors are discussed in more details, all showing the crystal structure beyond that of the simple perovskites. In particular: 1) the A-site layered $\text{RE}(\text{Ba,Sr})\text{Co}_{2/3}\text{M}_y\text{O}_{5+\delta}$ (RE: selected rare-earth cations; M: Mn, Fe, Cu, etc.) double perovskites, in which Co-rich materials are known to exhibit very high mixed conductivity, high electrocatalytic activity, enabling application in the high temperature Solid Oxide Cells. In comparison, one of the possible chemical composition end-members, $\text{REBaMn}_2\text{O}_{5+\delta}$, show a desirable set of physicochemical characteristics for the oxygen storage-related usage; 2) the Cu-based $\text{RE}_{1-x}(\text{Ba,Sr})\text{CuO}_{3-\delta}$ oxides, having either RE-(Ba,Sr) cation-ordered or cation-disordered sublattice, as well as the linked ordered or disordered oxygen sublattice defects. It is documented that the Cu-based complex perovskites may also exhibit attractive physicochemical properties regarding the high temperature oxygen electrode application; 3) the YMnO_3 -derived perovskite-type and hexagonal oxides, which show unusual reactivity with oxygen for compositions close to the phase transition border. The oxides may be tuned for the temperature-swing processes involving uptake and release of substantial amount of oxygen. Some guidelines are also given regarding rational designing of the chemical composition in the discussed groups, with the aim to enhance the useful properties.

12:05 PM DT21.04

Explaining the Interference Between Electronic and Ionic Movement—A Case Study in Ceria [John P. Arnold](#) and Manfred Martin; Rheinisch-Westfälische Technische Hochschule Aachen, Germany

Inorganic mixed ionic-electronic conductors (MIECs) play a crucial role in green technologies, for example as electrode in solid oxide fuel cells or as electrolyte in gas membranes. In contrast to Kohlrausch's law of independent motion, these materials show an interference between the ionic and electronic flux, but the origin of this effect is not clear yet. Using ceria as a model system, we conducted density functional theory simulations and found a vehicle-like mechanism in which electron polarons and oxygen vacancies perform a joint migration. We quantified the influence of this novel mechanism with subsequent kinetic Monte Carlo simulations and show that its consideration is crucial to reproduce the experimentally reported interference effect. Because other materials with coupled fluxes show polaronic behavior as well, our results may be more widely applicable and help in the improvement of MIECs in general.

12:20 PM DT21.05

Unraveling, with *Ab Initio* Modeling—The Connection Between Electronic Structure and Dynamical Properties of the Sodium Bismuth Titanate [Marcin Krynski](#)¹, Marcin Malys¹, Franciszek Krok¹, Isaac Abrahams² and Wojciech Wrobel¹; ¹Politechnika Warszawska, Poland; ²Queen Mary University of London, United Kingdom

Solid electrolytes with high oxide ion conductivity have drawn significant attention as they find applications in wide range in electrochemical devices like oxygen sensors, oxygen pumps and solid oxide fuel cells [1]. Recently, ceramic compounds based on the perovskite $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ (NBT) attracted major attention due to their high Curie temperature (~ 325 °C), large remnant polarization ($38 \mu\text{C}\cdot\text{cm}^{-2}$) and exceptional fast oxygen-ion conduction. Interestingly, NBT shows high ionic conductivity only if the molar ration between Na and Bi atoms is above unity. Below this value, a sudden drop of conductivity is observed. Despite significant scientific effort in explaining this phenomenon, a satisfactory explanation has proved elusive.

In this project we employ state of the art Density Functional Theory, using the Strongly Constrained and Appropriately Normed functional (SCAN) together with the Dudarev approach of on-site Coulombic interaction to model the oxide ion dynamics in the NBT electrolyte. For the first time, we correlate the dynamical properties of mobile ions with the behaviour of the Bi $6s^2$ lone pair, showing the role of the lone pair has in the diffusion process. Furthermore, we look at the charge transfer during the dynamical processes, change of the dipole moment, as well as the bond strength. All this allows us to form a coherent picture of the diffusion processes being strongly correlated to the electronic structure features, such as the ferroelectric behaviour of NBT, and how these two aspects of this system are modulated by the composition.

This work was supported by the National Science Centre, Poland under grant number UMO-2018/30/M/ST3/00743.

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SESSION DT22: Beyond Classical Electrochemical Characterization

Session Chair: Francesco Ciucci

Wednesday Morning, July 20, 2022

Mezzanine Level, Second Floor, Arlington

11:00 AM *DT22.01

Photo-Enhanced Ionic Grain Boundary Conductivity in Solid Electrolytes [Dino Klotz](#)^{1,2}, Thomas Defferriere², Juan Carlos Gonzalez-Rosillo³, Jennifer Rupp⁴ and Harry Tuller^{2,1}; ¹Kyushu Daigaku, Japan; ²Massachusetts Institute of Technology, United States; ³Institut de Recerca en Energia de Catalunya, Spain; ⁴Technische Universität München, Germany

Materials development has provided us with a variety of oxide-based ionic conductors, tailored for the different requirements for specific technical applications such as fuel cells, batteries, permeation membranes and nano-electronic memory and sensing devices.

One of the performance-limiting factors for technical devices are grain boundaries, which are unavoidable for most cost-effective production methods, and which lead to significantly decreased effective conductivities and a decreased performance as compared to what is practically possible with the respective

bulk conductivities. Due to large activation energies, this limitation is especially relevant for low temperature applications. Space-charge potential barriers, featuring depletion zones and band bending, have been used to explain the blocking nature of grain boundaries.

In photoelectrochemistry, above band-gap light is well-known to reduce band bending at interfaces by providing additional charge carriers which screen potential barriers. Here, we show that the same principle can be applied to ionic conductors, and that we can significantly decrease the grain boundary impedance contribution.

In this talk, we will show photo-enhanced ionic conduction in a thin film of 3% Gd-doped ceria upon illumination by UV light. The chosen photon energy is slightly above ceria's band-gap and decreases the resistance of the thin film in a consistent and reversible fashion. In fact, the grain boundary resistance can be reduced by 72% at 250°C and its activation energy nearly halved from 1.12 eV in the dark to 0.68 eV under illumination. We further demonstrate that this effect is not caused by heat, electronic conductivity, or surface catalysis. Our findings are based on electrochemical impedance spectroscopy (EIS) and intensity-modulated photocurrent spectroscopy (IMPS), performed on polycrystalline and epitaxial samples, and backed by theoretical considerations of grain boundary potential height and space-charge regions.

EIS is the main analysis technique to demonstrate this opto-ionic effect. However, some characteristics can only be assessed through dynamic measurements with macroscopic external triggers, such as the conductivity enhancement under illumination. The dynamic evolution of relevant parameters following a change in the measurement conditions can help to provide additional information for an in-depth analysis, which is not accessible via classic EIS.

Here, the concept of single-frequency impedance transients (SFIT) comes into play, where the impedance at one specific frequency is measured continuously. For example, high-frequency SFIT measurements have been used to determine the temperature evolution in fuel cells and batteries by relating the Ohmic resistance to the electrolyte temperature. Similarly, we use SFIT to monitor the impedance at a specific frequency and analyze the dynamics in relevant parameters such as resistance and capacity in the time domain. Those parameter evolutions can be used as indicators for a specific process or behavior.

In this talk, we introduce the opto-ionic effect, and in the second part, enter into more detail regarding the measurement approach including the use of advanced impedance methods such as SFIT and IMPS that are very useful for investigating opto-electronic and opto-ionic systems, with their full potential yet to be utilized. In another contribution to this conference, we will discuss the opto-ionic effects at even lower temperatures.

This work was supported by JSPS Core-to-Core Program, A. Advanced Research Networks: "Solid Oxide Interfaces for Faster Ion Transport", Kakenhi Grant-In-Aid for young scientists (18K13993 and 20K15028), Department of Energy (Basic Energy Sciences award number DE-SC0002633), the Swiss National Science Foundation (grant number BSSG10_155986/1) and Equinor (Agr No.4502981450).

11:20 AM DT22.02

Evolution of Defect Ensembles in β -Ga₂O₃ with Illumination, Bias and Temperature [Mike Scarpulla](#); University of Utah, United States

The ultrawide bandgap semiconductor β -Ga₂O₃ sits at the interface between traditional semiconductors and insulators. Its projected high breakdown field has driven efforts to develop its technology to realize high-voltage and high-power devices. Understanding the thermodynamic forces and kinetic rates of defect formation and migration are required for maturing this technology and assessing prospects for long-term reliability. In this work, we will report on three types of experiments aimed at elucidating defect formation and transport: first, isovalent superlattices are used to determine native cation vacancy diffusion rates, next bias and moderate temperature stressing of Schottky diodes result in compensation close to the interface, and lastly we demonstrate modifications of defect ensembles in the near-surface region using both below-gap and above-gap illumination. These investigations help to quantify difficult-to-measure parameters like the gallium vacancy diffusion constant as well as offering fundamental insights into the influences of non-equilibrium electrochemical potentials on charged defects.

11:35 AM *DT22.03

Descriptors of Oxygen Ion Migration to Accelerate New Ion Conductor Discoveries [Daniele Vivona](#)¹, [Kiarash Gordiz](#)¹, [Randall Meyer](#)², [Sumathy Raman](#)² and [Yang Shao-Horn](#)^{1,1,1}; ¹Massachusetts Institute of Technology, United States; ²ExxonMobil Research and Engineering Company Annandale, United States

Solid-state oxygen ion conductors are essential to a variety of energy applications, ranging from catalysts to solid oxide fuel cells, batteries, and sensors. However, the success of these technologies is usually impeded by the slow diffusion of ions. Therefore, it is of primary importance to accelerate the discoveries of fast ion conductors that can enable energy paradigms to mitigate climate change. Research efforts dedicated to searching for new materials with high ionic conductivity have been dominated by trial-and-error approaches. Recently, researchers have used computational tools coupled with experimental measurements to accelerate the discovery of ion conductors by relating lattice dynamics to ion migration barrier. Such research allows us to gain atomic scale insights into ion hopping processes and understand how the specific features of crystal structure, chemical bonds or lattice dynamics should be tuned to increase ionic conduction. In this talk, we will discuss descriptors for oxygen ion transport in mixed conducting and pure oxygen ion conductors building on recent work that has shown that lowering the average vibrational frequency of lithium ions in the lattice is correlated with reduced migration barrier in pure lithium-ion conductors. We will discuss the coupling between electronic structure and lattice dynamics and relationships between the activation barrier for oxygen ion migration and defect formation - features of the local chemical bonding environment and vibration of lattice moieties. Design principles and descriptors of oxygen ion conductors based on the lattice dynamics and the nature of chemical bond are proposed, which can be used for searching new solid-state oxygen ionic conductors.

11:55 AM DT22.04

Characterization of Anisotropic Strain in Anelastic Materials by Raman Spectroscopy [Daniel Freidzon](#)¹, [Olga Kraynis](#)¹, [Ellen Wachtel](#)¹, [Igor Lubomirsky](#)¹ and [Tsachi Livneh](#)²; ¹Weizmann Institute of Science, Israel; ²Nuclear Research Center Negev Library, Israel

Raman spectroscopy has recently been applied for non-destructive characterization of strain in crystalline thin films. It makes use of the numerical value of the mode Grüneisen parameter γ , which equals (minus) the ratio of the relative change in the frequency of a Raman-active vibrational mode and the strain-induced relative change in the unit cell volume. In the presence of in-plane, compressive biaxial strain, aliovalent doped CeO₂-films exhibit values of γ which are ~30% smaller than the literature values for the bulk ceramics under isostatic stress. This discrepancy is due in large part to the negative contribution from the anelastic (time-dependent) mechanical properties of oxygen-deficient ceria, thereby raising questions concerning the relationship between Raman mode frequency and anelastic strain. Here we propose a way to "separate" anelastic and elastic contributions to the Grüneisen parameter. 500-650nm thick films, $x=0.1-0.2$, were deposited by RF magnetron sputtering on (100) *p*-Si wafers (1 Ω -cm, $t_{Si}=280$ nm). The films (S-films) were in the fluorite phase with pronounced (111) texture and exhibited biaxial, compressive strain. The in- and out-of-plane lattice parameters (a_s^{\parallel} , a_s^{\perp}) of the S-films were determined by XRD at different sample tilt angles. The in-plane stress (σ_{bi}) in the S-films was determined by profilometry from the change in Si-

wafer curvature following film deposition. From σ_{bi} and the film biaxial modulus, the elastic component of the in-plane compressive strain (u_e) was calculated ($\sim -0.2\%$).

Strain-free (relaxed) R-films were obtained by partial substrate removal, forming 2 mm diameter self-supported membranes. Pronounced membrane buckling indicated that residual strain was negligible ($\mathbf{aR}^{\parallel} \approx \mathbf{aR}^{\perp}$). From the increase in area upon substrate removal, measured with optical profilometry, the total S-film in-plane strain (u_i) was calculated from $\mathbf{aS}^{\parallel}/\mathbf{aR}-\mathbf{I} \approx -0.5\%$. The anelastic strain component may be calculated as $u_a = u_i - u_e$. The small, anisotropic strain-induced blue shift of the frequency of the F_{2g} -phonon mode for S-films suggests that the F_{2g} mode responds primarily to the elastic component of the strain.

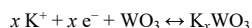
As a control, 430nm thick films of mechanically elastic Y_2O_3 were deposited by sputtering on a Si wafer covered with a 1.5 μm thick PECVD deposited SiO_2 layer. This layer supported the Y_2O_3 -films upon membrane formation, but prevented complete strain relaxation. The Y_2O_3 -films were in the double fluorite phase with strong (222) texture and, as with the S-films, were under in-plane compressive strain. The Y_2O_3 S-film lattice parameters were determined by acquiring XRD-patterns at different sample tilt angles, while membrane in- and out-of-plane lattice parameters were determined with XRD in the transmission and reflection modes, respectively. The values of γ calculated from the Raman frequency of the $[F_g+A_g]$ peak position were close to the literature values for bulk yttria under isostatic stress.

This work should serve as a sample protocol for strain characterization of doped ceria thin films. It supports the concept that the discrepancy between the behavior of Raman modes of isostatically and anisotropically strained doped ceria is related to anelasticity. Our results shed light upon strain characterization by Raman spectroscopy and may lay the foundation for future studies to elucidate selective sensitivity to various strain components.

12:10 PM DT22.05

In Situ Raman-spectroscopic Investigation of Phase Transitions in Polycrystalline WO_3 Thin Films During Ion Insertion and Extraction Markus S. Friedrich, Alexander Strack, Jan L. Dornseifer and Peter J. Klar; Justus Liebig Universitat Giessen, Germany

In 2016 approximately one fifth of the global energy consumption was accounted to the building sector. A large portion of this consumed energy is used for space heating or air conditioning.¹ The installation of windows with switchable optical properties, so called "smart windows", can play a key role in the reduction of the energy demand for such applications. Functional components of "smart windows" are thin films of electrochromic materials such as tungsten trioxide (WO_3).² The electrochromic coloration and bleaching of the WO_3 is based on the reduction respectively oxidation of the tungsten ions by the reversible insertion or extraction of small ions like H^+ or Li^+ into the octahedral sites of the crystal structure of the WO_3 . This reaction follows the equation



where K^+ denotes H^+ or Li^+ ions and x is between 0 and 2.³ The insertion of ions leads to a reduction of the tungsten ions from the +6 oxidation state to the +4 oxidation state, which leads to a change of the electronic structure in the thin film and therefore leads to a change in the photon absorption behavior of the material.

It is obvious that ion diffusion in the WO_3 plays a key role in this process and therefore needs to be understood in depth in order to enable the optimization of future devices. Burkhardt et al. investigated the diffusion of hydrogen in amorphous and polycrystalline WO_3 thin films by in situ transmission spectroscopy and proclaimed a diffusion mechanism, where the hydrogen diffusion coefficient is dependent on the concentration of W^{4+} species in the material.³ They showed, that in the case of polycrystalline WO_3 the hydrogen diffusion coefficient increases with an increasing concentration of W^{4+} .³ It is suggested that the change of the hydrogen diffusion coefficient originates from changes in the crystal structure of the thin films.

To substantiate this suggestion in situ Raman spectroscopy experiments were performed on polycrystalline WO_3 thin films, prepared by electron beam evaporation deposition, during potentiostatic hydrogen insertion and extraction. The Raman experiments reveal that the WO_3 undergoes two structural transitions during hydrogen insertion, from its initial structure to a tetragonal structure, and from the tetragonal structure to a cubic structure. These findings enable targeted examinations on the electrochromic behavior of H_xWO_3 phases with a defined crystal structure. Therefore, a more precise characterisation of the diffusion of small ions in WO_3 thin films can be achieved.

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12:25 PM DT22.06

Advanced Characterization Using Coherent X-Rays for Materials Joshua Turner; Stanford Linear Accelerator Center, United States

We discuss advanced characterization of materials based on coherent x-rays which can be useful for defect and transport in solid electrolytes or mixed conductor type materials. This is possible using bright x-ray sources, which allows for studies of dynamics to be carried out on a range of time and length scales. We will discuss the potential and the limitations of this method as a way to explore solid state ionics and potential for future advanced characterization techniques.

SESSION DT23: In-Situ/Operando Characterization Techniques

Session Chair: Kelsey Stoerzinger

Thursday Morning, July 21, 2022

Mezzanine Level, Second Floor, Georgian

9:10 AM **DT23.01

In Situ Characterization of Radiation-Induced Transport Cortney Kreller, Blas Uberuaga, James Valdez, Benjamin Derby and Yong Wang; Los Alamos National Laboratory, United States

Many materials studied for nuclear energy applications – such as pyrochlores and other fluorite derived materials and spinels – also have application as functional materials such as fuel cells, fast ion conductors, and batteries. In both fields, mass transport is a critical factor that dictates their suitability for application. Electrochemical impedance spectroscopy (EIS) has been extensively applied to these types of materials from the point of view of their conductivity and functionality. Ex situ characterization of irradiated materials has provided significant insight into their overall response to damage. What is missing, however, is an understanding of how these materials behave in situ: how irradiation impacts transport through defect formation/annihilation and

their mobility.

Los Alamos National Laboratory (LANL) recently established the capability of performing in situ EIS measurements at the Ion Beam Materials Laboratory (IBML). Proof of principle was demonstrated on yttrium-stabilized zirconia (YSZ) with 200 keV He ion irradiation. YSZ is known to be a very rad tolerant material, and as expected, our ex situ analysis of irradiated YSZ showed no change in ionic conductivity. However, the in situ characterization under irradiation showed an enhanced ionic conductivity under irradiation that depended upon both sample temperature and irradiation conditions.

9:40 AM DT23.02

Study of Ion Transport and Defects in Electrode Thin Films by Operando Spectroscopic Ellipsometry [Alex Morata](#)¹, Juan Carlos Gonzalez-Rosillo¹, Yunqing Tang¹, Valerie Siller¹, Francesco Chiabrera¹, Michel Stchakovsky², Marc Nuñez¹, Nerea Alayo¹ and Albert Tarancón^{1,3}; ¹Institut de Recerca en Energia de Catalunya, Spain; ²Horiba Scientific, France; ³Institució Catalana de Recerca i Estudis Avançats, Spain

Ion-based devices such as batteries, fuel cells and electrolyzers are called to play a major role in the future carbon-free societies. Understanding interfacial and diffusion phenomena taking place during operation is key for improving performance and develop next-generation materials and architectures. The sophistication of some of the most powerful techniques, such as isotopic ion exchange methods, in situ TEM and synchrotron radiation based techniques, limits the routine access to essential information for developing next-generation devices. In addition, commonly available techniques have also been explored including X-ray diffraction, atomic force microscopy, Raman spectroscopy and Fourier transform infrared (FTIR) spectroscopy showing different compromises between spatial and time resolutions. Despite the well-known capabilities of Spectroscopic Ellipsometry (SE) to infer the properties of thin film and multilayers, such as thickness, crystallinity, materials ratio in mixtures, roughness, structure of the interfaces, electronic band structure etc., the use of this affordable, non-destructive technique for the study of ion-transport under operation is very limited. In this talk, we will discuss the implementation of Spectroscopic Ellipsometry to perform operando experiments thanks to its fast response and the strong effect of the oxidation state on the optical properties of the films. We will illustrate the power of the technique with several examples on the field of lithium-ion batteries and solid oxide cells. First, we will show the use of SE to monitor Li^+ transport properties and degradation phenomena through real-time tracking of the oxidation-state and volume changes associated with lithium insertion and extraction along LiMn_2O_4 and $\text{Li}_4\text{Ti}_5\text{O}_{12}$ electrodes. The layers were grown on top of Pt coated Si chips with Pulsed Laser Deposition (PLD), using a layer-by-layer, multi-target strategy to compensate for Li loss. An air-tight chamber with optical windows was developed to perform the operando measurements, able to host different liquid electrodes adapted on the electrode potential range (e.g. LiSO_4 , LiPF_6).

In a second example, we use SE for studying the concentration of point defects in $\text{La}_{1-x}\text{Sr}_x\text{FeO}_{3-\delta}$ (LSF) thin films as a function of equivalent oxygen partial pressure, temperature and Sr concentration. LSF thin films were deposited on YSZ (001) substrate by PLD and the evolution of their optical properties was measured while electrochemically reducing/oxidating the layers in the temperature range 350 to 500 C. A low energy optical transition was univocally related to the concentration of electronic holes in the layers and a non-dilute defect chemistry model was developed for explaining the defects evolution with the oxygen partial pressure.

The results provide evidence of the applicability of operando SE for determining the oxidation-state and point defects concentration of electrodes, linking changes under operation with degradation mechanisms, unveiling non-ideal behavior in oxides at intermediate temperature and providing guidelines for future durable electrodes.

9:55 AM *DT23.03

Studies of Point Defects in Ionic System with Scanning Transmission Electron Microscopy, from Static Displacements to Migration Dynamics [James LeBeau](#); Massachusetts Institute of Technology, United States

In this talk, we will discuss how aberration corrected scanning transmission electron microscopy (STEM) can be used to probe the atomic scale dynamics of point defects in functional oxide materials. As prototypical examples, we will report on the direct quantification of point defect formation and migration in Ga_2O_3 and a MgCr_2O_4 . In these systems we can observe the dynamics of interstitial formation through STEM imaging, which is found to depend on electron dose and energy. In both example systems, the interstitials are observed to reversibly migrate back and forth from the host crystal structure to the interstitial positions. Spectroscopy will be shown to provide evidence of preferential mass loss of the lighter species, i.e. forming vacancies within the structure. By probing these materials at various dose rates, we will discuss how to gain insight into defect formation and migration energies through a combination with theory. We will also highlight how light element imaging techniques, such as iDPC STEM can be used to observe the distortion of cation-anion tetrahedra and octahedral during imaging. For example, with the formation of interstitials in MgCr_2O_4 , the tetrahedra bend away from the mid-plane in response to the presence of charged point defects. Furthermore, we will use the intensities of the point defect positions to infer the exchange with neighboring vacancies or migration deeper into the crystal. Such approaches with STEM imaging will be show to provide direct insights into mechanisms of ionic conduction, particularly in non-stoichiometric material.

Beyond isolated point defects, we will also explore the modification of point defect stability at planar defects, such as anti-phase boundaries. This is important, for example, when controlling the response of multiferroic materials to applied magnetic and electric fields. We will focus our discussion on the structure and chemistry of anti-phase boundaries in Y-rich multiferroic YFeO_3 thin films. Combining imaging with atomic resolution energy dispersive X-ray spectroscopy, we find that Fe_γ anti-sites, which are not stable in the film bulk, periodically arrange along anti-phase boundaries due to changes in the local structural environment. The impact that the point and planar defects have on properties will also be explored through theory. Using density functional theory, we will show that the anti-phase boundaries are polar and bi-stable, where the presence of Fe_γ anti-sites significantly decreases the switching barrier. Finally, we will discuss how these results suggest that anti-phase boundaries in doubled perovskite structures can stabilize point defects that would otherwise not be expected to form within the structure.

10:15 AM DT23.04

In Situ Solid-Phase Crystallization of Functional Ceramics in the Transmission Electron Microscope Jenna Wardini¹, Jairo Gonzalez¹, George Harrington^{2,3} and [William Bowman](#)^{1,4}; ¹University of California Irvine, United States; ²Kyushu Daigaku, Japan; ³Massachusetts Institute of Technology, United States; ⁴University of California Irvine Materials Research Institute, United States

Many technologically relevant materials are not at their true thermodynamic free energy minimum but instead are kinetically stabilized [1]. These metastable polymorphs can show improved functionality over their thermodynamically stable counterparts, however, controlling the formation pathways to target specific polymorphs presents a formidable challenge. Heat treatment of amorphous pulsed laser deposited (a-PLD) films provide a unique route to control the crystallization kinetics of amorphous films, providing a means to control the crystallized area fraction and potentially to target favorable polymorphs from a given starting composition.

Previous work has shown that structural aspects of amorphous films can create a preference for the formation of certain polymorphs upon annealing [1]. Here, we show that in addition to the structure of the starting a-PLD film, subsequent annealing steps applied to a-PLD complex-oxide thin films under various heating schedules and oxygen partial pressures ($p\text{O}_2$) will also impact the resulting polymorphs and their stability. We refer to this processing

approach solid-phase crystallization (SPC) to distinguish it from solid-phase epitaxy (SPE) which implies the substrate acts as a seed crystal. Here, the a-PLD films are deposited on an amorphous Si_xN_y substrate such that the resulting phases are free of epitaxial constraints, providing a very open phase space. SPC provides an opportunity to explore the formation of new polymorphs nucleating within the amorphous far-from-equilibrium starting matrix, where even metastable states are energetically preferred over the a-PLD film.

Here, SPC is applied to $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ (LSM82) *in situ* in the transmission electron microscope. In the perovskite form, LSM is a prototypical mixed ion and electron conductor (MIEC) often used as a cathode material in commercially available solid oxide cells (SOC). Grain boundaries and other crystalline defects within LSM have been shown to act as pathways for fast oxygen transport [2]. Since SOC efficiency is intimately tied to the ease of oxygen transport, the correlation between structural disorder and enhanced ion transport seen in LSM and demonstrated other amorphous complex oxides may provide an approach to lower the operating temperature of SOCs through the use of partially amorphous cathodes without sacrificing performance [3].

Using *in situ* SPC, scanning and transmission electron microscopy paired with electron energy-loss and energy-dispersive x-ray spectroscopies (EELS, EDXS) are used to monitor the structural (e.g., morphology, grain size, crystal structure) and chemical (e.g., elemental distribution, bonding environment) state of the film during annealing, while temperature-dependent charge transport is intermittently measured. In both vacuum and air anneals, the amorphous LSM82 film does not form the single-phase perovskite structure as predicted by bulk equilibrium thermodynamics [4]. Rather, upon vacuum annealing, the local film morphology leads to preferred crystallization of particular polymorphs, likely due to the presence of local strains and greater oxygen deficiency with increased surface exposure to the low-pO₂ environment. Multi-cation segregation and oxidation from the crystallized phases occurs at higher temperatures (~700-800 °C) followed by the formation of multiple other decomposition products. The air anneal also results in a multi-phase system which implies that thin-film effects (rather than oxygen deficiency alone) are responsible for the departure from the predicted structure.

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SESSION DT24: MIEC: Chemo-Mechanics

Session Chair: Courtney Kreller

Thursday Morning, July 21, 2022

Mezzanine Level, Second Floor, Georgian

11:00 AM **DT24.01

Achieving Near-Zero Chemical Strain in Perovskites by Tailoring Metal-Oxygen Bond Charge Distribution and Angles [Nicola H. Perry](#); University of Illinois at Urbana-Champaign, United States

The relative angles and charge distribution of B-O bonds in ABO_3 perovskites are known to impact many properties, from electronic and ionic mobilities, to ferroelectricity, nonlinear optical behavior, catalytic activity, and magnetic order. Here I will present our recent work demonstrating how these features of the B-O bonds can also impact coefficients of chemical expansion (CCEs). Redox and hydration induced chemical strains can lead to large stresses and mechanical degradation in devices leveraging the ability of proton, mixed ion/electron, and triple conducting oxides to change stoichiometry. Crystal chemical design rules for zero-chemical-strain materials would enable more chemo-mechanically durable devices.

We have recently synthesized and precisely measured CCEs for mixed-conducting $\text{Pr}(\text{Ga},\text{Mg})\text{O}_{3-x}$, triple-conducting $\text{Ba}(\text{Pr},\text{Y})\text{O}_{3-x}$, and the primarily proton-conducting solid solution $\text{Ba}(\text{Zr},\text{Ce},\text{Y})\text{O}_{3-x}$ [1,2]. Isothermal chemical strains were monitored by *in situ* X-ray diffraction (for axis-specific strain) and dilatometry at different oxygen and steam partial pressures. Stoichiometry changes were evaluated isothermally under identical conditions by thermogravimetric analysis. The CCEs at each temperature were determined from the slopes of plots of chemical strains vs. stoichiometry changes.

Collaborative density functional theory simulations were performed in concert with impedance spectroscopic measurements to evaluate theoretical chemical strains and charge localization as a function of varied compositional, structural, and electronic features.

For the Pr-bearing systems, the redox CCEs were significantly lower than any reported for perovskites by a factor of 2-5, regardless of Pr A- or B-site placement. This behavior is inconsistent with predictions of an ionic radius model that assumes a cubic structure and redox fully on Pr. The anomalously low CCEs observed were attributed to a combination of hybridization of Pr and O states, redox on O not just Pr, and crystallographic distortions away from the cubic phase leading to anisotropic strain. Similarly for the proton conductors, the hydration CCEs were lowered by a factor of 5, to near-zero values, by distorting the structure away from cubic symmetry through Ce replacement of Zr.

While both B-O-B angles less than 180 degrees and metal-oxygen covalency may be individually beneficial for lowering redox CCEs, they are somewhat contraindicated when trying to optimize both. However, our results suggest that, more than metal-oxygen sharing of charge (holes), locating redox and holes fully on oxygen, with or without distortions, may lead to near-zero CCEs.

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11:30 AM DT24.02

Chemical Expansion of Cerium Oxide Based Thin Films Hendrik Wulfmeier¹, Dhyan Kohlmann¹, Thomas Defferriere², Carsten Steiner³, Marvin Schewe¹, Christian Rembe¹, Ralf Moos³, Harry Tuller² and [Holger Fritze](#)¹; ¹Technische Universität Clausthal, Germany; ²Massachusetts Institute of Technology, United States; ³Universität Bayreuth, Germany

Nonstoichiometry in oxides governs many key materials properties including electronic and ionic conductivity, oxygen and cation diffusion and chemical expansion. While the atomic transport processes are well studied, the chemical expansion generally receives less attention. Materials with high chemical expansion can be utilized for the development of a new generation of high-temperature actuators. On the other hand, related induced mechanical stress in e.g. fuel cells contributes to limited lifetime and should be avoided. The focus of this work is the investigation and understanding of chemical expansion at high temperatures and its correlation with other key properties such as nonstoichiometry and electrical conductivity. In this context thin films are of particular interest as they enable miniaturization and, consequently, fast response due to short transport paths. However, their properties might differ from their bulk counterparts.

In addition to the material aspects, specially tailored methods are of particular importance for the investigation of thin films at high temperatures. Here, a special Differential Laser Doppler Vibrometer (DLDV) is described [1] and applied. As it is based on differential measurements, external disturbances are largely suppressed. As a consequence, determination of displacements on the order of picometers for periodic movements down to 1 mHz is achievable up

to 1000 °C.

$\text{Pr}_{0.1}\text{Ce}_{0.9}\text{O}_{2-x}$ (PCO) is taken as reference material as it shows a well-defined non-stoichiometry plateau at intermediate oxygen activities. Starting from this plateau, the chemical expansion at temperatures up to 800 °C was determined as a function of oxygen activity. At 650 °C, independently determined values [2] match well, confirming the functionality of the DLDV. Moreover, the data correspond to calculated displacements for dense PCO films.

Thin-film ceria shows a similar trend to PCO with respect to the excitation frequency dependent displacement, including the tendency to reach a constant displacement at low frequencies, suggesting the ability to reach a near equilibrium state for periodically adjusted oxygen activity at 0.1 Hz. Furthermore, $\text{Ce}_{0.8}\text{Zr}_{0.2}\text{O}_{2-\delta}$ (CZO) thin films are investigated. They show cracks that partially accommodate chemical expansion. As a consequence, the calculated film thickness change for dense CZO films is larger than measured values for films with cracks.

The chemical expansion of films induces sample bending. Note that the films are deposited on single crystalline yttria stabilized zirconia substrates that simultaneously serve as oxygen pumps to adjust the oxygen activity in the films. The substrate bending and the film thickness change match very well if the Stoney equation used to correlate both effects.

The chemical expansion is furthermore correlated with the non-stoichiometry of the films (determined by resonant nanogravimetry) and electrical conductivity (impedance spectroscopy).

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11:45 AM *DT24.03

Investigation of Thermo-Chemical Expansion in Doped Ceria by Temperature Modulated Dilatometry Yoed Tsur and Ashok K. Baral; Technion Israel Institute of Technology, Israel

Many metal oxides exhibit thermo-chemical expansion due to change in the chemical potential of oxygen. It is difficult to study thermal and chemical effects separately in a qualitative manner, as both occur simultaneously. In this work, we demonstrate the separation of chemical expansion and pure thermal expansion at various temperatures, by using temperature modulated dilatometry. Such separation is possible if different processes occur on significantly different timescales. However, the case in our model materials - doped ceria and for comparison doped zirconia - is more complex due to different chemical effects that are predominant at different temperatures. Values of coefficient of modulated temperature thermal expansion (MCTE) are compared with the coefficient of linear thermal expansion (CTE). The CTE remains independent of heating rate, whereas the MCTE generally depends on the modulation rate. As defect associates disappear over temperatures, and cation valence changes kick in, the latter dependence of the MCTE is affected greatly.

<https://doi.org/10.1016/j.jeurceramsoc.2021.12.040>

12:05 PM DT24.04

Chemo-Mechanically Driven Hierarchical Structure Evolution in Crystallizing $\text{SrTi}_{0.65}\text{Fe}_{0.35}\text{O}_{3-d}$ Films and Correlation to Electrical Conductivity Haley Buckner¹, Qing Ma², Joshua Simpson-Gomez¹, Emily J. Skiba¹ and Nicola H. Perry¹; ¹University of Illinois at Urbana-Champaign, United States; ²Argonne National Laboratory Advanced Photon Source, United States

Mechanical strain arising from oxygen stoichiometry changes in mixed ionic/electronic conductors (MIECs) can be quite pronounced in compositions with multi-valent cations. This effect is generally considered detrimental due to mechanical failure associated with the large oxygen gradients relevant for solid state electrochemical device operation. Instead, our recent work^{1,2} has harnessed this chemo-mechanical coupling to actuate hierarchical structures through low-temperature crystallization of amorphous-grown perovskite oxide thin films. The *in-situ* crystallized films exhibit enhanced oxygen exchange kinetics, as the low-temperature fabrication route kinetically limits deleterious A-site cation surface segregation. In the present work³, the complex, multi-scale chemical and structural evolutions from crystallization and the implications for the electronic transport properties were explored.

This presentation will discuss the observed changes in oxygen non-stoichiometry and atomic- and micro-scale structure in crystallizing $\text{SrTi}_{0.65}\text{Fe}_{0.35}\text{O}_{3-x}$ (STF35) thin films on (0001)-oriented sapphire substrates and their correlation to changes in in-plane electronic conductivity, measured through *in-situ* a.c. impedance spectroscopy. Synchrotron X-ray absorption spectroscopy at the Ti and Fe K-edges gives direct evidence of oxidation occurring with the onset of crystallization through an increase in the average Fe oxidation state. The rapid oxidation results in an increase in B-site polyhedra symmetry and alignment of neighboring B-site coordination units, thus increasing the O 2p and Fe 3d orbital overlap. High resolution transmission electron microscopy and spectroscopy shows compositional homogeneity at various stages of crystallization and the development of extensive nano-porosity consistent with the expected solid phase contraction from both oxidation and crystallization. For further insight into the microstructural evolution, distributions of relaxation times (DRT) were extracted from the impedance spectra. The DRT reveal a narrowing distribution of time constants during crystallization, as expected from an increase in more homogenous crystalline regions and decrease in grain boundary/amorphous blocking behavior as oxidation and crystallization proceed.

This chemo-mechanically driven structural evolution and concomitant point defect concentration changes have significant implications for the electronic conductivity. We suggest oxidation leads to an increase in hole concentration; the associated increase in symmetry and alignment of B-site cation coordination units increases the hole mobility through the O-2p/Fe-3d orbital overlap; and resulting porosity and grain growth influences the connectivity of crystalline grains. The combination of oxidation and dynamic nano-structuring from crystallizing STF35 thin films may also help to explain the previously reported emergence of rapid surface oxygen exchange kinetics during crystallization. Given the resulting combination of high electronic conductivity and rapid surface exchange kinetics, the promise of the fabricated semi-crystalline hierarchical mixed conductors for low to intermediate temperature solid state electrochemical applications will be addressed.

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12:20 PM DT24.05

Oxygen Nonstoichiometry in Lanthanum-Cerium Cuprate Thin Films Determined by Resonant Nanogravimetry Hendrik Wulfmeier¹, Thomas Defferriere², Harry Tuller² and Holger Fritze¹; ¹Technische Universität Clausthal, Germany; ²Massachusetts Institute of Technology, United States

Mixed ionic and electronic conducting (MIEC) oxides play a key role in energy conversion applications such as reversible solid oxide fuel cells (SOFCs) or in automotive catalysts as oxygen storage materials. Among those, cuprate-based oxides such as lanthanum cerium cuprate ($\text{La}_x\text{Ce}_{1-x}\text{CuO}_{4-\delta}$, LCCO) are materials of great interest due to their high achievable non-stoichiometry δ , electrical conductivity and rapid oxygen exchange kinetics.

Thin films are of technological interest as they can be integrated into miniature devices such as thin film fuel cells, batteries, and memory devices. In addition, they serve as model systems for examination of defect and transport processes given short diffusion lengths and ability to reproducibly control

composition, morphology and dimensions. Electronic and ionic transport in these oxides, as well as other properties such as chemical expansion depend strongly on δ which, in turn, depends on temperature and the oxygen partial pressure p_{O_2} in the surrounding atmosphere. Precise determination of nonstoichiometry is crucial, but very difficult to achieve for thin films where conventional thermogravimetry is insufficiently sensitive. To overcome this limitation, we introduce the use of high-temperature resonant nanogravimetry. In this work LCCO thin films on the order of 1 μm in thickness are grown by pulsed laser deposition on high-temperature stable piezoelectric resonators that serve as nanobalances. The preferential orientation of the LCCO films perpendicular to the substrate is along their crystallographic c-axis. The nanobalance consists of high-temperature stable piezoelectric langasite ($\text{La}_3\text{Ga}_5\text{SiO}_{14}$, LGS) single crystals equipped with platinum electrodes. Such LGS nanobalances show mass sensitivity of ~ 5 ng/Hz when operated at ~ 5 MHz. This results in a theoretical resolution for the oxygen nonstoichiometry of $\Delta\delta = 0.0005$ for the given films. The LCCO thin films are characterized systematically with respect to variations in sample temperature and oxygen partial pressure. The mass change of the films is determined isothermally at temperatures up to 600 $^\circ\text{C}$, while the p_{O_2} in the surrounding atmosphere is varied stepwise between $-0.67 < \log(p_{O_2}) < -15$ by an electrochemical oxygen pump fed with a buffer gas mixture of 0.5 % H_2 in Ar. For example, a $\text{La}_{1.85}\text{Ce}_{0.15}\text{CuO}_{4-\delta}$ film heated to 590 $^\circ\text{C}$ shows a change in oxygen nonstoichiometry of $\Delta\delta \approx 0.16$ at a p_{O_2} of 10^{-15} bar with respect to 0.2 bar in fair agreement with values derived from earlier reported chemical capacitance measurements. Further, the thermodynamic parameters derived from conductivity and nanobalance measurements allow for detection of possible differences between values obtained for bulk vs thin-film samples. Nanogravimetric measurements are complimented by chemical expansion measurements by high-temperature laser-Doppler vibrometry providing additional insights towards understanding the potential role of strain on the thermodynamic parameters.

SESSION DT25: Mixed Conductors II
 Session Chair: Yoed Tsur
 Thursday Afternoon, July 21, 2022
 Mezzanine Level, Second Floor, Georgian

2:00 PM **DT25.01

***In Situ* Raman Spectroscopy—Novel Approaches to Study Oxygen Defect Dynamics in Mixed Conducting Oxides** Alexander Stangl¹, Adeel Riaz¹, Odette Chaix-Pluchery¹, Dolores Pla¹, Caroline Pirovano², Stefano Ambrosio¹, Federico Baiutti³, Albert Taracón³, Carmen Jimenez¹, Michel Mermoux⁴ and Monica Burriel¹; ¹Laboratoire des Matériaux et du Génie Physique, France; ²Université de Lille, France; ³Institut de Recerca en Energia de Catalunya, Spain; ⁴Laboratoire d'Electrochimie et de Physico-chimie des Matériaux et des Interfaces, France

Oxygen point defects, which in oxides can exist both as oxygen vacancies and as oxygen interstitials, are essential to the functionality of a broad range of solid state oxide devices. Their presence and, more importantly, their migration under a particular driving force, such as temperature, oxygen partial pressure, voltage or electrochemical potential, defines the performance of oxides when used as functional components in solid oxide fuel cells, electrolyzers, oxygen permeation membranes and memristive devices. The presence of oxygen defects creates changes in the oxygen sublattice, in the cation-anion interactions and, in some cases, can also lead to changes in crystal symmetry. The relationship between oxygen defects and structural modifications is not always well understood and is particularly difficult to characterize for thin films and under *in situ* conditions.

In this work we have focused on the study of common mixed conducting oxides in the form of thin films, such as the $\text{La}_2\text{NiO}_{4+\delta}$ Ruddlesden-Popper oxide prepared by Metalorganic Chemical Vapor Deposition or the $(\text{La,Sr})(\text{Mn,Co})\text{O}_{3-\delta}$ perovskite prepared by Pulsed Laser Deposition. With the purpose of relating the functional properties to the structural characteristics of mixed conducting oxides, a number of unconventional Raman experiments were designed.

We have developed a novel *in situ* methodology using Raman spectroscopy for the characterization of kinetic transport properties, such as self-diffusion and surface exchange coefficients of electrode materials based on isotopic exchange using a conventional temperature cell and Raman setup. The strengths of this new approach will be showcased with our proof of concept study on $(\text{La,Sr})(\text{Mn,Co})\text{O}_{3-\delta}$ thin films. Raman Spectroscopy is primarily known as a vibrational spectroscopy technique. As such, isotopic labelling indeed provides a mass contrast, leading to line shifts of some of the material Raman-active modes. Hence, changes in the isotopic composition due to isotopic exchange can be directly followed *in situ*, with spatial and temporal resolution, not accessible with conventional methods, such as isotope exchange depth profiling. This innovative approach therefore enables complementary insights for the study of ion transport properties of functional materials. Captivating benefits of this elegant *in situ* approach are its cost efficiency, speed, simple setup and sample preparation and its non-destructive nature.

Furthermore, $\text{La}_2\text{NiO}_{4+\delta}$ has been studied by *in situ* Raman spectroscopy for the first time under different temperature and p_{O_2} conditions.

$\text{La}_2\text{NiO}_{4+\delta}$ presents a complicated phase diagram in which subtle changes in oxygen stoichiometry induce structural variations, which provoke changes in the $\text{La}_2\text{NiO}_{4+\delta}$ functional properties. At ambient temperature the structure of the stoichiometric compounds $\text{La}_2\text{NiO}_{4.00}$ is orthorhombic, made of a stacking sequence of La_2O_2 bilayers, intrinsic positively charged, and NiO_2 monolayers, intrinsic negatively charged. The strain may be released by either a tilting of the NiO_6 octahedra in the [100] direction, or by an oxygen intercalation in the La_2O_2 double layers, resulting in overstoichiometric phases $\text{La}_2\text{NiO}_{4+\delta}$. As a function of δ , at room temperature the system shows a sequence of pure phases Low Temperature Orthorhombic \rightarrow Low Temperature Tetragonal \rightarrow High Temperature Tetragonal separated by biphasic regions. These phase changes have been studied both *by ex situ* and *in situ* Raman spectroscopy. With p_{O_2} changes, the appearance and disappearance of certain Raman modes have been monitored and have been related to structural changes due to oxygen content differences. Furthermore, the kinetics of the oxygen exchange process has been measured combining *in situ* Raman and electrical conductivity relaxation measurements.

Through these examples, we will discuss what kind of information these unconventional Raman experiments can bring and review their merits, weaknesses and prospects.

2:30 PM DT25.02

Selected Examples of High-Throughput Experimental Studies in Solid State Ionics and Solid State Electrochemistry Sossina Haile; Northwestern University, United States

The pace of materials development efforts has accelerated dramatically over the past several years, with increasing attention being given to computational prediction of new materials and machine learning of structure-processing-relationships. Key to the ultimate success of such approaches is the acquisition of large amounts of experimental data, which serve as inputs for machine learning, provide validation of simulation methods, and culminate in the realization of computational predictions. High throughput studies of high-temperature, solid state systems are, however, difficult to implement for a variety of reasons. Here we describe an environmental scanning electrochemical impedance spectroscopy apparatus designed for automated data acquisition from libraries of hundreds of samples and present several examples of studies performed in this system: oxygen ion conductivity in Lu doped zirconia; oxygen electroreduction/evolution on $(\text{La,Sr})\text{MnO}_3$; and oxygen electroreduction/evolution on $(\text{La,Sr})(\text{Co,FeO})\text{O}_3$.

2:45 PM *DT25.03

Simultaneous Electrical Impedance and Optical Absorption Measurements for Rapid Characterization of Defect and Transport Properties of Praseodymium Substituted Ceria Dmitri Kalaev and Harry Tuller; Massachusetts Institute of Technology, United States

While mixed ionic-electronic conductivity (MIEC) in oxides is central to the efficient operation of multiple technologies, from an experimental point of view, it is challenging to systematically characterize MIEC over the broad range of experimental conditions of interest, thereby significantly limiting their study and potential applications. Here, we introduce a novel and highly efficient method to gain such information based on transient, out-of-equilibrium measurements of electrical conductivity and optical absorption of thin films that enables access to information about defect generation and transport efficiently, and with improved precision, as functions of oxygen partial pressure and temperature, over wide limits. We select for study the model MIEC $\text{Pr}_x\text{Ce}_{1-x}\text{O}_{2-\delta}$ (PCO) system, given detailed information existing for this system in the literature as obtained by classical methods, and its increasing consideration in various energy conversion and storage applications, as memory devices or as a key component in actively tunable optical devices. Here we show that simultaneous transient measurement of the electrical and optical properties of PCO thin films, with $x = 0.1$ and 0.2 , enables rapid characterization of its optical molar extinction coefficient, and thereby its defect chemistry in a continuous manner, while simultaneously enabling decoupling of the partial ionic and electronic transport contributions. The transport and the optical properties of PCO measured in this study were found to be consistent with previously published results obtained by classical methods. This work, therefore, opens up the possibility to efficiently study the potentially confounding effects of variations in microstructure, substrate and deposition induced strain structure and various other external stimuli on the defect and transport properties of the PCO compounds and related MIEC materials.

3:05 PM DT25.04

Peculiarities of Ionic Conductivity Mechanisms in $\text{Bi}_{1-x}\text{Pr}_x\text{O}_{1.5}$ Rhombohedral System Jan Jamroz¹, Wojciech Wrobel¹, Marcin Krynski¹, Marcin Malys¹, Isaac Abrahams² and Franciszek Krok¹; ¹Politechnika Warszawska, Poland; ²Queen Mary University of London, United Kingdom

The rhombohedral-type structure observed in some lanthanide doped bismuth oxides exhibits ionic conductivity almost as good as that of the fluorite $\delta\text{-Bi}_2\text{O}_3$ type compounds [1] and is more resilient during long-term annealing [2]. This type of structure is often observed in many bismuth oxide based systems doped with rare earth metal oxides of a large ionic radius e.g. in praseodymium doped bismuth oxides, $\text{Bi}_{1-x}\text{Pr}_x\text{O}_{1.5}$. The step change of ionic conductivity observed at ca. 700 °C in these compounds is believed to be associated with ordering processes in the oxide ion sublattice and the activation of an additional conductivity pathway [3] and is also dependent on doping level. Therefore, this system can be considered as a model system to study some peculiarities of the ionic conductivity mechanism as a function of praseodymium content and temperature using a combination of experimental and computer modelling results.

Compounds of general formula $\text{Bi}_{1-x}\text{Pr}_x\text{O}_{1.5}$ $x = 0.200, 0.225, 0.250, 0.275, 0.300, 0.325$ were synthesized by solid-state reaction with sintered pellets exhibiting densities, above 95% of theoretical values. XRD and neutron scattering (Polaris Diffractometer at ISIS) data were collected over the temperature range 25 – 800 °C. Electrical properties were studied by the means of ac impedance spectroscopy combined with dielectric property analysis. Conductivity data were modelled on the basis of the modified “cube-root” model using self-made fitting procedures in MATLAB software package. *ab initio* molecular dynamics was studied with the VASP simulation package.

Investigation of structural properties by powder X-ray and neutron diffraction confirmed rhombohedral structure throughout the studied temperature and composition ranges, with an order-disorder type phase transition ($\beta_2 \leftrightarrow \beta_1$) at ca. 700 °C. Rietveld analysis of diffraction patterns reveals a variation of a lattice parameter, related with changing of Bi : Pr ratio. Data show that both the difference in ionic radii and in preferred local coordinations of cations plays major role in structural and electrical properties in this system. Redistribution of oxide ions between the fluorite like blocks and van der Waals gap results in step change of conductivity at the $\beta_2 \leftrightarrow \beta_1$ phase transition. In order to shed more light on the dynamics within and between the blocks we employ van der Waals corrected Density Functional Theory within molecular dynamics setting. The study shows that the oxide ion dynamics of $\text{Bi}_{1-x}\text{Pr}_x\text{O}_{1.5}$ exhibits high level of dynamical heterogeneity, with centers of the diffusion processes migrating between the fluorite-like block and the van der Waals gap with varying Bi : Pr ratio.

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Acknowledgements

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3:20 PM DT25.05

Novel Model-Building Tools for the Development of Near-Surface Mixed Ionic-Electronic Conducting Emulator Models for High-Temperature CO₂ Electrolysis Cells Alejandro Mejia^{1,2} and David S. Mebane¹; ¹West Virginia University, United States; ²Idaho National Laboratory, United States

Current research interests in the design and commercialization of solid-state energy storage and conversion devices, such as solid oxide fuel/electrolysis cells, have led to an ongoing development of advanced model fitting and model building techniques. In this field, we at the Energy Systems and Materials Simulation group in West Virginia University, have developed a set of model building routines, based on the BSS-ANOVA framework, that allow us to construct an emulator for the near-surface defect chemistry of mixed ionic-electronic conducting thin films, typically used in high-temperature CO₂ electrolysis. This methodology allows us to replace complex, nonlinear differential equations with a simplified, empirical surrogate computer model that can effectively describe the nonhomogeneous near-surface chemistry, given the bulk parameters and operating conditions. Using the Multiphysics Object-Oriented Simulation Environment (MOOSE) framework, developed at INL, to initially run sets of parameter combinatorial pseudo-experiments, we can obtain a parameter input/output emulator to replicate the function behavior of the computationally intensive multiscale MOOSE models. With these large datasets, the emulator routine can provide an accurate and fast scheme for replacing the near-surface defect chemistry models. Applying this technique to a two-dimensional operating CO₂ electrolysis cell, we can effectively build equilibrium and kinetic models for a real-life cell. Combining these models with actual experimental data, we can additionally apply a Bayesian calibration routine to obtain posterior parameter distributions that can provide further insight into the underlying science and effectively test different hypotheses for CO₂ adsorption and incorporation reaction mechanisms. Current results and emulator model-building demonstration will be presented to highlight the main achievements of this ongoing project and share the framework code for other interested research groups.

SESSION DT26: Field and Strain Effects
 Session Chair: Clement Nicollet
 Thursday Afternoon, July 21, 2022
 Mezzanine Level, Second Floor, Georgian

4:00 PM *DT26.01

Mechanically Induced Dislocations and Their Effects on Electrical Properties of Oxide Ceramics Till Frömling, Qaisar Khushi Muhammad, Lukas Porz and Jürgen Rödel; Technische Universität Darmstadt, Germany

The functional properties of ceramics are usually tailored by designing point defects and interfaces. Dislocations as heavily charged nanoscale one-dimensional line defects have so far been underappreciated as a means to tune functionality but are finding increasing attention today. For example, the opportunity to tune ceramics beyond what can be achieved by chemical doping, hampered by the solution limit of the dopants, is of significant interest. Here, we demonstrate on the model materials TiO_2 , SrTiO_3 , and yttria-stabilized zirconia that mechanically introduced dislocations possess the ability to induce quantitatively equivalent conductivity enhancements into oxide ceramics to conventional chemical doping. We combine the understanding of mesoscopic dislocation structure and its behavior at elevated temperatures. The impact of dislocations on the functional properties of ceramics depends on a convolution of dislocation character, core properties, possibly existing space charges, and mesoscopic structure. This is difficult to control as ceramics are usually not plastically deformable. The interaction of dislocations and bulk properties is thus both complex and exciting as it allows for multiple modification possibilities such as anisotropic conductivity change in semiconductors and solid electrolytes.

4:20 PM DT26.02

Understanding the Structure-Strain-Ion Conduction Relationships in Fluorite-Bixbyite Heterostructures Gene Yang, Mohammad El Ioubani and Dongkyu Lee; University of South Carolina, United States

Achieving fast ion transport at reduced temperatures is a key requirement to develop advanced oxide-based energy applications. In recent years, rapidly growing attention has been directed to the investigation of ionic conductivity in oxide heterostructures due to their ability to enhance ion conduction. Such an increase of ionic conductivity is mainly associated with interfacial strain effects and space charge effects in oxide heterostructures. In particular, interfacial strain plays a key role in controlling the oxygen ion migration and oxygen vacancy formation. However, the nanoscale thickness required for maintaining strain along the lateral direction of the substrate surface is impractical as many practical devices require ions to move across electrode-electrolyte interfaces. Furthermore, only a few studies have experimentally demonstrated the effect of strain on ion transport properties owing to the difficulty in deconvoluting the strain contribution from both strain and space charge effects. New design concepts are therefore required to realize heterostructures with the increased number of strained interfaces and thickness in micron-scale for commercial applications, and to address the effect of interfacial strain on ionic conductivity.

In this work, a combination of the fluorite Gd-doped CeO_2 (GDC) and a bixbyite RE_2O_3 (RE = Y and Sm) is used in the form of both lateral multilayer thin films with nanoscale thickness and vertically aligned heterostructures (VAHs) with micron-scale thickness to provide the direct insight into the structure-strain-ion conduction relationships. Pulsed laser deposition is performed to synthesize epitaxial GDC- RE_2O_3 (RE = Y and Sm) multilayer thin films and VAHs. Considering the lattice mismatch between GDC and RE_2O_3 (RE = Y and Sm), Sm_2O_3 ($a = 10.935 \text{ \AA}$) and Y_2O_3 ($a = 10.607 \text{ \AA}$) introduce tensile (~1%) and compressive (~2.1%) strain, respectively, into GDC ($a = 5.418 \text{ \AA}$). We access the strain state of GDC depending on its counterpart with High-resolution X-ray diffraction (HRXRD) reciprocal space maps. The difference in the oxygen vacancy concentration induced by strain is evaluated by Raman spectroscopy and in-situ HRXRD. Measurements of in-plane and out-of-plane ionic conductivity demonstrate how the ionic conductivity of GDC is influenced by strain states and ion flow directions. By altering the thickness and ratio of GDC in multilayer films and VAHs, respectively, the ionic conductivity of GDC significantly increased (decreased) as tensile (compressive) strain increased. These results imply that tensile strain may significantly reduce the energy barriers for either oxygen vacancy formation or oxygen ion migration at the interface in contrast to compressive strain. We demonstrate the effect of strain on ion conduction by successfully deconvoluting the strain contribution from multiple factors to the interfacial ionic conductivity in oxide heterostructures. Our work provides previously inaccessible insights into the vertical strain-ion transport relationship and a rational design strategy to precisely control ionic conductivity at the atomic level critical for developing high-performance energy and ionotropic devices.

This research was funded by the U.S. Department of Energy (DOE), Office of Science (OS), Basic Energy Sciences (BES), grant number DE-SC0021363.

4:35 PM DT26.03

Large Non-Classical Electrostriction in Aliovalent and Isovalent Doped Ceria Maxim Varenik, Ellen Wachtel, David Ehre, Elad Gaver and Igor Lubomirsky; Weizmann Institute of Science, Israel

The majority of commonly used electrostrictive ceramics are based on lead manganese niobate. These ceramics display large electrostriction strain coefficients $\approx 10^{-16} \text{ m}^2/\text{V}^2$ at frequencies up to a few kHz. However, they suffer from major drawbacks: they require high driving currents (dielectric constant >10000), contain toxic elements, and are incompatible with thin film Si-microfabrication techniques.

We have recently reported that ceria ceramics doped with aliovalent cations having crystal radii smaller than that of cerium, display increased high frequency ($f > 100 \text{ Hz}$) longitudinal electrostriction strain coefficients $|M|$. For instance, with 10 mol% Lu^{3+} or Yb^{3+} lanthanide dopants, $|M| \sim 10^{-17} \text{ m}^2/\text{V}^2$ is observed for $f > 100 \text{ Hz}$. Despite $Y_{\text{ceria}} \sim 200 \text{ GPa}$ and $\epsilon_{\text{ceria}} \sim \dots$, these electrostriction strain coefficients are 100-fold larger than estimated on the basis of Newnham's scaling law for "classical" electrostrictors. Such "non-classical" behavior has been attributed to the formation of highly polarizable, elastic dipoles reorienting under external electric field.

Surprisingly, doping with small isovalent dopants, such as Zr and Hf, produces an increase in $|M|$ to, independent of frequency up to several kHz, as determined by converse electrostriction measurements. The introduction of Zr raises the dielectric constant more than predicted by the Clausius-Mossotti relation. This suggests that the presence of a small dopant creates a highly polarizable unit which may be responsible for the large electrostriction strain coefficient. Our results demonstrate that, by systematically adjusting the composition of ceria-based solid solutions, the possibility exists for development of technologically useful electrostrictive materials which are, at the same time, ecologically sound and fully compatible with Si-microfabrication.

4:50 PM DT26.06

Understanding Delamination of Oxygen Electrode by Electro-Chemical and Mechanical Coupled Modeling Puvikkarasan Jayapragasam¹, Yeting Wen², Xinfang Jin¹ and Kevin Huang²; ¹University of Massachusetts Lowell, United States; ²University of South Carolina, United States

Critical long-term goal of reducing global greenhouse gas emissions can be achieved by use of sustainable alternatives to fossil fuels. Hydrogen is considered as one of the most promising green energy sources, due to its zero-carbon emission and high gravimetric energy density than gasoline [1,2]. Steam methane reforming or coal gasification is the primary source of hydrogen generation, unfortunately, with utilization of fossil fuels. Water splitting is

a cleaner way of generating hydrogen through an electrolysis process. Solid Oxide Electrolysis Cell (SOEC), operating at high temperature, is one of the most important electrolysis devices and generates hydrogen efficiently with reduced requirement of electric voltage [2,3]. SOEC is a reversed mode of Solid Oxide Fuel Cell (SOFC), consisting of an oxygen electrode (OE), an electrolyte (EL) and a hydrogen electrode (HE).

Degradation of SOECs' performance is mainly due to delamination of oxygen electrode from electrolyte [3,4]. Delamination becomes severe during long-term use beyond 1000h, causing technology barriers for its commercialization [5]. There are two theories about the delamination mechanism at OE/EL interface. Some researchers predict that delamination is due to accumulation of oxygen partial pressure at the OE/EL interface [3,5]. Another group of researchers think diffusion and migration of oxygen ions from electrolyte to electrode causes oxygen stoichiometry variation and lattice expansion at OE/EL interface [4]. In this work, we will use Nernst-Planck equation to simulate the diffusion and migration of oxygen ions, predict oxygen stoichiometry variation at the interface and the resulted delamination by chemical expansion [1]. Our preliminary results show that improving oxygen evolution electrokinetics at 2PB (two phase boundary) can minimize the accumulation of oxygen ions at interface and eventually eliminates faster cleaving of OE and electrolyte.

We will explore two OEs: Porous Lanthanum Strontium Cobalt Ferrite (LSCF) as a baseline OE and LSCF coated with Strontium Cobalt Tantalum Oxide (SCT) as a bilayer OE. An Electro-Chemical-Mechanical coupled model will be used to correlate the crack length at the OE/EL interface with voltage-current curve and results will be validated by experimental measurements. Long-term performance of bilayer design will be compared against the baseline cell and their degradation mechanism will be investigated. J-integral method will be employed to evaluate the crack growth as a function of time, under 1 A/cm² and 700°C. Furthermore, this model will be used as an optimization tool for choosing favorable operating conditions (like current density, temperature) mitigating delamination rate.

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SESSION DT27: Poster Session III: Batteries
Thursday Afternoon, July 21, 2022
6:00 PM - 8:00 PM
Mezzanine Level, Second Floor, Stadler

DT27.02

Electrical and Structural Studies on the Li_{1.3}Al_{0.3}Ti_{1.7}(PO₄)₃-LiAlSiO₄ Ceramic Li⁺ Conductor Konrad Kwatek¹, Wioleta Slubowska¹, Jan Nowinski¹, Agnieszka Krawczynska¹, Isabel Sobrados² and Jesus Sanz²; ¹Warsaw University of Technology, Poland; ²National Research Council, Spain

Lithium aluminum titanium phosphate (LATP) with NASICON-like structure is considered to be one of the possible promising candidates as a solid electrolyte in all-solid-state batteries due to good thermal and mechanical stability, good chemical stability against moisture in the air and high bulk ionic conductivity of the order of 10⁻³ Scm⁻¹ at room temperature. However, the total conductivity of LATP is lower by one order of magnitude because of highly resistive grain boundary phases. Therefore, it is necessary to increase the conductivity of grain boundary region e.g. by introducing additives with good ionic conductivity [1]. For this purpose, the LiAlSiO₄ (LASO) additive was introduced into the LATP matrix. Similar approach has already been applied in our previous works with (0.75Li₂O•0.25B₂O₃) [1] glass and LiF [2] additives as sintering agents, where the enhancement of the total ionic conductivity was also observed.

The electrical and structural properties of the LATP-xLASO ceramics, where 0 ≤ x ≤ 0.2, were studied applying several different and complementary methods, like high temperature X-ray diffractometry (HTXRD), ⁶Li, ²⁷Al, ²⁹Si and ³¹P nuclear magnetic resonance (MAS NMR), scanning electron microscopy (SEM), thermogravimetry (TGA), impedance spectroscopy (IS) and density (Archimedes) methods. The obtained materials were studied not only in a function of LASO content but also in a function of sintering conditions. The experimental data indicate that the addition of LiAlSiO₄ to LATP results in the enhancement of its total ionic conductivity with reference to pristine LATP. The highest value of $\sigma_{tot} = 2.5 \times 10^{-4}$ Scm⁻¹ has been obtained for LATP-0.1LASO material sintered at 1000 °C for 2 h. Based on collected results, we suggest that there may be two factors determining the enhancement of total ionic conductivity in the LATP-xLASO system. The first one refers to the microstructure of the material, which is sensitive to sintering parameters (temperature and/or sintering time affect the average grain size and the thickness of grain boundary region). The second one, even more significant, is related to the occurrence of another lithium-ion conductor (LiTiPO₅) formed during the sintering process.

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DT27.03

Impact of Li-Excess Sources on the Electrical Properties of LiTa₂PO₈ Material—A Novel Solid Lithium-Ion Conductor Konrad Kwatek¹, Wioleta Slubowska¹, Jan Nowinski¹, Cezariusz Jastrzebski¹, Agnieszka Krawczynska¹, Isabel Sobrados² and Jesus Sanz²; ¹Warsaw University of Technology, Poland; ²National Research Council, Spain

Among inorganic solid lithium-ion conductors considered for application in all-solid-state batteries, various metal oxide-based compounds have already been studied, e.g., perovskite-type $\text{Li}_{3-x}\text{La}_{2/3-x}\text{TiO}_3$ (LLTO), garnet-type $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZO), NASICON-structure phosphates $\text{Li}_{1+x}\text{Al}_x\text{Ti}_{2-x}(\text{PO}_4)_3$ (LATP) and LISICON-type. However, there is still a strong demand for better solid electrolytes with high ionic conductivity as well as good thermal, mechanical and chemical stability. Recently, a new compound emerged, lithium tantalum phosphate LiTa_2PO_8 (LTPO), which meets the requirements mentioned above [1]. LTPO has excellent bulk ionic conductivity of the order of 10^{-3} Scm^{-1} at room temperature. However, its total ionic conductivity is one order of magnitude lower because of highly resistive grain boundaries and relatively high porosity [1]. The overall electric properties of this ceramic material strongly depend on processing conditions, e.g., time and temperature of sintering [2]. LTPO requires high sintering temperatures of above 1000°C at which the evaporation of Li_2O becomes highly probable and is detrimental for its ionic conductivity. To compensate for Li^+ loss at high temperatures, we modified and optimised the synthesis procedure by introducing an excess of lithium varying from 5 to 15 wt.% (with reference to the stoichiometric amount). Also, different lithium sources, like Li_2CO_3 , LiNO_3 , $\text{LiOH}\cdot\text{H}_2\text{O}$ and Li_2O were used and their impact on secondary phase composition, porosity and ionic conductivity was thoroughly examined. The electrical and structural properties of the LiTa_2PO_8 ceramics, with excess Li source were studied applying several different and complementary methods, like high-temperature X-ray diffractometry (HTXRD), ^6Li and ^{31}P nuclear magnetic resonance (MAS NMR), Raman spectroscopy, scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDX), thermogravimetry (TGA), impedance spectroscopy (IS), density (Archimedes) and Hebb-Wanger polarization methods. Besides different compositions of the formed ceramics, also the impact of the sintering conditions on the electrical properties was investigated. The highest value of $\sigma_{\text{tot}} = 5.2 \times 10^{-4} \text{ Scm}^{-1}$ has been obtained for LiTa_2PO_8 (LiNO_3 source) material sintered at 1075°C for 8 h. The correlations between the sintering conditions, structure, microstructure and electrical properties will be pointed out and discussed.

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DT27.04

Synthesis of $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ -Type Structured $\text{Li}_{9+k}\text{P}_{3+k}\text{S}_{12-k}\text{O}_k$ Solid Solution Phases Subin Song, Miao Xu, Satoshi Hori, Kota Suzuki, Masaaki Hirayama and Ryoji Kanno; Tokyo Kogyo Daigaku, Japan

Inorganic fast lithium conductors can be applied as solid electrolyte in all-solid-state lithium batteries, which may have enhanced energy- and power-features, and properties of the solid electrolyte are important for developing the batteries. A superionic conductor $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ [1] (LGPS) and its structural analogous $\text{Li}_{10}\text{MP}_2\text{S}_{12}$ ($M = \text{Si}, \text{Sn}$) have been intensively studied because they show especially high ionic conductivity of 10^{-3} – 10^{-2} Scm^{-1} . Recent studies reported LGPS-type crystalline phase in Li-P-S-O system. [2, 3] However, their neutron crystal structure analyses have not been performed, though such analysis can facilitate the optimization of the material's properties. The present study reports on the $\text{Li}_{9+k}\text{P}_{3+k}\text{S}_{12-k}\text{O}_k$ (LiPISO) solid solutions, which synthesized by both mechanochemical (M-LiPISO) and melt quenching (Q-LiPISO) methods. The relationships between crystallinity, crystal structure, and electrochemical properties were clarified.

The start materials of Li_2S , P_2O_5 , P, and P_2S_5 were weighted in the designed molar ratio and mixed by ball milling. The specimens were pressed in pallet, sealed in the quartz tube, and heated in a furnace. For mechanochemical synthesis, the annealing temperature was 493–553 K for 4h. For melt-quenching synthesis, the pellet was heated at 1223 K for 5h and rapidly quenched in ice water. The crystal structure was analyzed based on neutron diffraction. The phase and crystallinity change were conducted by X-ray diffraction (XRD) and transmission electron microscopy (TEM). Ionic conductivity was determined by the electrochemical impedance spectroscopy.

Both M-LiPISO and Q-LiPISO synthesis methods provided the LGPS-structure phase; the XRD pattern of the synthesized samples with a specific k range were indexed by the same space group as the LGPS ($P4_2/nmc$). For determining the occupancy and sites of lithium and oxygen atoms, the structure analysis based on neutron diffraction data was performed for Q-LiPISO ($k = 3$), which showed higher sample crystallinity than M-LiPISO ($k = 3$) in TEM observation. During the refinement, the occupancy of Li4 site, which is one of the four Li sites reported for the original LGPS, becomes zero. Since the Li4 site was considered as a component of the conduction pathway over the ab -plane in the original LGPS, the lithium distribution change observed for the Q-LiPISO implies a decrease in the lithium conduction pathways of the ab -plane. Oxygen atoms selectively replaced sulfur atoms at the S1 site, which is one of the three sulfur sites in LGPS-type crystal. Such selective occupation of oxygen would induce the electrostatic attracting interaction between oxygen atoms at the substitution site and Li ions around the substitution site. The deduced change in the lithium distribution along conduction pathways was further investigated by the density functional theory (DFT) *ab-initio* molecular dynamics (MD) calculation. The probability density for the Li site positions along c -axis was found unconnected even in 700 K, indicating the absence of the c -axis diffusion pathway that was reported for the original LGPS. These Li distribution changes associated with oxygen substitution were ascribed to the reason for the low ionic conductivity (0.07 mScm^{-1}) for the Q-LiPISO ($k = 3$). However, this study found that the solid solution phase with a low degree of sulfur/oxygen substitution (M-LiPISO with $k = 0.9$) showed a high ionic conductivity of above 1 mScm^{-1} . In addition, the all-solid-state cell with Li metal anode and M-LiPISO ($k = 0.9$) separator keeps discharge capacity retention rate of 97 %. These preliminary result indicated that LiPISO electrolytes with low substitution degree possesses is a promising candidate solid electrolyte for all-solid-state lithium batteries.

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DT27.05

Adhesion Strength Between Solid Components of Sulfidic ASSBs—Influence of the Process Routes on Microstructural Changes Celestine Singer^{1,2}, Milot Aruqaj², Lorenz Kopp^{1,2}, Hans-Christoph Töpper^{1,2} and Rüdiger Daub²; ¹TUMint. Energy Research GmbH, Germany; ²Technische Universität München, Germany

All-solid-state batteries (ASSBs) seem to be a promising future cell concept to enhance energy densities and create an advantage in safety aspects in comparison to conventional LIBs. ASSBs are built up from solid components/thin layers, including a composite cathode and potentially a lithium metal anode as well as a solid electrolyte separator, which is responsible for the ion conduction. To guarantee the functionality and high performance of the galvanic cells, a good interface between those layers is essential to reduce electrochemical resistances and enhance mechanical stability. Especially, the physical contact of the composite cathode/solid electrolyte interface and the solid electrolyte/anode interface require attention.

As known from the conventional lithium-ion battery production, several process steps have a significant influence on the microstructure and therefore the binder distribution, which is mostly responsible for the adhesion strength. Since the final process route to building up a galvanic cell is not yet established, the advantages of respective routes can be evaluated by analyzing the adhesion strength as a quality criterion. In general, there are three possibilities to

fabricate the final galvanic cell: A so-called cathode-supported cell design is built up by coating the solid electrolyte directly onto the cathode. Another process route includes the use of a carrier foil to coat a free-standing solid electrolyte and press single layers to one compound afterward. In a third, the solid electrolyte is coated and first pressed onto the lithium metal anode.

To evaluate these routes, parameters of essential processes were varied and the adhesion strength between different compounds are measured by a tensile strength test in argon atmosphere. Besides the influence of the drying temperature on the binder migration and decrease of adhesion strength, also the parameters of pressing/laminating the layers in different sequences are analyzed for the sulfidic materials $\text{Li}_6\text{PS}_5\text{Cl}$ (LPSCI) and a respective composite cathode made of the raw materials NMC622, LPSCI, HNBR and C65 as well as pure lithium metal as anode.

As a first result, the high influence of the drying temperature on the adhesion strength is shown. At temperatures around 60 °C, there seems to be no major impact on the binder migration. Rising to 100 °C a clear decrease of the adhesion strength and a higher binder concentration on the top of the sample are then observed. With regard to the sequence of combining the solid electrolyte with an electrode, a difference in the adhesion strength is measured for the process flows. Directly coated solid electrolytes onto cathodes do show a significantly higher adhesion strength than subsequently pressed solid electrolytes. For the compound of lithium metal and the solid electrolyte, the adhesive properties of both materials are advantageous, and therefore, the adhesion strength is higher than in between the cathode and solid electrolyte. With regard to industrial production, major advantages in mechanical stability can thus be achieved following these process flows to ensure high performance of sulfidic all-solid-state batteries.

DT27.06

Stepwise Reaction and Degradation in Solution Synthesis of $\text{Li}_6\text{PS}_5\text{Br}$ from P_4S_{10} Raheed Bolja^{1,2}, Bjorn Joos^{1,2,3}, Alexander Tesfaye⁴, Marlies Van Bael^{1,2,3} and An Hardy^{1,2,3}; ¹Hasselt University, Institute for Materials Research (imo-imomec), DESINE team, Belgium; ²EnergyVille, Belgium; ³imec, imec, Belgium; ⁴Umicore, Corporate Research & Development, Belgium

Transport is the only sector to have increased its CO₂ emissions since 1990, and regular passenger cars make up the largest part of these transport emissions. Thus, a growing need for sustainable mobility is clear, leading to an expanding electric vehicle market. Lithium-ion batteries are considered most suitable for these vehicles owing to their large volumetric and gravimetric capacities. The need for increased battery performance as well as improved safety makes solid-state batteries the main contender for next-generation Lithium-ion batteries in all battery development roadmaps. Among solid-state electrolytes, sulfide-based materials such as LGPS ($\text{Li}_{10}\text{GeP}_2\text{S}_{12}$), lithium thiophosphates (Li_3PS_4 and related compounds), and lithium argyrodite-type (generally $\text{Li}_4\text{PS}_5\text{X}$, X being Cl, Br, or I) materials are attracting much attention because of their high ionic conductivity, which is comparable in magnitude to that of known liquid electrolytes, potential for improved safety, and potential for more sustainable production.

Synthesis of both lithium thiophosphates and their derived products, lithium argyrodites, can be performed in several ways: solid-state methods offer proven ways to achieve these materials, although they come at significant cost in both reaction time as well as energy consumption. Solution-based methods have been shown to produce these materials with lower reaction times, requiring a smaller energy investment, and offering access to metastable phases. A solution-based route starting from the precursor P_4S_{10} towards the final $\text{Li}_6\text{PS}_5\text{Br}$ argyrodite-type product has been described in literature by Yubuchi *et al.*, whereby P_4S_{10} and Li_2S are first reacted in a tetrahydrofuran (THF) solvent to form Li_3PS_4 , followed by addition of Li_2S and LiBr in ethanol to form the $\text{Li}_6\text{PS}_5\text{Br}$ product in a mixed-solvent solution. This work examines the presence of intermediate compounds in the first step of this synthesis (performed in THF), and the formation of ethanolic degradation products over time in the second step of the synthesis (performed in the THF-ethanol mixed solvent system) by a combination of analytical techniques including MAS-³¹P-NMR, liquid ³¹P-NMR and ICP-OES.

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DT27.07

Enhancement of Superionic Conductivity by Halide Substitution in Strongly Stacking Faulted $\text{Li}_3\text{HoBr}_{6-x}\text{I}_x$ Phases Maximilian A. Plass^{1,2}, Sebastian Bette¹, Robert E. Dinnebier¹ and Bettina V. Lotsch^{1,2}; ¹Max-Planck-Institute for Solid State Research, Germany; ²Ludwig-Maximilians-University Munich, Germany

Fossil fuels are limited and their combustion products have severe effects on climate and health. This is the reason why several governments aim to reduce average carbon dioxide emissions of new cars.^[1] A smart way to face this challenge is to establish electric and hybrid electric vehicles (EVs) for individuals or within the public transport system, in which rechargeable energy storage technologies are used. Thus, EVs have the potential not only to reduce the environmental pollution, but also the dependence on fossil fuels.^[2]

Because of their high power and energy density, low weight and cost, lithium ion batteries (LIBs) are among the most promising energy storages for EVs. The most established and commercialized electrolytes in LIBs are liquid organic electrolytes, because they show high ionic conductivities of up to 10^{-2} S cm^{-1} . A major disadvantage, however, is a lack of safety. A promising alternative are solid inorganic electrolytes (SIEs), which feature higher thermal stabilities and eliminate safety concerns due to their non-flammability. In addition, all-solid-state batteries (ASSBs) based on solid electrolytes promise a simplified design based on Li metal anodes, which allows for significantly higher energy densities compared to conventional LIBs.^[3,4]

Due to their high ionic conductivities^[5-8] of up to 10^{-2} S cm^{-1} , sulfide-based SIEs are promising candidates for ASSBs. Unfortunately, sulfidic SIEs exhibit narrow theoretical electrochemical stability windows vs. Li.^[9,10] In contrast, halides show much wider theoretical electrochemical stability windows and

promise higher stabilities against high-voltage cathodes. Since halide-SIEs exhibit comparably high ionic conductivities, they show promise as a new generation of both bulk SIEs and conductive coatings for catholyte materials.^[11–14]

Here we present the structure, microstructure and Li transport properties of the strongly stacking faulted rare earth halides Li_3MX_6 with M = rare earth metal and X = Br, I and highlight the influence of cation disorder and halide substitution on the superionic conductivity across the solid solution series $\text{Li}_3\text{HoBr}_{6-x}\text{I}_x$. We demonstrate that the optimum in ionic conductivity ($2.7 \times 10^{-3} \text{ S cm}^{-1}$ at 20°C) and activation energy (0.21 eV) is observed at $x \approx 3$, revealing a complex influence of composition, microstructure and disorder on the ionic transport properties in the system $\text{Li}_3\text{HoBr}_{6-x}\text{I}_x$.

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DT27.09

Effect of Nanostructure Control on Li-Garnet Electrolyte Thin Film for Li-Ion Solid-State Battery Haemin Paik and Jennifer Rupp; Massachusetts Institute of Technology, United States

To achieve high power and energy densities with long cycle life for all-solid-state Li-ion batteries (SSBs), solid electrolyte with thinner and high Li-ionic conductivity as well as high resistance to Li dendrite propagation is essential. Ceramic Li-garnet is a promising candidate for the solid-state electrolyte due to its high Li-ion conductivity and structural and electrochemical stability. Li-garnet polycrystalline thin-film with high Li-ion conductivity can be achieved by introducing multilayer processing with Li_3N as Li reservoirs using pulsed laser deposition (PLD) technique. This process enables to obtain thin and continuous dense Li-garnet polycrystalline film with unusual low processing temperature. However, the film contains nanoporous structure inside the film formed by decomposing of Li_3N layers during the post annealing process. Although closed pores formed in the Li-garnet film have not affected its Li ionic conductivity significantly, it could give other potential issues such as the sites for Li dendrite growth. Here, we developed a new thin-film growing process to control the density of the nanopores in the Li-garnet thin-film while keeping desired cubic phase with high Li ionic conductivity and low processing temperature. We investigated how this new ceramic processing approach affects the atomic structural properties of the film and the correlation with its Li ion transport kinetics. This gives new perspective on developing advanced Li-ion solid-state electrolyte to design safe and stable all-solid-state Li-ion battery architecture allowing more room for cathode volumes as well as reduced fabrication processing temperature.

DT27.10

Quantitative Measurement of Li-Ion Concentration and Diffusivity in Solid-State Electrolyte Gun Park¹, Hongjun Kim¹, Jimin Oh², Youngwoo Choi¹, Olga Ovchinnikova³, Seokhwan Min¹, Young-Gi Lee² and Seungbum Hong¹; ¹Korea Advanced Institute of Science and Technology, Korea (the Republic of); ²Electronics and Telecommunications Research Institute, Korea (the Republic of); ³Oak Ridge National Laboratory, United States

Reliable analysis based on quantitative measurement is a prerequisite for exploring the electrochemical phenomena of battery materials, which eventually allows for successful materials design based on in-depth understanding. However, current macroscopic measurement lacks the ability to fully decipher local properties as materials design rule approaches the nanoscale or even atomic scale. Recently, many visualization methods have been developed based on atomic force microscopy (AFM) with nanoscale resolution. Among various modes of AFM, electrochemical strain microscopy (ESM) has the advantage of visualizing the ion distribution and movement, which reflects the internal ion conduction channel in battery materials. Also, ESM enables us to investigate the ionic behavior with nanoscale spatial resolution, which can unveil unknown electrochemical mechanism in battery research. Here, we present a quantitative method to calculate the concentration and diffusivity of Li-ion in a solid-state electrolyte. We design an optimal DC bias voltage pulse to induce ion movement detected by an AFM cantilever and investigate the change in ESM signals as a function of Li-ion concentration. We calibrate the Li-ion concentration based on time-of-flight secondary ion mass spectroscopy (ToF-SIMS), X-ray photoelectron spectroscopy (XPS) and inductively coupled plasma optical emission spectroscopy (ICP-OES). We confirm that the measured ESM signal changes and calibration result (effective ion concentration) are strongly correlated with R-square of 0.91. We also calculate diffusivity of Li-ion based on relaxation curves of Li-ion after removal of DC bias voltage pulse and show the diffusivity change with nanoscale spatial resolution. Our study can be widely used to explore the ionic behavior in various electrochemical system with nanoscale resolution and eventually will provide new insight into electrochemical phenomena at nanoscale.

DT27.11

Li-Ion Conductivity in Metal Hydride-Based Nanocomposite Electrolytes—The Effect of Nanoscaffold Porosity and Surface Chemistry Laura M. de Kort, Petra de Jongh and Peter Ngene; Universiteit Utrecht, Netherlands

The development of energy storage technologies, such as rechargeable batteries, is crucial for the transition to a sustainable energy supply. Lithium-ion batteries are an effective means of electricity storage, which is demonstrated by their wide application ranging from mobile phones to electric vehicles. Unfortunately, Li-ion batteries suffer from safety issues arising from their combustible organic electrolytes. All-solid-state batteries (ASSBs), in which the common liquid organic electrolyte is replaced by a solid-state electrolyte (SSE), could potentially lead to safer batteries with increased energy density.

Recently, metal hydrides (e.g. LiBH_4 and $\text{LiCB}_{11}\text{H}_{12}$) have gained attention as promising solid electrolytes due to their stability, low density and high ionic conductivity albeit at elevated temperatures. However, for successful incorporation of metal hydride SSEs in ASSBs, sufficient ionic conductivity at room temperature is required. Therefore, the development of strategies that enhance room temperature conductivity in complex hydrides is of crucial importance.

In this contribution, we report on the combination of two promising strategies to enhance the ion mobility in metal hydrides, namely, partial ionic

substitution and nanoconfinement, which led to highly conductive metal hydride-based nanocomposites. Notably, via partial ion substitution with LiNH_2 , followed by nanoconfinement in a mesoporous oxide scaffold, $\text{LiBH}_4\text{-LiNH}_2/\text{oxide}$ nanocomposites with conductivities reaching $5 \times 10^{-4} \text{ S cm}^{-1}$ at 30°C were obtained^[1], compared to $2 \times 10^{-8} \text{ S cm}^{-1}$ for pristine LiBH_4 .

Interestingly, the conductivities of the nanocomposite electrolytes are strongly influenced by the chemical and physical nature of the mesoporous metal oxide. We studied this effect systematically using mesoporous silica (SBA-15) scaffolds with varying surface chemistry and pore structure. Remarkably, the conductivity varied over three orders of magnitude when tuning the porosity and surface chemistry of the metal oxide scaffold.^[2] For example, changing the SBA-15 surface chemistry through aluminium improved the conductivity of $\text{LiBH}_4\text{-LiNH}_2/\text{oxide}$ nanocomposites by a factor of two. On the other hand, the conductivity varied from $4 \times 10^{-7} \text{ S cm}^{-1}$ to $5 \times 10^{-4} \text{ S cm}^{-1}$ by increasing the scaffold pore volume from 0.51 to $1.00 \text{ cm}^3 \text{ g}^{-1}$, showing that the conductivity in this system is mainly dictated by the scaffold pore volume. Notably, this is different from pure $\text{LiBH}_4/\text{oxide}$ nanocomposites. Although their conductivity improves significantly compared to pristine LiBH_4 as well, in this case the conductivity does not depend on the scaffold pore volume at all. Instead, the surface chemistry plays a predominant role.

These results demonstrate that the origin of the conductivity enhancement in nanocomposites based on LiNH_2 -substituted LiBH_4 is different from $\text{LiBH}_4/\text{oxide}$ nanocomposites. The nanocomposite conductivity is greatly affected by the properties of the scaffold material in both cases, however, the exact impact can differ between the metal hydride ion conductors. The fundamental insights on the influence of scaffold properties on ion mobility in nanocomposite materials are relevant for other cation- and anion substituted ion conductors as well. Therefore, this work provides useful insight for the design of novel solid-state electrolytes with excellent ionic conductivity, essential for the development of next generation batteries.

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DT27.12

Li^+ NASICON- $\text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3$ Dispersed with Ionic Liquids—Electrical Transport and Applications to Electric Double Layer Supercapacitors Gurpreet Kaur, S. C. Sivasubramanian and Anshuman Dalvi; Birla Institute of Technology & Science Pilani, India

NASICON structured Li^+ ion conductor $\text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3$ (LTP) has been synthesized by the sol-gel route. To prepare fast ionic composites, the LTP was further dispersed with a small amount (2-13 wt%) of various ionic liquids (viz. EMIM BF_4 , EMIM CF_3SO_3 and BMIM BF_4). Structural, thermal, and electrical investigations carried out on these composites show interesting results. High-temperature XRD and TGA results reveal that these composites are stable at least up to 300°C . Composites containing ionic liquid (IL) interestingly exhibit a conductivity up to $\sim 10^{-3} \Omega^{-1}\text{cm}^{-1}$ at 25°C , thus have been used as electrolytes for electric double layer supercapacitors (EDLCs). The EDLCs were prepared by pressing the IL added-LTP powder between the activated carbon electrodes (diameter $\sim 14 \text{ mm}$) by ~ 2 tons, and subsequently packed in 2032 cell configuration. The EDLC behavior is confirmed by Nyquist plots, linear galvanostatic discharge curves, and featureless CV scans. A maximum specific capacitance of $\sim 200 \text{ F/g}$ has been observed at 0.6 A/g , 1 V . The EDLCs are stable at least up to \sim galvanostatic 15000 charge-discharge cycles without any notable degradation. It has also been observed that the choice of IL, and the conductivity of Li^+ NASICON, both play important role in supercapacitor performance. An assessment of the correlation of conductivity of the composite electrolyte has been made with EDLC performance via a systematic compositional variation of the electrolyte composition. These supercapacitors are successful in glowing 2 W LEDs up to ~ 30 mins at 15°C .

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DT27.13

Synthesis of Highly Li-Ion Conductive Garnet-Type Solid Ceramic Electrolytes by Solution-Process-Derived Sintering Additives Nataly C. Rosero-Navarro, Akira Miura and Kiyoharu Tadanaga; Hokkaido Daigaku, Japan

The sintering of garnet-type solid ceramic electrolytes (e.g., $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$, LLZ) is rather challenging considering the easy volatilization of the lithium at high temperatures. Liquid-phase sintering using sintering aids such as Li_3BO_3 and Al_2O_3 has effectively used to sinter LLZ solid electrolyte at low temperatures. However, the presence of sintering additives strongly affects the total lithium-ion conductivity of the solid electrolyte. As the lithium-ion conductivity of Li_3BO_3 is approximately two orders of magnitude lower than LLZ, the addition of a large amount of the sintering additive increases the resistance of the composite solid electrolyte, while an insufficient amount leads to a poor densification and insufficient lithium pathway for the ionic conductivity.

In this study, we propose an **alternative route to sinter garnet-type solid ceramic electrolytes using solution-process-derived sintering additives** to overcome the limitations of current sintering additives. We utilized Li_3BO_3 and Al_2O_3 as well-known sintering additives for the Ta-doped LLZ solid electrolytes by varying the processing using the solution-derived sintering additives. **This approach enables the significant reduction of the sintering additives and consequently, the enhancement of the lithium-ion transport properties** achieving a high ionic conductivity of 0.8 mS cm^{-1} with low activation energy (9 kJ mol^{-1}) and almost negligible contribution of grain boundary resistance (10% reported so far).

DT27.15

Exhaustive Investigation of NASICON-Type Na-Ion Conductors Using Molecular Dynamics Simulation and Bayesian Optimization Judith Schütt^{1,2}, Shuta Takimoto³, Steffen Grieshammer¹ and Masanobu Nakayama³; ¹Rheinisch-Westfälische Technische Hochschule Aachen, Germany; ²Forschungszentrum Jülich GmbH, Germany; ³Nagoya Institute of Technology, Japan

Ionic conductivity is a key property of solid electrolytes for application in energy storage technologies. NASICON (Na Super Ionic Conductors) materials are attracting a great share of attention among ceramic electrolytes since the observation of fast ionic conductivity in $\text{Na}_{1-x}\text{Zr}_2\text{Si}_x\text{P}_{3-x}\text{O}_{12}$ ($0 \leq x \leq 3$) by Hong and Goodenough in 1975. The NASICON structure exhibits the rhombohedral symmetry above 150°C , but at room temperature the monoclinic phase occurs in the compositional range of $1.8 \leq x \leq 2.2$. The three-dimensional structural framework of corner-sharing ZrO_6 octahedra and PO_4 tetrahedra with multiple sodium sites provides ionic migration in a , b and c direction resulting in high mobility of the monovalent charge carriers. Additional sodium

ions are introduced into the structure on regular lattice sites by doping zirconium and/or phosphorus sites.

In this study, NASICON materials are optimized regarding sodium ion conductivity by doping Sc^{3+} on Zr^{4+} sites and Si^{4+} on P^{5+} sites. Multi-element doping leads to an enormous search space and the investigation of NASICON structures with wide compositional range comes along with large time-consuming and cost-intensive computational demand. We present an efficient, automated, high-throughput computational approach that combines materials simulation and informatics-aided methods to exhaustively evaluate ionic conductivities of various derivate NASICON materials.

We study the ionic conductivity of multi-doped $\text{Na}_{1+x+y}\text{Zr}_{2-x}\text{Sc}_x\text{P}_{3-y}\text{Si}_y\text{O}_{12}$ by force-field molecular dynamics (FFMD) simulations. Accordingly, force-field parameters were generated using reference data obtained by high-precision first-principal MD (FPMD) simulations based on DFT. An implementation of the metaheuristic cuckoo search (CS) optimization was applied for the rhombohedral structure with co-doped composition $\text{Na}_3\text{Zr}_1\text{Sc}_y\text{P}_2\text{Si}_1\text{O}_{12}$ ($x = 1; y = 1$) to fit the set of parameters. We were able to obtain one FF parameter set that reproduces DFT results of rhombohedral as well as monoclinic structure with various compositions accurately. Subsequent FFMD simulations were performed for the entire compositional range of $\text{Na}_{1+x+y}\text{Zr}_{2-x}\text{Sc}_x\text{P}_{3-y}\text{Si}_y\text{O}_{12}$ between 298 K – 798 K with 100 K steps. Large supercells with around 4000 – 5000 atoms were generated, and 1 ns was simulated for each temperature and composition. In total, 419 compositions of rhombohedral as well as monoclinic structure were considered. The diffusivity of the ions was investigated based on the mean squared displacements (MSDs) of the ions showing that only Na ions are mobile in the structure. Ionic conductivities at different temperatures and activation energies for sodium ion migration were obtained.

In addition, we conducted low-cost high-efficient informatics-aided computations using BO machine-learning algorithm for the search for promising multi-doped NASICON materials with high ionic conductivity. As a proof of concept, we introduced an automated BO scheme using the prior exhaustively computed conduction property dataset. Our results validate that the BO approach is more efficient than the random search.

DT27.16

Li and Mg Intercalation in Hexagonal TiS_2 —A DFT Study [Shamik Chakrabarti](#) and AK Thakur; Indian Institute of Technology Patna, India

Spinel TiS_2 has been demonstrated, previously, to exhibit Li intercalation long ago [1, 2]. It established the pathway for development of lithium-ion battery (LIB). In the present work, we report our DFT analysis results, on Li and Mg intercalation feasibility in layered hexagonal TiS_2 . TiS_2 has a hexagonal structure with space group P-3m1 comprising a layered Vander wall gap of 6.5 Å. This is large enough to accommodate alkali cations like Li^+ (ionic radius 0.90 Å) and Mg^{2+} (0.86 Å). We have studied the structural properties for Li^+ and Mg^{2+} intercalation in layered TiS_2 by including Vander wall interaction between two Ti-S layers. Our DFT analysis confirmed that the two TiS_2 layers are separated by Vander wall gap ~6.5 Å. The electronic structure has been studied with modified Becke-Johnson (MBJ) approach and intercalation voltage was evaluated using GGA + U approach ($U = 2.5$ eV for Ti in ATiS_2 , $A = \text{Li}^+/\text{Mg}^{2+}$). Study showed that with Li^+ and Mg^{2+} intercalation, there is an volume expansion by 1.2% and 5.1% for Li^+ and Mg^{2+} respectively. Simulation of electronic structure exhibited that TiS_2 has a band gap of 0.426 eV before cation intercalation and it becomes metallic after Li and Mg intercalation in TiS_2 . The magnetic moment of Ti in LiTiS_2 and MgTiS_2 are noted to be 0.83417 μ_B and 1.55452 μ_B respectively. This may be a signature of the presence of $\text{Ti}^{4+}/\text{Ti}^{+3}$ and $\text{Ti}^{4+}/\text{Ti}^{+2}$ redox couple in LiTiS_2 and MgTiS_2 respectively. Further, Li and Mg intercalation voltage has been estimated to be 1.73 V and 0.528 V respectively with electrode capacity of 239 mAh/g and 478 mAh/g. The results indicate that hexagonal layered TiS_2 can be suitable as anode for Mg ion battery with adequate control over volume strain. However, experimental confirmation is essential and this work is under progress in our laboratory.

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DT27.18

3D Benzimidazole Based Triptycene Ionic Covalent Organic Frameworks with High Li-Ion Conductivity [Yoonseob Kim](#); The Hong Kong University of Science and Technology, Hong Kong

Ionic covalent organic frameworks (iCOFs) with high crystallinity, porosity, and ion conductivity are promising for applying batteries and fuel cells. 2D iCOFs received extensive investigation due to their tunable ionic functional groups and ability to transport ions efficiently. However, the research on 3D iCOFs with unique properties is limited. In addition, monomers with abundant amino groups are difficult to obtain because they are extremely sensitive to oxygen. Here, we employed a stable 2,3,6,7,14,15-Hexaaminotriptycene hexahydrochloride as an amino monomer to synthesize a series of highly crystallized benzimidazole-based triptycene iCOFs, which can be used as a solid-state electrolyte for Li battery. In addition, we have synthesized the corresponding covalent organic polymers (COPs) for comparison. After ionizing with Li^+ , the structure-property-conductivity relationship of the synthesized iCOFs and iCOPs are investigated. The iCOFs show a high Li-ion conductivity and transference number, larger than that of the iCOPs. The reason for the improved Li^+ conductivity and transference number of iCOFs is that the high crystallinity and periodic structure compared with iCOPs. This report extends the synthetic scope of 3D iCOFs and provides a design strategy for solid-state electrolyte.

DT27.19

Electrical, Structural, and Thermal Properties of Poly(Ethylene Oxide)- Tetramethyl Succinonitrile Blend for Redox Mediator of Dye-Sensitized Solar Cells [Ravindra K. Gupta](#), Ahamad Imran and Hamid Shaikh; King Saud University, Saudi Arabia

Research for electricity generation and storage is currently focused on the development of non-fossil fuel-based solid-state electrochemical devices. Solid-state rechargeable batteries, supercapacitors, fuel cells, and dye-sensitized solar cells rely on the fast ion conducting solid polymer electrolytes (SPEs). The solid nature of electrolytes makes the device economical, robust, lightweight, and easy in manufacturing. In the present paper, we will discuss electrical, structural, and thermal properties of (1-x)poly(ethylene oxide): x tetramethyl succinonitrile blend, where $x = 0 - 0.25$ and 1 in mole fraction. The tetramethyl succinonitrile (TMSN) is a plastic crystal, which has two extra methyl groups at the cyano radical of the succinonitrile, resulting in a higher value of solid-solid transition temperature (71 °C) and melting temperature (170 °C). This blend is new utilizing the plasticizing property of the TMSN, which is confirmed by electrical conductivity – temperature, XRD, FT-IR spectroscopy, Raman spectroscopy, DSC, and TGA studies. Though the electrical conductivity is nearly same, $\sim 10^{-9}$ S cm^{-1} at room temperature for blends with $x = 0.1-0.25$ mole, there is a phase separation starting from $x = 0.1$ mole and quite visible for $x = 0.2$ and 0.25 mole. This blend is used for preparing an I^+/I_3^- redox mediator, [0.85 PEO₈: 0.15 TMSN]-LiI-I₂. This mediator exhibits electrical conductivity of $\sim 10^{-4}$ S cm^{-1} at room temperature and dye-sensitized solar cell efficiency of $\sim 3.5\%$ at 1 sun; while, PEO₈-LiI-I₂ exhibits electrical conductivity of $\sim 10^{-5}$ S cm^{-1} at room temperature and cell efficiency of $\sim 0.5\%$ at 1 sun.

DT27.20

Ionic Conductivity of Amorphous and Crystalline β -Li₃PS₄ C. Mandl, Katharina Hogrefe, Martin Wilkening and B. Gadermaier; Graz University of Technology, Austria

Solid electrolyte manufacturing and processing is a major challenge in all-solid-state battery assembly. Processing at high temperatures is often necessary to assure intimate contact between the crystallites and high conductivity. Sulfide-based electrolytes are particularly interesting as their synthesis often does not rely on high temperatures.[1] This property makes them compatible to be processed with active materials with low thermal stability. The solid electrolyte Li_3PS_4 , for example, belongs to the group of thiophosphates which can be obtained by a simple solvent-assisted synthesis route [2]. Therefore,

the synthesis of Li_3PS_4 can be carried out with ordinary lab equipment and without high-temperature treatment. Here, Li_3PS_4 prepared by wet-chemical methods is characterized by X-ray powder diffraction (XRPD), ^6Li , and ^{31}P magic-angle spinning (MAS) NMR as well as conductivity spectroscopy to study both structural aspects and ion dynamics. The sample initially obtained after the final drying step turned out to be X-ray amorphous and shows a specific ionic conductivity (σ) of 0.03 mS/cm at room temperature. Annealing this amorphous sample at 120 °C leads to an increase in conductivity reaching 0.07 mS/cm while the amorphous state is retained. Both, results from X-ray analysis and MAS NMR do not indicate significant changes on the length scales to which the methods are sensitive. Crystallization initiated by annealing at 170 °C increases the conductivity even further leading to $\sigma = 0.13$ mS/cm; ^6Li and ^{31}P MAS NMR revealed significant structural changes in the direct vicinity of the NMR active nuclei. In any state, Li_3PS_4 as obtained by a solvent-assisted synthesis is characterized by an improved ionic conductivity compared to its counterpart prepared by classical mechanochemical synthesis routes [3]; $\sigma = 0.03$ mS/cm. Importantly, such wet-chemical preparation routes are highly scalable and, most importantly, enable the direct synthesis of cathode composites. Using carbon-coated LiFePO_4 as a model substance, we show that the solvent-assisted synthesis is successful even if other foreign phases are present. Moreover, the one-pot synthesis allows for the direct preparation of all-solid-state composite cathodes.

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SESSION DT28: Grain Boundaries/Interfaces
 Session Chair: William Bowman
 Friday Morning, July 22, 2022
 Mezzanine Level, Second Floor, Georgian

9:10 AM **DT28.01

Recent News in the Development of Useful and Scientifically Accurate Models of the Electrochemical Interface in Solids David S. Mebane^{1,2}; ¹National Energy Technology Laboratory, United States; ²West Virginia University, United States

Interfaces and surfaces in materials consisting of charged particles develop strong gradients in both concentration and electrostatic potential. Numerous microscopic observations have proven that the thermodynamic treatment of these starkly inhomogeneous systems cannot simply ignore the inhomogeneity. However the resulting phase-field models -- of either the Cahn-Hilliard (conservation preserving) or Allen-Cahn (non-conserved) variety -- require specialized knowledge and computationally demanding software. This renders them ill-suited for use by the majority of researchers in chemistry and materials science in the interpretation of experiments. This talk will discuss the steps taken at West Virginia University in applying advanced techniques in nonparametric regression to this problem, with the goal of releasing computationally light software tools that encapsulate the phase-field formulations and can be deployed in models of macroscale devices and experiments. In addition we will discuss using these same data science approaches in the interpretation of microscopic data, through which direct measurements of inhomogeneous thermodynamic excess free energy functions can be made.

9:40 AM DT28.02

A Molecular-Dynamics Study of Oxygen Diffusion in Polycrystalline $(\text{La,Sr})\text{FeO}_3$ Alexander Bonkowski¹, John A. Kilner² and Roger A. De Souza¹; ¹Rheinisch-Westfälische Technische Hochschule Aachen, Germany; ²Imperial College London, United Kingdom

$(\text{La,Sr})\text{FeO}_3$ is a well-known mixed ionic and electronic conducting perovskite oxide [1-5], with application in Solid Oxide Fuel Cells (SOFCs) and Solid Oxide Electrolysis Cells (SOECs).

In this study we employed molecular-dynamics (MD) simulations based on empirical force fields [6,7] to investigate oxygen transport in the solid solution $\text{La}_{1-x}\text{Sr}_x\text{FeO}_{3-x/2}$ ($x = 0, 0.1, 0.25$ and 0.4). Simulations were performed at temperatures $1000 \leq T / \text{K} \leq 3000$. Oxygen tracer diffusion coefficients obtained for both orthorhombic and cubic structures are compared with experimental data [1-5], and are found to give a satisfactory description of the oxygen transport behaviour as a function of T and x . Subsequently, we examined oxygen tracer diffusion in polycrystalline cells of $\text{La}_{1-x}\text{Sr}_x\text{FeO}_{3-x/2}$ with differing numbers of grain boundaries. In all cases, we find that oxygen tracer diffusion in the polycrystalline systems is lower than in the single-crystal systems. Our results thus indicate that in perovskite-oxide ceramics with homogeneous cation distributions there is no faster diffusion of oxygen along grain boundaries. A detailed analysis of diffusion data for polycrystalline simulation cells is demonstrated with a new in-house analysis tool [8].

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9:55 AM *DT28.03

Photo-Enhanced Ionic Conductivity Across Grain Boundaries in Polycrystalline Solid Oxide Electrolytes at Reduced Temperatures Thomas Defferrere¹, Dino Klotz², Jennifer Rupp^{3,1} and Harry Tuller¹; ¹Massachusetts Institute of Technology, United States; ²Kyushu Daigaku, Japan; ³Technische Universität München, Germany

We recently demonstrated the ability to use photogenerated charge carriers to modulate the grain boundary resistance of a model polycrystalline oxygen solid electrolyte thin film (Gd doped CeO_2)^{*}. These findings were inspired by the recognition that above bandgap light is well known to reduce band bending at interfaces by providing additional charge carriers to screen potential barriers. Such findings could pave the way for novel and dynamic means of modulating ionic transport in solid electrolytes and as such requires further investigations to better understand the limitations of this approach. While our initial observations were limited to temperatures above 250 °C, where only a maximum factor of 3 enhancement in conductance was observed, we anticipate that much larger conductivity enhancements could be realized at lower temperatures due to the large observed activation energy change of the

grain boundaries resistance between light and dark.

To demonstrate the feasibility of modulating grain boundary ionic conductivity in our model oxygen solid electrolyte, Gd doped CeO₂, over a broad temperature range, we extended our studies both for our polycrystalline and epitaxial samples down to room temperature. Deviations from the intermediate temperature behavior are observed with much shallower activation energies below 150 °C indicating that photogenerated charge carriers are participating in current conduction at these lower temperatures. However, the transition between the intermediate temperature ionic conduction and this lower temperature electronic conduction appears over a broad temperature range indicating that a superposition of the grain boundary ionic optical effect and electronic contributions, with the latter dominant at lower temperatures (150 °C). To better understand how photogenerated charges carriers interact in the oxide lattice and participate in the conduction mechanism, we systematically varied materials parameters such as thickness, grain size and doping. We designed and studied a polarization cell to isolate the ionic from the electronic contributions and were able to demonstrate extended enhancements in the ionic conductivity by optical illumination down to 150 °C. These insights are invaluable as they allow us to understand the limitations of our technique and provide with us a path towards engineering our materials to reduce the contributions of electronic photoconductivity.

The findings in this work pave the way for a novel and dynamic means of modulating ionic transport in solid electrolytes. While only demonstrated here for the case of a model oxygen solid electrolyte, we believe this strategy can be more widely applied to other ion conductors such as proton or Li ion conductors, all of which have relevant electrochemical energy applications that would benefit from reduced grain boundary resistance. This is essential for guiding the efforts towards more efficient and better performing electrolytes for fuel cells, electrolyzers, batteries and other (photo-) electrochemical energy conversion systems. Likewise, it can provide new design guidelines for mitigating ion migration in devices operated under optical illumination such as perovskite solar cells and photodetectors.

* Please see also presentation by D. Klotz, et. al. *Photo-Enhanced Ionic Grain Boundary Conductivity in Solid Electrolytes in this symposium*

10:15 AM DT28.04

Oxygen In/Excorporation Kinetics by Electrical Conductivity Relaxation—Application in Dual-Phase Ce_{0.9}Gd_{0.1}O_{2-δ}:La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-δ} Composites and Single-Phase La_{0.8}Sr_{0.2}FeO_{3-δ} Thuy Linh Pham¹, Ji Haeng Yu², Hohann Bae¹, Sun-Ju Song¹ and Jong-Sook Lee¹; ¹Chonnam National University, Korea (the Republic of); ²Korea Institute of Energy Research, Korea (the Republic of)

To determine the chemical diffusion coefficient D and surface exchange reaction coefficient K of mixed ionic-electronic conductors (MIECs), the electrical conductivity relaxation (ECR) technique is often used. It measures the time variation of the electrical conductivity of a sample after a small stepwise change in the ambient oxygen partial pressure. Oxygen transport kinetic parameters are estimated from fitting the relaxation curves to the solution of diffusion equations depending on the different geometries of samples. Numerous studies using this method have been conducted on single-phase perovskite La_{0.6}Sr_{0.4}Co_{1-y}Fe_yO_{3-δ} (LSCF). In contrast, few investigations have been performed so far on dual-phase composites comprising an oxygen ionic conductor and a mixed conductor like Ce_{0.9}Gd_{0.1}O_{2-δ} (GDC): La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-δ} (LSCF). In this work, the GDC: LSCF composites as a function of GDC phase volume fraction, which is above the percolation threshold, were prepared [1]. 4-probe DC conductivity (van der Pauw method) was applied at different temperatures (800, 770, and 750 °C), and the change in the conductivity upon oxygen potential change between air and nitrogen atmosphere was monitored. Disk-shaped samples were measured, which allows the diffusion problem as 1-dimensional. It is shown that the oxygen equilibration kinetics in the range of oxygen partial pressure (pO₂) from 0.002 to 0.21 atm is limited by the surface exchange rate where normalized conductivity transient after a pO₂ step change is given by a simple exponential decay function. Python was employed to deal with the fitting of a large number of data and their calculations. Large initial time t_0 values were obtained in ECR of GDC: LSCF composites, suggesting the surface reactions enhanced at the triple-phase boundaries. The oxygen transport kinetics of La_{0.8}Sr_{0.2}FeO_{3-δ} (LSF82), had been reported in the previous publication, which was conducted using a conventional bar-shaped sample [2]. Absolute minima or physically more probable local minima in solution space (D , K , t_0 , conductivity at the equilibrium state σ_{eq}) can be more easily explored using self-coded Python for the manual iterative root-finding process [3]. In the published result with t_0 values closely representing the experimental parameters, slower relaxation in the reduction process was attributed to D parameters, while K parameters are similar in oxidation and reduction. Reevaluation in this study shows that the characteristic of substantially large t_0 leads to physically correct behavior of oxygen kinetics with the difference between oxidation and reduction explained by the difference in K parameters while D parameters remain almost unchanged. The large t_0 , different from the experiments is considered to indicate surface reaction kinetics, which is not probably described by the present theory.

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SESSION DT29: Transport Mechanisms

Session Chair: Thomas Defferriere

Friday Morning, July 22, 2022

Mezzanine Level, Second Floor, Georgian

11:00 AM DT29.01

Hydride Ion Conductivity in Materials with K₂NiF₄-Type Structure Henrik Rodenburg and Peter Ngene; Universiteit Utrecht Faculteit Betawetenschappen, Netherlands

Hydride ion conducting materials are interesting for their ability to potentially supply highly reactive hydride ions to participate in electrochemical reactions in future electrochemical devices, such as hydride-based batteries or solid-state hydrogen sources for electrochemical conversion of various molecules, such as hydrogenation of N₂ to ammonia. Unfortunately, current hydride ion conductors typically only show high conductivity (10⁻⁶-10⁻⁵ S cm⁻¹) around 300 °C, especially those with the K₂NiF₄-type structure, such as La_{2-x-y}Sr_{x+y}LiH_{1-x+y}O_{3-y} [1], Ln₂LiHO₃ (Ln = La, Nd, Pr) [2] and Ba₂SrCoHO₃ [3]. Other materials, such as (modified) BaH₂ [4,5] and oxygen-doped LaH₃ [6] can achieve measurable conductivities below 200 °C.

In this presentation, we will discuss the hydride ion conductivity of new complex hydrides with the K₂NiF₄-type structure. Electrochemical measurements reveal some of the highest hydride ion conductivity reported in complex hydrides with the K₂NiF₄-type structure, reaching 10⁻⁶ S cm⁻¹ at only 100 °C, and appear to show previously unreported phase behaviour in some of these materials. The phase behaviour is further investigated and the nature of the conductivity in the complex hydrides is studied in detail. We will show that the conductivity in some of the materials is best explained by hydride transport, while other materials seem to exhibit substantial electronic conductivity in combination with hydride ion conductivity. By combining experimental and theoretical results, we will discuss the ion transport mechanism and possible approaches to further increase the hydride ion conductivity of the compounds at moderate temperatures.

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11:15 AM DT29.02

Al States in Al₂O₃-Doped Sc₂O₃ Stabilized ZrO₂ Studied by Al-27 NMR [Itaru Oikawa](#)¹, Akihiro Fujimaki¹, Fuminori Tamazaki², Hiroshi Okamoto² and Hitoshi Takamura¹; ¹Tohoku Daigaku, Japan; ²Daiichi Kigenso Kagaku Kogyo Co Ltd, Japan

Sc₂O₃-stabilized ZrO₂ (ScSZ) is a candidate electrolyte of solid oxide fuel cells due to its three-times higher ionic conductivity than YSZ. Conductivity degradation at long term operation is one of the drawbacks of this material for practical applications. This degradation is correlated with the phase transition from the cubic phase to the tetragonal phase and oxygen vacancy ordering accompanied by the phase transition to the rhombohedral phase. Doping of the third element such as Y and Al can suppress this degradation. Y-doping can stabilize the cubic phase of ScSZ by substituting the Zr sites. Meanwhile, for the Al-doping, several mechanisms for the stabilization of the cubic phase have been proposed. One is the introduction of the strain in the lattice and the other is the segregation of Al in the grain boundary. So far, the role of Al to the suppression of the conductivity degradation is unclear. Understanding the role of Al is important to control the degradation behavior of ScSZ and design the material for practical use. In this study, the Al states in Al₂O₃-doped 10 mol% Sc₂O₃ stabilized ZrO₂ (Al: 10ScSZ) and 10ScSZ co-doped with 1 mol% Y₂O₃ (Al: 10Sc1YSZ) are investigated by Al-27 NMR spectroscopy combined with DFT calculations to clarify the role of Al in these materials.

In the Al-27 magic-angle spinning NMR spectrum of Al: 10ScSZ, two peaks at 15 and -9 ppm are observed. The peak at 15 ppm is assigned to α -Al₂O₃ from its chemical shift and the other peak is assigned to Al dissolved in the 10ScSZ. From the peak area of each peak, more than 80% of Al is α -Al₂O₃ in Al: 10ScSZ which indicates limited solubility of Al in the lattice. Meanwhile, in addition to these peaks, one more peak at 38 ppm is observed in the NMR spectrum of Al: 10Sc1YSZ and assigned to the dissolved Al in the different chemical environment from the peak at -9 ppm. Roughly estimated the amounts of Al corresponding to each Al peak, the two dissolved Al sites are the dominant Al states in Al: 10Sc1YSZ.

To clarify the detail Al states in the materials, DFT calculations are carried out. The calculated Al-27 chemical shifts indicate that the peaks at -9 and 38 ppm are derived from 6-coordinated Al and 7- or 8-coordinated Al, respectively. Interestingly, the chemical shift of 38 ppm is unusual for 7- or 8-coordinated Al; however, these Al are effectively 4-coordinated with the other three or four oxygen atoms residing too far from the Al atom to contribute to the effective coordination number of the Al. This effective 4-coordinated Al can be observed at 38 ppm which is typical for 4-coordinated Al even though the Al is surrounded by seven or eight O atoms. The effective 4-coordinated Al as well as the 6-coordinated Al in usually 8-coordinated Zr sites of ScSZ may be caused by the large ionic size mismatch between Al and Zr. This study suggests that these unique Al states contribute to stabilize the cubic phase in the 10ScSZ-based materials.

11:30 AM DT29.04

Crystal Structure and Ionic Conductivity of Novel Rare Earth Niobate LnNbO₄ (Ln = Nd, Sm, Eu, Gd) by Substituting Nb with W [Yue Jin Shan](#), Ryo Kawaguchi, Ryoji Akizawa and Keitaro Tezuka; Utsunomiya University, Japan

Rare-earth niobates LnNbO₄ (Ln = rare-earth) have a monoclinic fergusonite-type structure (space group *I12/a* (No.15)) at room temperature, and are known to undergo structural phase transition to a tetragonal scheelite-type structure (space group *I41/a* (No.88)) at about 500-850 °C. Substitution of Nb with a small amount of W in LnNbO₄ (Ln = La, Pr, Nd) has been reported, in which there is no structural change at room temperature and the oxide ion conduction is remarkable at high temperatures. The main purpose of our research is to synthesize unreported the solid solution system LnNb_{1-x}W_xO_{4+δ} (Ln = Nd, Sm, Eu, Gd; 0.0 ≤ x ≤ 1.0), and to investigate their changes in crystal structure and effects on oxide ion conductivity due to differences in the amount of W substitution and rare earth elements.

The synthesis of LnNb_{1-x}W_xO_{4+δ} (Ln = Nd, Sm, Eu, Gd; 0.0 ≤ x ≤ 1.0) was carried out by the solid-phase reaction method with changing the amount of W substitution and the rare earth elements. Making a survey on the relationship between the W substitution amount and the crystal phase of the obtained sample, it can be found that is formed only in a certain amount range of substitution, and the lower limit of W substitution at which the high temperature scheelite-type phase appears at room temperature is about 0.3 regardless of rare-earth elements. In addition, the phase transition temperature decreases with increasing the amount of W substitution, and the substitution (solid solution) range tends to increase with decreasing ionic radius of the rare-earth elements. Impedance measurements were carried out on single scheelite-type phase or multi-phase (scheelite-type and fergusonite-type phases) samples without impurities. The ionic conductivity of all the samples increases significantly with increasing W substitution, and NdNb_{0.8}W_{0.2}O_{4+δ} shows the highest conductivity among these samples. It was also demonstrated that the difference in activation energy between high-temperatures and low-temperatures was insignificant in the W-substituted samples.

11:45 AM DT29.05

Exploring Charged Defects and Dopability Limits of Solid Electrolytes, a Computational Study [Yasmine Benabed](#)^{1,2}, Diana Dahliah², Mickaël Dollé¹ and Geoffroy Hautier^{3,2}; ¹Université de Montreal, Canada; ²Université catholique de Louvain, Belgium; ³Thayer School of Engineering at Dartmouth, United States

All-Solid-State Lithium Batteries (ASSLBs) are a new generation of lithium batteries that is developed to meet high expectations in terms of safety, stability and high energy density. The liquid electrolyte of conventional Li-ion batteries is replaced in ASSLBs by a safer and more stable solid electrolyte (SE). These solid electrolytes must meet a number of requirements before they can be considered in ASSLBs, including a wide electrochemical stability window, a high ionic conductivity and a negligible electronic conductivity [1]. For a long time, researchers have focused on achieving the highest ionic conductivity possible on these materials, comparable to the one of liquid electrolytes. The ionic conductivity in SEs has been successfully increased by the introduction of defects (doping) and Li_{1.3}Al_{0.3}Ti_{1.7}(PO₄)₃ and Li_{1.5}Al_{0.5}Ge_{1.5}(PO₄)₃ solid electrolytes are both excellent examples of such achievement. However, the formation of defects can also have a significant effect on the SEs electronic conductivity [2],[3],[4]. Increasing the electronic conductivity in solid electrolytes is detrimental to the ASSLBs safety and integrity. Therefore, it is essential to understand the defect chemistry in SEs. Due to their negligible concentration, characterizing point defects is hardly possible using standard characterization techniques, justifying the need for first-principles calculations. In this work, we have investigated the defect chemistry of most common solid electrolytes Li_xM₂(PO₄)₃ (M = Zr, Ti, Ge, Al), Li₇La₃Zr₂O₁₂, LiLaTi₂O₆, Li₁₀Ge(PS₆)₂, Li₇P₃S₁₁, Li₃PS₄, Li₃PO₄ and LiPO₃. For each SE, we computed the formation energies for intrinsic defects and assessed the dopability limits as a function of the synthesis conditions. We found that the position of the Fermi level and dopability limits depend strongly on lithium and oxygen/sulfur chemical potentials but also on the nature of the solid electrolyte. We advocate that it is imperative to better regulate the synthesis

conditions if we want to gain control over the formation of defects in solid electrolytes. The outcoming properties of these materials, such as the ionic and electronic conductivities, depend on it.

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Energy and Fuels Conversion

Energy and Fuels Conversion

July 18 - July 22, 2022

Symposium Organizers

Sean Bishop, Sandia National Laboratories

Georgios Dimitrakopoulos, Massachusetts Institute of Technology

* Invited Paper

SESSION EF01: Oxygen-Ion Conducting Fuel Cells I
 Session Chairs: Georgios Dimitrakopoulos and John Irvine
 Monday Morning, July 18, 2022
 Lobby Level, Avenue 34, Studio 1

9:10 AM **EF01.01

Towards the Next Generation of Solid Oxide Cells Natalia Kostretsova¹, Radostin S. Pavlov¹, Lucile Bernadet¹, Maritta Lira dos Santos¹, Marc Nuñez¹, Federico Baiutti¹, Alex Morata¹, Marc Torrell¹ and Albert Tarancón^{2,1}; ¹Institut de Recerca en Energia de Catalunya, Spain; ²Institució Catalana de Recerca i Estudis Avancats, Spain

Hydrogen technologies are crucial for the foreseen transition towards a more sustainable society based on renewable energy. The most efficient of those technologies is based on high temperature operation devices such as Solid Oxide Cells. Solid Oxide Fuel and Electrolysis Cells have been developed during many decades and, nowadays, reached a level of maturity for a mass market entry.

Conventional manufacturing technologies such as tape casting or screen printing enabled the existing generation of high temperature solid oxide cells. This successful story ended up in a feasible technology currently reaching the MW scale and thousands of hour of continuous operation. Complementary, novel fabrication approaches are recently presented pushing the limits of some classical constraints such as simple shape or slow startup opening new application scenarios.

In this talk, we will present recent advances in 3D printing of solid oxide cells that increase the performance of SOCs made of state of the art materials as well as the interest of incorporating thin film layers for improving the performance and durability of currently existing designs.

9:40 AM *EF01.02

Interaction of SOFC Fuel Electrodes with Different Fuels and Therein Contained Impurities Andre Weber; Karlsruhe Institute of Technology (KIT), Germany

Solid Oxide Fuel Cells are renowned for their unique fuel flexibility. Even state of the art anode supported cells, exhibiting an anode functional layer and a substrate based on Ni/8YSZ-cermet, can convert a wide variety of fuels as reformed hydrocarbons, carbon monoxide, ammonia, ethanol and AdBlue™ besides hydrogen [1]. In this contribution performance of SOFCs operated with different fuels respectively reformates thereof will be discussed. A particular focus will be on stability issues and the observed interactions of fuel electrode and substrate with these fuels and hardly avoidable contaminants as sulfur species [2],[3] and higher hydrocarbon residues acting as soot precursors [4]. Examples of these interactions will be illustrated by means of cell performance degradation, changes in the impedance spectrum and distribution of relaxation times [5] as well as microstructural changes and macroscale defects observed in post-test analyses. Possible countermeasures by the expensive adjustment of the operating conditions on the system level or modifications of the fuel electrode itself will be discussed.

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10:00 AM *EF01.03

Materials Development for High-Performance Solid Oxide Cells [Christian Lenser](#)¹, Alexander Schwiers^{1,2}, Jun Zhang³, Norbert H. Menzler^{1,2} and Olivier Guillon^{1,2,4}; ¹Forschungszentrum Jülich GmbH, Germany; ²Rheinisch-Westfälische Technische Hochschule Aachen, Germany; ³Danmarks Tekniske Universitet, Denmark; ⁴JARA, Germany

Solid Oxide Cells (SOC) are electrochemical energy conversion devices that can convert chemical energy carriers into electricity (fuel cell mode, SOFC) or vice versa (electrolysis mode, SOEC). The operating parameters (temperature, current density, fuel gas composition) depend on the cell architecture, the choice of materials and the intended application. Forschungszentrum Jülich has been developing fuel-electrode supported cells (FE-SOC) for over 25 years. Among the achievements are the development of the Crofer 22 APU stainless steel for interconnects, the operation of an SOFC stack for over 10 years with an average voltage degradation rate of ~0.5% / 1000 hours, and the development of a reversible SOC system with a round-trip efficiency of 44 %. In this work, an analysis of the impedance contributions of a 3-layer SOFC stack will be presented. These results identify the Ni-YSZ fuel electrode and the stack contacting as the most significant sources of cell impedance. Based on these insights, different approaches to alleviate these problems will be presented. Special attention will be paid to the substitution of YSZ by doped ceria, the resulting consequences for cell manufacturing and architecture, and the electro-chemo-mechanical stresses induced during cell operation.

10:20 AM *EF01.04

Designing Multi-Elemental Oxide Catalysts with High-Throughput Simulations and Machine Learning Jessica Karaguesian, James Damewood, Jaclyn Lunger, Daniel Schwalbe-Koda, Yang Shao-Horn and [Rafael Gomez-Bombarelli](#); Massachusetts Institute of Technology, United States

New materials are needed in order to achieve a low-carbon sustainable economy. Electrocatalysts, for instance, are an exciting technology for generating sustainable fuels, such as hydrogen production from water electrolysis. In particular, finding catalysts for the oxygen evolution reaction (OER) is both urgent and challenging. Metallic catalysts typically rely on rare and expensive noble metals, while oxide catalysts are challenged by lower activity and poor stability. It has been hypothesized that complex, multi-element oxides may afford a sweet spot in activity and stability, by generating atomic environments that are both kinetically and thermodynamically stable, and also highly active. Promising oxide electrocatalysts such as $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ perovskite have very complex compositions (quinary if the role of oxygen vacancies is considered). Exploring such high-order compositional landscapes, through experiments, or even through simulations is daunting.

Here, we have developed and deployed a suite of computational tools, involving both simulation and data science, to design of optimized, thermodynamically stable, complex oxide materials.

Using perovskites as a materials platform, our approach utilizes high-throughput (HT) DFT simulations of bulk materials to generate stability metrics (energy above the convex hull), and performance descriptors (oxygen 2p band center, which is correlated to OER activity). We have calculated tens of thousands of candidate materials in senary and higher design spaces. The HT-DFT platform also handles the generation and simulation of surfaces, as well as the simulation of adsorbates. This allows promoting those materials that show promising bulk descriptors to a more explicit calculation of binding energy of intermediate species in the OER mechanism, and thus to estimating the reaction overpotential.

Because DFT simulations are relatively accurate, but not scalable to the design space of 1^{20} or more senary combinations, we trained surrogate machine learning (ML) models, based on graph-convolutional networks, to bypass these expensive simulations. The ML predictors showcase multiple innovations to address the combinatorial nature of the design space, the need to execute predictions from idealized structures, so lattice relaxations can be avoided, and to predict per site properties. In the space of complex perovskites, we achieve fidelity with respect to DFT of 20 meV/atom in energy above the convex hull and 100 meV in the O₂p band center.

These predictive models can then be combined with fast materials optimization strategies to navigate the discrete decision space of elemental substitution that maximizes stability and activity. In particular, we utilize discrete optimization strategies combining exploration and exploitation to identify promising elemental combinations and lattice configurations with desired O₂p values around -1.70 eV and within 50 meV of the convex hull energy. We observe orders of magnitude in acceleration compared with random exploration in design spaces that are too large to fully enumerate.

This self-driving computational platform can identify promising materials, and also regions of the combinatorial space where the ML models are uncertain, and thus automatically acquire new training data to refine such models. By exploring the large combinatorial design space of senary perovskites, including oxygen vacancies, we single out promising new materials. Experimental synthesis, characterization, and catalytic testing confirm the performance of these materials for the oxygen evolution reaction.

10:40 AM BREAK

11:00 AM *EF01.05

SOFCs—Recent Trends and Selected Materials Challenges [Peter V. Hendriksen](#), Xiufu Sun, Francesco Mondì, Ming Chen, Anke Hagen and Henrik Lund Frandsen; Danmarks Tekniske Universitet, Denmark

Solid oxide fuel cells are these years being deployed in different commercial and semi-commercial applications; for domestic heat and power supply, in UPS systems as well as in APU'S for transport applications. The detailed requirements vary between these applications, but for extending the use of SOFCs further, it is highly desirable to reduce cost and improve reliability. The overall cost of acquiring and operating an SOFC can be reduced if power density can be increased, cheaper materials can be applied and the overall lifetime can be extended. On improving reliability – one key challenge inherent to the technology is the brittle character of the ceramic materials applied. In the presentation, selected efforts to improve overall component reliability as well as efforts to improve performance shall be presented.

Reliability: Recent efforts at DTU Energy to improve the toughness of the applied zirconia [1] shall be presented as shall efforts in improving the mechanical reliability at interfaces in the stack [2,3]; at current carrying interfaces as well as in sealing areas.

Performance and lifetime: Reducing the area specific polarization resistances of the electrodes can directly benefit cost competitiveness via increased power density at operation, but also in enabling a reduced temperature of operation, that will in turn allow use of cheaper steels for the interconnects. How cell performance can be boosted via post firing infiltration at both electrodes [4] shall be discussed as shall be the use of a similar process to boost interconnect lifetime [5]

A recent trend in SOFC R&D is the use of ammonia as a fuel. Ammonia is being considered a promising green fuel that can help the global maritime sector

in reaching zero emission. It can also be seen more broadly as an energy vector – a compound that facilitates transport of hydrogen. It is an excellent fuel for an SOFC [6,7], but imposes certain challenges in use, which shall be discussed.

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11:20 AM EF01.06

Optimisation and Performance Evaluation of Rh/Ceria Co-Impregnated Catalyst Systems for La_{0.20}Sr_{0.25}Ca_{0.45}TiO₃ Solid Oxide Fuel Cell Anodes Robert Price¹, Ueli Weissen², Holger Bausinger², Jan G. Grolig², Andreas Mai² and John T. Irvine¹; ¹University of St Andrews, United Kingdom; ²HEXIS AG, Switzerland

Solid Oxide Fuel Cells (SOFC) are ceramic devices which operate at high temperatures (600 °C to 900 °C) to simultaneously generate electricity and heat via electrochemical oxidation of a fuel gas. Therefore, SOFC lend themselves to application in combined heat and power (CHP) systems that may be used to satisfy the heat and electricity demand of residential properties, for example. Typically, state-of-the-art SOFC employ an anode comprising a ceramic-metal composite (cermet) of nickel and yttria-stabilised-zirconia (YSZ) or cerium gadolinium oxide (CGO) as these materials offer high performance for the electrocatalytic oxidation of fuel gases at a relatively low cost.

However, these materials also present some challenges that must be overcome in order to improve durability and performance in next generation SOFC. These include poor tolerance to coking and sulphur poisoning in unprocessed natural gas feeds, severe degradation at high fuel utilisations and redox instability. Recent research into Rh/CGO co-impregnated La_{0.20}Sr_{0.25}Ca_{0.45}TiO₃ (LSCT_A) SOFC anodes, as replacements for the Ni-based cermet, has led to demonstration of high performance and excellent durability (3.3 mV kh⁻¹ degradation) under the aforementioned harsh operating conditions at short stack scales.¹

In this research, we present results concerning the electrochemical performance of several SOFC containing Rh/ceria co-impregnated LSCT_A anode 'backbones', including Rh/CeO₂, Rh/Ce_{0.90}Zr_{0.10}O₂, Rh/Ce_{0.90}Gd_{0.10}O_{1.95} and Rh/Ce_{0.80}Gd_{0.20}O_{1.90}, in order to identify the most electrochemically active catalyst combination. SOFC testing performed at 850 °C in non-humidified H₂ indicated that the 'backbone' impregnated with 2 wt. % Rh (with respect to the LSCT_A anode mass) and 13 wt. % Ce_{0.80}Gd_{0.20}O_{1.90} (CG20) gave rise to the lowest area specific resistance (ASR) of 0.45 Ω cm². Furthermore, AC impedance spectroscopic studies of SOFC containing LSCT_A anodes impregnated with individual components, including 2 wt. % Rh (ASR = 0.86 Ω cm²), 27 wt. % CG20 (ASR = 1.24 Ω cm²) or unimpregnated LSCT_A anode scaffolds (ASR = 2.23 Ω cm²), highlighted that significantly enhanced performance was obtained by co-impregnation of Rh and CG20, in comparison to singly impregnated anodes, and identified the existence of a mutualistic interaction between these two catalyst components.

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11:35 AM EF01.07

Novel Strategy to Reactivate Poisoned Oxygen Exchange Kinetics in Mixed Conducting Oxides by Controlled Surface Acidity Han Gil Seo¹, Anna Staerz¹, Dennis S. Kim¹, Dino Klotz^{2,1}, Clement Nicolle³, James LeBeau¹ and Harry Tuller¹; ¹Massachusetts Institute of Technology, United States; ²Kyushu Daigaku, Japan; ³Institut des Matériaux Jean Rouxel, France

The performance and viability of applications ranging from energy conversion and storage devices (solid oxide fuel/electrolyser cells (SOFCs/SOECs), permeation membranes, batteries), and sensors are presently limited by performance degradation due to impurity poisoning, for example in SOFCs, due to chromia and silica impurities coming from metal interconnects and furnace refractories respectively. We recently showed that the oxygen surface exchange kinetic (k_{chem}) values of the mixed conducting oxide, Pr_{0.1}Ce_{0.9}O_{2-δ} (PCO), can be systematically varied by over 6 orders of magnitude by infiltrating the surface with binary oxides ranging from strongly acidic to strongly basic [1]. Basic lithia increased k_{chem} by nearly 1,000 times over that of pristine PCO, while acidic silica depressed k_{chem} by nearly the same factor with variations in k_{chem} attributed to the induced relative accumulation or depletion of surface electrons. With this insight, we hypothesized that surface acidity could be used not only to predict the effect of a single additive on oxygen exchange, but also to compensate for poisoning by an acidic additive.

Here, we demonstrate that the degradation in the oxygen exchange kinetics of PCO induced by infiltration of acidic binary additives such as chromia and silica, can be fully recovered by subsequent infiltration of basic additives such as lithia and calcia. Electrical conductivity relaxation measurements on porous PCO specimens were used to examine the impact of serial infiltration of basic additives on the degraded exchange rate of oxygen. In parallel, the electrochemical performance of screen-printed PCO symmetric cells (cathode|electrolyte|cathode) with serial infiltration of basic additives were evaluated by electrochemical impedance spectroscopy in terms of area-specific resistance with similar trends observed. Surface microstructures of the respective infiltrated specimens were examined by scanning transmission electron microscopy with electron energy loss spectroscopy to characterize the chemical nature and distribution of the additives.

11:50 AM EF01.08

Reactivation of Exsolved Ni- and Ru-Doped Strontium Iron Titanate Solid Oxide Fuel Electrodes Travis A. Schmauss¹, Alessandro Donazzi², Yubo Zhang¹, Jakob Reinke¹ and Scott Barnett¹; ¹Northwestern University, United States; ²Politecnico di Milano, Italy

Cation exsolution has emerged as a useful technique for the generation of stable, high areal density metal nanoparticles on the surface of mixed ionic-electronic conducting (MIEC) perovskites for solid oxide fuel electrodes. Redox cycling, normally observed to degrade the microstructure and performance of conventional cermet (e.g., Ni-YSZ) fuel electrodes, does not necessarily degrade performance in the case of MIEC oxide and oxide-exsolution electrodes and has been reported in some cases to recover degraded performance. Exsolved electrodes sometimes show reversible exsolution/re-solution of the metal phase from the perovskite oxide phase, with re-reduction able to regenerate active area. Here we present results on life testing of Ni-doped Sr(Ti,Fe)O_{3-δ} electrodes that show degradation and subsequent electrochemical performance recovery after redox cycling, with in-situ X-ray diffraction data and post-test scanning transmission electron microscopy for mechanistic determination. Reduction results in the formation of a Ruddlesden-Popper phase in conjunction with coarsening and composition changes in the exsolved Fe-Ni nanoparticles, both contributing to the observed degradation. Reoxidation then returns the parent oxide back to the perovskite structure alongside a partial re-incorporation of the Fe-Ni binary alloy into the oxide, resulting in the observed performance recovery. Redox cycling also has a potential application for removing deposited carbon from anodes after catalyst deactivation via coking from carbon-containing fuels. In a separate set of experiments, cells with Ru-doped Sr(Ti,Fe)O_{3-δ} and conventional Ni-YSZ composite anodes were operated with ethanol fuel. The Ni-YSZ anodes were unrecoverably degraded, whereas the oxide anodes continued to operate well in ethanol, including after redox cycling.

12:05 PM EF01.10

Significantly Reduced Area Specific Resistance of Pr₄Ni₃O_{10+δ} – Ce_{0.75}Gd_{0.1}Pr_{0.15}O₂ Composite Cathode by Optimizing Microstructure for IT-SOFCs Zheng Xie and Stephen J. Skinner; Imperial College London, United Kingdom

Ruddlesden-Popper (RP) phases, Ln_{n+1}Ni_nO_{3n+1} (Ln=La, Nd or Pr, n= 1, 2 or 3)), are promising candidates for cathode materials for intermediate temperature (600 °C-800 °C) solid oxide fuel cells (IT-SOFCs) because their mixed electronic and ionic conducting (MIEC) properties enlarge the electrochemically active region from the triple phase boundary (TPB) to the double phase boundary (DPB). Among these materials, Pr₄Ni₃O_{10+δ} (PNO) is selected to be the cathode material because of its higher electrical conductivity and chemical stability at intermediate temperatures. A composite electrode is prepared by mixing PNO and an ionic conducting phase, Ce_{0.75}Gd_{0.1}Pr_{0.15}O₂ (CGPO), which enhances the ionic conductivity and length of the TPB. The performance of composite cathodes was characterized by electrochemical impedance spectroscopy (EIS). The size of synthesized PNO particles was 1000 times greater than that of the synthesized CGPO particles, which was considered to hinder the formation of a well-connected network and hence the performance of the cell. This was confirmed by the impedance spectroscopy (IS) of cells composed of PNO with reduced particle sizes. In this case, the area specific resistance (ASR) was reduced to 0.04 Ωcm² from 0.12 Ωcm² at 680 °C.

To investigate how the microstructure affects the cell performance, focused ion beam-scanning electron microscopy (FIB-SEM) was applied to characterize the microstructure and quantitative image analysis and 3D reconstruction of representative volume elements were achieved by using Avizo and MATLAB plug-in TauFactor [1]. The results show that the TPB and DPB were significantly increased after reducing the PNO particle size. Also, the tortuosity of PNO was reduced, which means the percolation of the PNO network is better. IS under air, pure oxygen and argon have been carried out and confirmed that one of the electrochemical processes is related to oxygen reduction reactions. A series of IS measurements will be carried out under different oxygen partial pressures to assign electrode processes as the dependence of polarization resistance on the oxygen partial pressure gives information on the species involved in the reactions. Once this is confirmed, comparison of impedance between electrodes with different microstructures will be carried out to investigate how microstructure affects electrochemical processes of these new composite cathodes.

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SESSION EF02: Solar Cells I
Session Chairs: David Cahen and Yang Yang
Monday Morning, July 18, 2022
Lobby Level, Avenue 34, Studio 2

9:10 AM **EF02.01

Addressing the Stability and Reliability Challenges in Perovskite Solar Cells via Microstructural and Interfacial Tailoring Nitin P. Padture; Brown University, United States

Most commercial devices, including photovoltaics (PVs), have gone through a familiar research and development trajectory — increasing performance, upscaling, improving stability, and enhancing mechanical reliability — before making it to the marketplace successfully. In this context, perovskite solar cells (PSCs) are likely to be no exception, but little attention has been paid to the latter issue of mechanical reliability. In fact, enhancing the mechanical reliability of PSCs is particularly important and challenging because the low formation energies of MHPs that makes them easy to solution-process renders them inherently poor in mechanical properties: they are compliant (low Young's modulus), soft (low hardness), and brittle (low toughness). To address this perhaps final hurdle in the path towards PSCs commercialization, several rationally designed microstructural- and interfacial-tailoring approaches are used. These include grain-coarsening, grain-boundary functionalization, and interfacial engineering, all of which involve solid-state ionics. Most importantly, these approaches are designed such that they not only enhance the PSCs mechanical reliability but also increase performance and improve stability. The scientific rationales for these approaches are discussed, together with the presentation of the current results.

9:40 AM **EF02.02

Manufacturing Perovskite Solar Cells with Passivated Interfaces—Approaching Efficiency Limits with Scalable Chemistry David Ginger; University of Washington, United States

Halide perovskite semiconductors offer the opportunity to rapidly mass-produce high-efficiency photovoltaic cells in both single-junction and tandem (e.g. perovskite/silicon and perovskite/perovskite) formats. Controlling interface chemistry in these cells, both within the perovskite layers, and between the perovskite semiconductor and the other layers of the device, is essential to obtain high efficiency and long lifetimes. I think talk I will review the importance of interfacial recombination in current perovskite semiconductor devices, and discuss recent results of scalable chemical processes for controlling surface recombination velocities down to < 10 cm/s, including high quality interfaces even in contact with electron and hole extraction layers. Using hyperspectral

photoluminescence and nano-infrared microscopy, I will also discuss the impact of various processing methods on the compositional heterogeneity that is ubiquitous in many perovskite formulations and identify opportunities for further improvements.

10:10 AM *EF02.03

Tin-Lead-Metal Halide Perovskite Solar Cells with Enhanced Crystallinity and Efficiency Maria Antonietta Loi; Rijksuniversiteit Groningen, Netherlands

Highly performing mixed Sn/Pb-perovskite solar cells (PSCs) are among the most promising options to reduce Pb content in perovskite devices and enable the fabrication of all-perovskite tandem solar cells owing to their reduced band gap. Here, I will show that the introduction of 2,3,4,5,6-pentafluorophenethylammonium cations in a perovskite active layer of composition $(\text{FASnI}_3)_{0.5}(\text{MAPbI}_3)_{0.5}$ enhances the crystallinity of the active layer, reduces the voltage losses and increases the material stability. The addition of the fluorinated cations allows the fabrication of highly oriented films with improved thermal stability. Moreover, the treated films exhibits merged grains with no evidence of 2D structures, which we believe leads to the passivation of trap states at the grain boundaries. Solar cells fabricated adding to the active layer the fluorinated cation display reduced trap-assisted recombination losses and lower background carrier density, which led to enhanced open-circuit voltage than the reference sample using phenethylammonium cations. The best perovskite solar cell showed an efficiency of 19.13%, with an open-circuit voltage of 0.84 V, which is substantially improved respect to the reference sample which exhibits 17.47% efficiency and 0.77 V as open-circuit voltage. More importantly, the fluorinated cations' addition help to improve the device's thermal stability, maintaining 90.3 % of its initial efficiency after 90 min of thermal stress at 85 °C in Nitrogen atmosphere.

10:30 AM EF02.04

Wasted Photons—Photogeneration Yield and Charge Carrier Collection Efficiency of Metal Oxide Photoanodes for Photoelectrochemical Water Splitting Yifat Piekner¹, David S. Ellis², Daniel A. Grave^{2,3} and Avner Rothschild²; ¹Technion Israel Institute of Technology, Technion Israel Institute of Technology, Haifa, Haifa, IL, academic, Israel; ²Technion Israel Institute of Technology, Israel; ³Ben Gurion University of the Negev, Israel

At the heart of solar cells is a semiconductor photoabsorber: a material capable of absorbing photons and generating electrons and holes that contribute to the photocurrent. But where commercial photovoltaic cells use silicon for that purpose, photoelectrochemical water splitting cells for solar energy conversion to green hydrogen must rely on other materials that are suitable for operation in aqueous electrolytes. Selected transition metal oxides such as TiO_2 and $\alpha\text{-Fe}_2\text{O}_3$ (hematite) are known for their stability in alkaline electrolytes, which makes them prime candidates for photoanodes for water photo-oxidation. While transition metal oxides with empty d-shell configurations such as TiO_2 ($\text{Ti}^{4+} 3d^0$) and BiVO_4 ($\text{V}^{5+} 3d^0$) reach high internal quantum efficiencies, their lower bandgap counterparts with open d-shell configurations such as hematite ($\text{Fe}^{3+} 3d^5$) display low quantum efficiencies that limit their photoconversion efficiency. In the case of hematite photoanodes, less than half of the theoretical photocurrent limit has been reached, despite half a century of research efforts to improve their performance. Nearly all of these efforts address electron-hole recombination losses in the bulk and at the surface by nanostructuring and co-catalysis, respectively, whereas only few studies have considered the deleterious effect of localized d-d transitions that do not generate electrons and holes. Here we present an analytical way of assessing the actual limit that might be obtained from hematite, as a case-study for other correlated electron materials. To this end, a comprehensive method is introduced to extract both the spatial profile of the charge carrier collection efficiency and the photogeneration yield spectrum, defined as the wavelength-dependent fraction of absorbed photons that generate electron-hole pairs. Our results show that photogeneration yield in thin film hematite photoanodes is less than unity across the entire absorption range, limiting the maximal photocurrent that may be attained in an ideal hematite photoanode to about half of the theoretical limit predicted without accounting for this effect. Our method is applicable to other materials, and we hope that this study will inspire further research into the effect of noncontributing light absorption in photocatalytic materials with correlated electrons that often give rise to nontrivial physical phenomena that may affect their properties and performance.

10:45 AM BREAK

11:00 AM *EF02.06

Monolithic Photoelectrochemical Tandem Devices Consisting of Tunnel Oxide Passivated Contact Silicon and BiVO_4 Enabling Unassisted Water Splitting Choongman Moon¹, Gihun Jung¹, Filipe Martinho², Stela Canulescu² and Byungha Shin¹; ¹Korea Advanced Institute of Science and Technology, Korea (the Republic of); ²Danmarks Tekniske Universitet, Denmark

A tandem photoelectrochemical (PEC) water-splitting device for solar hydrogen production consists of two light absorbers with different bandgaps. It is important to enhance the performance of both cells to achieve high solar-to-hydrogen (STH) conversion efficiency. In this regard, silicon photoelectrodes have been widely investigated because of their bandgap (1.12 eV), which is suitable for the low bandgap bottom cell of a tandem device. Herein, we apply a tunnel oxide passivated contact (TOPCon) on the front and back sides of a Si wafer to prepare a TOPCon Si PEC device. Photocathodes and photoanodes based on TOPCon Si are demonstrated over a broad pH range (0–14), and they produce photovoltages of 640–650 mV under 1 sun illumination, which are the highest values obtained from crystalline Si photoelectrodes. TOPCon Si demonstrates excellent thermal stability, enduring a high processing temperature of up to 600 °C for 1 h in air. These advantages of TOPCon Si provide high efficiency and great design flexibility for monolithic tandem cells. TOPCon Si was coupled with BiVO_4 , a large bandgap top cell consisting of earth-abundant and non-toxic elements, in monolithic construction, i.e., a wireless PEC tandem cell. A photovoltage exceeding 1.7 V was produced by the BiVO_4/Si with a successful demonstration of unbiased PEC water splitting. I will discuss details of the challenges and our solutions in the monolithic integration of BiVO_4 and Si.

11:20 AM EF02.07

A Versatile, Scalable and Facile Aqueous Route Towards CuBi_2O_4 Photocathodes and Green Hydrogen Bjorn Joos^{1,2,3}, Jonathan Van den Ham⁴, Andreas Paulus^{2,1,3}, Ken Elen^{2,1,3}, Pascal Buskens^{5,4,1}, Marlies Van Bael^{1,2,3} and An Hardy^{1,2,3}; ¹Hasselt University, Belgium; ²Interuniversitair Micro-Elektronica Centrum, Belgium; ³EnergyVille, Belgium; ⁴The Netherlands Organisation for Applied Scientific Research (TNO), Netherlands; ⁵Brightlands Materials Center, Netherlands

Although solar energy is the cleanest and most abundant energy source available on the planet, the use thereof is hindered by its intermittent nature. The ability to harness and conserve the solar energy is of utmost importance to guarantee a continuous supply in order to satisfy our energy demands. Artificial photosynthesis is a promising and upcoming technology to store the captured solar energy into energy-dense chemicals such as hydrogen, methanol, or formic acid.[1] Such a solar-energy-to-chemical-energy conversion could be achieved at high efficiency through the use of photo-electrochemical devices. Herein, via the absorption of solar photons, semiconducting photocathodes or photoanodes (or a combination thereof) generate electrons and holes, that are capable to reduce water to hydrogen gas (H_2) or to oxidize water to oxygen gas (O_2) respectively.

Copper-based p-type semiconductors (Cu_2O , CuBi_2O_4 , CIGS, CZTS, etc.) take a prominent role as a photocathode due to their abundance, high theoretical photocurrents, and tunable bandgaps (1.0 to 3.5 eV).[1][2] Ideally, visible solar radiation should be absorbed by the photoelectrode to maximize the device's potential, limiting the bandgap to the 1.5 to 1.8 eV range. A good candidate is the spinel-type mixed copper bismuth oxide CuBi_2O_4 . The oxide displays a suitable bandgap of around 1.6-1.8 eV (~700nm onset) with a suitable conduction band edge for the reduction of protons to hydrogen gas. [3]

In recent work, the synthesis of CuBi_2O_4 occurs mainly through techniques such as pulsed laser deposition (PLD), atomic layer deposition (ALD), spray pyrolysis, electrodeposition, spin-coating, drop-casting, often requiring environmentally unfriendly organic solvents such as ethanol and acetic acid.[3] In this work, we develop a facile and versatile aqueous solution-gel route to deposit CuBi_2O_4 thin films on TCOs, omitting the use of harmful organic solvents. The aqueous route promotes the fine-tuning of the CuBi_2O_4 such as the elemental composition (Cu/Bi ratio), the thickness of the deposited layers, the facile and homogeneous introduction of dopants, etc. The deposited layers can easily be varied from 30 to 500 nm thickness to optimize the balance between the charge carrier lifetime and light absorption. The influence of the aqueous precursor's composition (Cu/Bi ratio) on the formation of crystalline CuBi_2O_4 on the FTO substrate and the suppression of side-phase formation is analyzed by X-ray diffraction and further supported by Raman spectroscopy. UV-VIS spectroscopy reveals the optical properties of the deposited semiconductor films. The electrochemical properties such as charge carrier mobilities are analyzed and compared to the state-of-the-art. Lastly, the photo-electrochemical performance towards the hydrogen evolution is analyzed with a solar simulator.

Acknowledgements

Financial support by TNO in the framework of the Early Research Program "Energy Conversion and Storage" and Catalisti moonschot project SYN-CAT is acknowledged. SYN-CAT is a cSBO in MOT3 Electrification & Radical Process Transformation

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11:35 AM EF02.08

Polarization and Internal Electric Field Screening in Mixed Conducting Hybrid Perovskite Devices Davide Moia^{1,2}, Ilario Gelmetti³, Philip Calado², Mina Jung¹, Jenny Nelson², Piers Barnes² and Joachim Maier¹; ¹Max-Planck-Institut für Festkörperforschung, Germany; ²Imperial College London, United Kingdom; ³Institut Catala d'Investigació Química, Spain

Hybrid perovskites are the first photovoltaic material class presenting competitive solar cell performance and, at the same time, significant mixed ionic electronic conduction at room temperature. [1] Early reports revealed the major contribution of iodide vacancies in the ion conduction of methylammonium lead iodide (MAPI), also demonstrating room temperature bulk stoichiometry control when varying the iodine partial pressure. [2] Recent investigations emphasized the influence of ionic interactions at the interfaces of hybrid perovskite films with contact materials in the determination of the interfacial space-charge situation, a paradigm-shift in the evaluation of mobile charge carrier equilibration in solar cells. [3] Further advance of experimental and computational tools is needed in order to harness the complexity of mixed conduction in MAPI and other hybrid perovskites, and to address its influence on device performance and stability. Specifically, accurate models of mixed conduction in solar cells accounting for the non-equilibrium electronic and ionic situations are currently missing and prevent the community from taking full advantage of common experimental characterization methods. In addition, novel experimental approaches are required to elucidate fundamental questions on the ion transport and polarization processes occurring in hybrid perovskite solar cells and their implications on the physical quantities, such as the internal electric field distribution, that are linked to the device's response.

In this contribution, we address these aspects by presenting on theoretical and experimental progress in the description of mixed conduction in hybrid perovskite devices. First, we discuss conductivity measurements performed on different device geometries to investigate the polarization dynamics of MAPI. The results help us discriminating between different polarization effects, upon application of electrical stimuli, which can be attributed to charging of the interfaces and to bulk stoichiometric polarization. Secondly, we developed frequency domain and time-resolved electroabsorption techniques that can be used to resolve the internal electric field in hybrid perovskite films. [4] By monitoring the signal strength of 1st harmonic and 2nd harmonic electroabsorption in devices to which an oscillating voltage perturbation is applied, we evaluate changes of the averaged electric field in the perovskite active layer. The results are consistent with data extracted from impedance spectroscopy and step-dwell-probe measurements performed in the dark and under light. We pursue a combined spectroscopic and optoelectronic study of the dynamics of internal electric field screening in perovskite solar cells, which highlights characteristic frequencies and time constants for each technique. We are then able to evaluate the role of device architecture and applied bias light in the determination of the screening kinetics. We propose our interpretation of the resulting trends in terms of electronic and ionic contributions influencing the internal electric field, also based on drift-diffusion simulations of the performed measurements. Finally, we discuss the implications of our findings to the development of appropriate equivalent circuit models describing solar cell devices.

Our contribution highlights the potential of combining experimental and computational approaches to address fundamental questions on the mixed ionic-electronic conduction in MAPI and other hybrid perovskites. Such approach can provide self-consistent analysis and interpretation of the complex electrical response of devices, by also enabling the design of appropriate models.

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11:50 AM EF02.09

Exsolution of CdS Nanoparticles on Lanthanum Strontium Titanate for H₂ Production Under Visible Light Shreyasi Chattopadhyay and John T. Irvine; University of St Andrews, United Kingdom

To address the current energy crisis and environmental issues, utilization of solar energy in terms of photocatalytic water splitting has good potential for producing green H₂ fuel. Being a potential semiconductor, SrTiO₃ is interesting due to its tuneable light absorption property. Changing stoichiometry or creating A or B site defects by incorporating cations with different valance and size can alter the electronic structure of SrTiO₃ and therefore, tune its photoactivity. Moreover, in situ growth of other photoactive nanoparticles on A-site deficient lanthanum doped strontium titanate would allow successful development of a new class of catalyst for efficient solar energy conversion. The strong surface interaction from exsolved nanoparticles would also offer stability under photocatalysis conditions.

In this approach CdS nanoparticles were prepared via combining sulfidation with exsolution from A-site cation deficient La_{0.40}Sr_{0.40}Cd_{0.05}Ti_{0.95}O_{3- δ} (LSCdT) has been made. It is noteworthy that, the low melting points of metallic Cd and CdO restricted high-temperature synthesis methods, therefore a room temperature route to CdS NPs has been designed after hydrothermal synthesis of LSCdT. Thorough characterization was carried out to confirm the formation of phase pure LSCdT prior to the exsolution done under the room temperature sulfidation reaction condition. Uv-vis absorption spectrum and a thorough TEM analysis confirmed successful creation of CdS nanoparticles with particle size of ~3-5 nm. Furthermore, photocatalytic activity of the

photocatalyst towards water splitting for H₂ production has been investigated under vacuum condition with full UV-vis range and visible range of light irradiation. A H₂ production rate of ~50 μmol h⁻¹ g⁻¹ has been obtained under visible light, and the rate was calculated to be ~1169 μmol h⁻¹ g⁻¹ with respect to the CdS content. Control experiment with undoped LST showed no H₂ evolution under visible light. Characterization of the photocatalyst recovered after photocatalysis confirmed the stability of CdS nanoparticles on perovskite oxide surface. Hence, we have successfully developed a new material with enhanced light absorption property and results detailing the material and its photoactivity towards water splitting will be presented.

12:05 PM EF02.10

Perovskite-Based Nanostructured Materials for CO₂ Conversion into Solar Fuels Using Localized Surface Plasmon Resonance Lorenzo

Rizzato¹ and Antonella Glisenti^{1,2}; ¹Università degli Studi di Padova, Italy; ²Istituto di Chimica della Materia Condensata e di Tecnologie per l'Energia Consiglio Nazionale delle Ricerche, Italy

In recent years, increasing CO₂ levels have gained much attention due to their correlation with climate change phenomena. In order to mitigate the effects of anthropogenic emissions, different pathways can be undertaken; amongst them, CO₂ photoconversion into solar fuels is interesting for its sustainability, circularity, and simplicity. In this work, nanostructured perovskite-based materials have been evaluated as potential candidates for efficient CO₂ conversion by means of photocatalytic processes. Sr_{1-x}TiO₃ was chosen as supporting material for its good electronic and transport properties; surface decoration with Cu nanoparticles was included to enhance the photocatalytic activity of the material by means of localized surface plasmon resonance (LSPR) [1]. The samples were prepared through a sol-gel method using citric acid as a chelating agent; surface decoration was obtained by means of ammonia deposition preparation (ADP) and exsolution. The latter method was found to be effective in the growth of metal nanoparticles caused by the migration of B-site perovskite cations to the surface when the material is exposed to a reducing atmosphere [2]. Moreover, A-site deficiency was found to help the migration of metallic B-site dopant cations towards the surface, as it equilibrates the structural stresses caused by the exsolution process. Different loads of Cu were inserted in the samples to study the effect of metal dopant concentration on the final materials structure.

Structural, morphological, and functional characterizations (XRD, SEM, EDX, XPS, H₂-TPR, CO₂-TPD, BET) were carried out to gain information over the properties of the catalysts. Interestingly, the surface decoration method strongly influences the nanoparticles structure, resulting in different shape, composition, dimension, and dispersion. Exsolved samples showed the presence of small copper nanoparticles, detected only with XRD and XPS analysis, while SEM images and EDX analysis of the catalysts treated in a more reducing atmosphere showed the formation of Cu-rich agglomerates; ADP resulted in the formation of large Cu particles on the surface of the supporting material.

An ad hoc versatile photo, electro-catalytic reactor was designed to study the influence of temperature, voltage, and electromagnetic field in the catalytic activation of CO₂ methanation with H₂. The experimental setup allows a full flexibility in the reaction conditions; it consists in a quartz-tube reaction chamber where the powders are inserted and the gas mixture flows in; temperature control is achieved by means of a small ceramic oven, while the photoactivation is possible by exposing the sample to a powerful LED visible light source. Catalytic tests were carried out using a stoichiometric mixture of CO₂ and H₂; mass spectrometry was used to analyse the final products. The results of this work indicate that Cu plays an important role in the activation of the catalyst when exposed to a light beam. Strontium titanate without surface decoration showed no catalytic activity towards CO₂ reduction reaction, while Cu-loaded samples resulted in the production of CO and CH₄. It seems that the electromagnetic field activates the charge carriers injection in the catalytic sites through the excitation of LSPR of the Cu nanostructures, leading to the detection of catalytic activity at low temperatures, as stated in other works [3]. From the qualitative point of view, materials with a lower amount of copper resulted to be more effective in the activation of carbon dioxide, leading to the production of methane instead of simple carbon monoxide. Thus, the activation of CO₂ could be enhanced by smaller and more dispersed nanoparticles, exploiting the LSPR effect more efficiently.

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SESSION EF03: PEM Fuel/Electrolysis Cells I
Session Chairs: Vito Di Noto and Sanjeev Mukerjee
Monday Afternoon, July 18, 2022
Lobby Level, Avenue 34, Studio 2

2:00 PM **EF03.01

Elucidation of the Factors Controlling Oxygen Evolution on Model Surfaces Ilan Stephens; Imperial College London, United Kingdom

It is particularly challenging to catalyse oxygen evolution under the acidic conditions of polymer electrolyte membrane (PEM) electrolyzers. All compounds, apart from IrO_x and RuO_x, are catalytically inactive or unstable. In alkaline electrolyzers, a wider range of materials are available, including non precious metals such as NiFeO_x. There are many open questions regarding the (a) the active site for oxygen evolution (b) the relationship between activity and dissolution (c) means of improving the stability.

In this contribution, I will attempt to address some of the questions.¹⁻⁴ The catalysts under investigation include single crystals, model-size selected nanoparticles, commercial high surface area catalysts, sputtered films and oriented thin films of oxides based on RuO_x, and IrO_x and doped Ni_xO_yH_z. We have probed these surfaces with electrochemical measurements, operando optical spectroscopy, X-ray photoelectron spectroscopy, low energy ion scattering spectroscopy, electron microscopy, X-ray absorption spectroscopy, crystal truncation rod measurements, electrochemical mass spectrometry and density functional theory calculations.

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2:30 PM **EF03.02

Advancing Fuel Cells for Heavy-Duty Applications Rod L. Borup¹, Adam Weber², Deborah Myers³, K C. Neyerlin⁴, Ahmet Kusoglu², Rajesh

Ahluwalia³, Rangachary Mukundan¹, David Cullen⁵ and Greg Kleen⁶; ¹Los Alamos National Laboratory, United States; ²E O Lawrence Berkeley National Laboratory, United States; ³Argonne National Laboratory, United States; ⁴National Renewable Energy Laboratory, United States; ⁵Oak Ridge National Laboratory, United States; ⁶DOE Golden Field Office, United States

While significant advances have been made and early commercial fuel cell light-duty vehicles (LDVs) are starting to be produced, fuel cells in the heavy-duty-vehicle (HDV) transportation sector (including trucks, long-haul semitrailers, maritime, trains, etc.) are nascent, despite the fact that advantages of fuel cells compared to both diesel and electric powertrains are very compelling in terms of emissions, charging time, efficiency, power-to-weight ratio, among others. However, the fuel-cell technology for HDVs requires a paradigm shift in fuel-cell research and development compared to LDVs, where the emphasis becomes efficiency and improvements in durability instead of a focus on increased power densities and lower cell costs.

Heavy-duty applications require significantly longer vehicle lifetimes (>25,000 hours/1,000,000 miles for heavy-duty trucks), and therefore require improved fuel cell durability compared to light-duty vehicles. Furthermore, because of this extended lifetime, hydrogen fuel costs comprise a greater proportion of heavy-duty vehicle lifecycle cost, making increased efficiency a key parameter for economic viability. In 2020, HFTO formed the Million Mile Fuel Cell Truck Consortium (M2FCT) that includes a core team of five national laboratories to overcome durability and efficiency challenges in PEMFCs for heavy-duty applications with an initial focus on long-haul trucks.

While targets and testing protocols have been developed for light-duty vehicles, the same level of targets and testing protocols have not been established for heavy-duty transportation. With operational times of greater than > 25,000 hours required, the need for well-developed accelerated stress tests (ASTs) is amplified. Results from these ASTs demonstrate the need for more durable electrode layers and well-controlled potential variations.

The presentation will provide an overview of the DOE's Fuel Cell R&D approach, highlighting past and current activities, as well as strategies to enable fuel cell competitiveness for heavy-duty applications.

Acknowledgments:

This work is funded through the DOE M2FCT Consortium with thanks to DOE EERE HFTO

3:00 PM *EF03.03

Activity, Degradation and Integration of Oxygen Reduction and Evolution Electrocatalysts in Polymer Electrolyte Fuel Cells and Water Electrolyzers [Deborah Myers](#), Nancy Kariuki, Jaehyung Park and A. Jeremy Kropf; Argonne National Laboratory, United States

The sluggish kinetics of oxygen electrocatalysis and the resulting high overpotentials necessary to achieve useful current densities, the degradation of the electrocatalysts, and the integration of the electrocatalysts with the ion-conducting phase to form an effective electrode are challenges to the development and widespread implementation of polymer electrolyte membrane fuel cells and electrolyzers (PEMFCs and PEMECs).^{1,2} The best catalysts for both the oxygen reduction and oxygen evolution reactions (ORR and OER, respectively) in acidic electrolyte are based on precious, platinum group metals, such as platinum and iridium. An additional challenge, thus, is to decrease the loading of precious metal catalysts or completely replace precious metal catalysts with earth-abundant materials, while maintaining efficiency and lifetime to enable cost effective implementation of these technologies.^{2,3} While replacement of platinum-group metal-based catalysts in PEMECs remains a challenge, incredible progress has been made over the past decade in increasing both the ORR activity and durability of PGM-free PEMFC cathode catalysts, most notably in the class denoted as "Fe-N-C".⁴

This presentation will describe application of *ex situ*, *in situ*, and *operando* synchrotron-based X-ray techniques and on-line inductively-coupled mass spectrometry to understand the mechanisms of oxygen catalyst degradation, to define conditions mitigating this degradation, and to understand means to form more effective oxygen electrodes. This presentation will also discuss the use of X-ray techniques to understand the mechanisms of active site formation in and degradation in PGM-free ORR electrocatalysts.

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Acknowledgements

This work was supported by the U.S. Department of Energy (DOE), Energy Efficiency and Renewable Energy, Hydrogen and Fuel Cell Technologies Office (HFTO) under the auspices of the Electrocatalysis Consortium (ElectroCat), the Million Mile Fuel Cell Truck Consortium (M2FCT), and the Hydrogen from Next-generation Electrolyzers of Water Consortium (H2NEW). This work utilized the resources of the Advanced Photon Source, a DOE Office of Science user facility operated by Argonne National Laboratory for DOE Office and was authored by Argonne, a DOE Office of Science laboratory operated for DOE by UChicago Argonne, LLC under contract no. DE-AC02-06CH11357.

3:20 PM *EF03.04

Optimization of Manufacturing Techniques for Highly-Performing Membrane-Electrode Assemblies in PEM Fuel Cells [Xianguo Li](#); University of Waterloo, Canada

PEM fuel cell technology is ready for large-scale commercial applications. Membrane-electrode assemblies (MEAs), in which electric power is generated, are the key component of PEM fuel cell power systems. One of the key challenges now is to manufacture MEAs at volume with low cost, consistency, reliability and repetitiveness among the same batch and different batches of manufacturing processes, within a specified quantifiable tolerance range. Three low-cost manufacturing techniques with volume capability have been evaluated: catalyst-coated substrate (CCS), catalyst-coated membrane (CCM) and decal-transfer method (DTM). For each method, systematic and consistent investigations were conducted for various sub-processes and conditioning parameters, such as DTM with different operation temperatures, and additional layers of Nafion and carbon at different locations and orders. We also studied the sensitivity of the platinum loadings on the MEA performance. It was observed that at the high Pt loading of 0.5 mg/cm², excellent MEA performance was achieved for all the three methods with almost identical results. When the Pt loading is reduced to 0.125 mg/cm² (75% reduction in the Pt loading), the performance of MEAs made by the different methods changes substantially, indicating significant sensitivity of the MEAs to the Pt loading.

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3:40 PM BREAK

4:00 PM *EF03.05

An Overview of the H2NEW Consortium [Bryan Pivovar](#); National Renewable Energy Laboratory, United States

The H2NEW (Hydrogen (H2) from Next-generation Electrolyzers of Water) consortium is a major new Department of Energy-Hydrogen and Fuel Cell

Technology Office funded effort with a vision is to enable large-scale production of hydrogen by splitting water into hydrogen and oxygen via low-temperature acidic polymer electrolyte membrane (PEM) electrolysis and high-temperature oxide-ion-conducting solid oxide electrolysis (HTE). The primary end-of-project goal of H2NEW is to enable hydrogen production from electrolysis for use as a clean, sustainable fuel or feedstock, at <\$2/kg production costs, making it cost competitive with fossil-derived hydrogen. To overcome the cost barrier, electrolyzers need to be fabricated at scale, more efficiently utilize low-cost electricity, and demonstrate durability under relevant intermittent and variable duty cycles. This talk will give an overview of the pillars of the H2NEW consortium targeting improved Durability, Performance and Manufacturing Scale-up and Integration with a focus on the PEM electrolysis efforts. Hydrogen has been growing in relevance and interest and one of the major needs in this space has been to enable lower cost electrolysis which serves as the primary goal of H2NEW.

4:20 PM *EF03.06

High Temperature Polymer Electrolyte Fuel Cells as a Unique Clean Power Technology for a Wide Array of Markets Vasilis Gregoriou; Advent Technologies SA, Greece

Advent Technologies is an innovation-driven company in the fuel cell and hydrogen technology space. Our vision is to accelerate electrification through advanced materials, components, and next-generation fuel cell technology. By using hydrogen produced from renewable energy sources, such as solar and wind, fuel cells can provide carbon-neutral power without any pollutants, such as SO_x and NO_x. Initial commercialization of clean, high-efficiency fuel cell electric vehicles is already underway, but further technological innovation is needed to improve the cost competitiveness of fuel cells in the marketplace. Fuel cells are promising devices for clean power generation in a variety of economically and environmentally significant applications. Low-temperature proton exchange membrane (PEM) fuel cells utilizing Nafion® require a high level of hydration, which limits the operating temperature to under 100 °C and requires high purity hydrogen as the fuel. In contrast, high-temperature PEM fuel cells utilizing acid imbedded engineering polymers can operate effectively at 80-200 °C, which greatly ameliorates the limitations of low temperature PEM.

This presentation will focus on how fuel cells that operate over 100 °C can significantly impact a wide array of markets, from portable power in the defense industry to stationary power systems providing clean power to cell phone towers in extreme environmental conditions. Operation at higher temperature provides a pathway to utilize multiple liquid hydrogen carriers, thus allowing hydrogen fuel cells to be deployed now while awaiting the infrastructure build-out for hydrogen gas. We will also discuss our next generation electrodes and membranes.

4:40 PM EF03.07

Synthesis of Proton-Conducting Inorganic-Organic Composites Based on Strong Acid Salts of Heterocyclic Compounds and Their Application to Medium-Temperature Anhydrous Fuel Cells Keiichiro Maegawa, Jin Nishida, Go Kawamura and Atsunori Matsuda; Toyohashi University of Technology, Japan

Polymer Electrolyte Fuel Cell operating under Medium Temperature condition (MT-PEFC) is one of the candidates as the next-generation energy to realize the carbon neutral. By increasing the operation temperature, higher power density, and reducing costs of PEFC can be achieved due to increasing the utilization of platinum catalysts at high temperatures. In order to enhance the performance of MT-PEFC, novel proton exchange membranes that can show high stability and high proton conductivity under medium temperature (~200°C), are needed. Phosphoric acid (PA)-doped Polybenzimidazole (PBI) is used as an electrolyte in common MT-PEFCs. The proton conductivity of PA-PBI can be improved by increasing the phosphoric acid doping level, but high PA doping leads to cell corrosion due to PA leaching. In this study, we proposed a new approach of adding solid proton conductors to the PBI membrane, to achieve high proton conductivity with a low PA doping level. We have found that an organic-inorganic composite material based on strong acid salts of the heterocyclic compound has high proton conductivity as a new solid proton conductor for the MT-PEFC. In this work, imidazole hydrochloride was chosen as the organic material and silica as the inorganic material, and they were combined by mechanical milling to obtain a new proton conductor. We have already investigated the proton conductivity of imidazole and found that it exhibits a high proton conductivity of around $1 \times 10^{-3} \text{ S cm}^{-1}$ under a wide range of temperatures. Therefore, we thought that imidazole hydrochloride, in which a hydrochloride group is introduced into imidazole, should exhibit even higher proton conductivity. Silica is chemically stable and effective in inhibiting phosphoric acid leaching. In addition, the addition of inorganic material into the organic material such as imidazole leads to the structure changing of the organic material and consequently improves the proton conductivity. Therefore, in this study, the effects of chemical, morphological structure of composite material mixing between imidazole hydrochloride and silica on the proton conductivity were examined. Finally, the fabricated proton conductor was incorporated into the PBI membrane and the performance of composite type PBI with low PA doping level was evaluated. The resulted membrane was electrochemically evaluated by impedance spectroscopic analysis (proton conductivity measurement), and fuel cell measurement using H₂/O₂ gases for anode and cathode, respectively, under 150°C anhydrous condition. The PA leaching properties of the composite PBI membrane were examined by exposing the PA doped films to steam at 100°C and measuring the weight change. Acknowledgment: This research is supported by New Energy and Industrial Technology Development Organization (NEDO) (JPNP20003).

4:55 PM EF03.08

Transition Metals High-Entropy Spinel Oxides Prepared by Spray Pyrolysis Technique—Microstructural and Electrical Investigations of Thin Films Bartosz Kamecki, Krystian Lankauf, Piotr Jasinski, Jakub Karczewski and Sebastian Molin; Politechnika Gdanska, Poland

The idea of high-entropy stabilized materials was initiated in 1995, but only in 2015 was it applied to oxide materials by Rost et. al[1]. The definition assumes the existence of multi-component materials with 5 up to 13 elements with a concentration between 5 and 35 at% in mostly equimolar ratios and certainly shows the essence of the whole concept of high-entropy materials. This research aims to fabricate and study a novel materials group broadly described as high-entropy oxides with a focus on thin films crystallized in the spinel structure. The novelty of the research is a detailed study of entropy stabilized spinels based on Transition Metal elements (Cr, Mn, Fe, Co, Ni, Zn) prepared by in-house developed spray pyrolysis technique in form of nanocrystalline thin layers (~ 500 nm). The facile spray pyrolysis technique seems to be well suited to fabricate and explore the spinel-based high-entropy oxides synthesized as thin films and studying new compositions containing transition metal cations. In this research different compositions of TM elements containing 5, 6, or 7 equimolar elements were deposited on amorphous SiO₂ or sapphire substrates. Prepared samples were evaluated in terms of microstructural and transport properties of materials in a temperature range of 400-700°C. Obtained layers were nanocrystalline and had a single-phase spinel structure observed after annealing at least 500°C confirmed by XRD measurements. The spray pyrolysis technique allows reducing sintering temperature by almost 400°C in comparison to the conventional solid-state sintering method. Selected compositions will be used to investigate electrocatalytic properties of nanocrystalline HEO layers on Oxygen Reduction Reaction in Alkaline Water Electrolysis. This work is supported by a project funded by National Science Centre Poland based on decision DEC-2019/35/N/ST5/01796

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5:10 PM EF03.09

Development and Characterization of Crosslinked PPO-Based Anion Exchange Membranes for AEM Fuel Cells Andrea Basso Peressut, Joelle

Montagna, Paola Moretti, Alessia Arrigoni, Saverio Latorrata, Chiara Bertarelli and Giovanni Dotelli; Politecnico di Milano, Italy

This work describes the synthesis and characterization of a series of poly (2,6-dimethyl-1,4-phenylene oxide) (PPO)-based anion exchange membranes (AEMs), crosslinked with bis-imidazolium cations, and investigated as potential ionic conductors for AEM fuel cells. PPO has excellent mechanical and thermal properties, and its backbone can be functionalized by means of several possible routes. Among them, bromination has been carried out with a quantitative control of the amount of the linked halogens. PPO with bromination degrees (BD) of 14% and 33% have been crosslinked by employing a novel procedure with 1,6-bis(2-methylimidazol-1-yl)hexane (bimh). This new crosslinking method has granted a fast and highly efficient crosslinking reaction, resulting in an almost quantitative substitution of bromine atoms (higher than 94%). The obtained cast membranes have been thoroughly characterized by ATR-FTIR and EDX spectroscopies, scanning electron microscopy (SEM), thermogravimetry and differential scanning calorimetry (DSC). Their functional properties have been assessed through four main tests, involving the evaluation of water uptake (WU) and swelling ratio (SR), ion exchange capacity (IEC), alkaline stability and ionic conductivity by means of electrochemical impedance spectroscopy (EIS). WU and EIS tests have been conducted as a function of temperature in the 20–100 °C range and in conditions of complete hydration (98% relative humidity). These analyses have revealed that the prepared AEMs are well-uniform with all the features properly controlled and affected by the increment of the bromination degree of PPO. This outcome is a consequence of the increased number of sites that can anchor OH⁻ ions and of the more crosslinked network, leading to the enhancement of ion exchange capacity and ionic conductivity. The membranes also exhibited a promising alkaline stability, since they have retained their robustness, transparency and functional properties with only minor changes, after being immersed in a strong alkaline environment (2 M KOH solution) for several days.

These promising features make the proposed AEMs worthy of application and further investigation is ongoing, aimed at assessing their mechanical behavior and fuel cell performance depending on the crosslinking degree.

5:25 PM EF03.10

Mesoscale Model for Ostwald Ripening of Catalyst Nano-Particles [Giovanna Bucci](#)¹ and W. Craig Carter²; ¹Palo Alto Research Center Incorporated, United States; ²Massachusetts Institute of Technology, United States

Polymer electrolyte membrane (PEM) fuel cells are increasingly regarded as the alternative for combustion engines in transportation (for instance as a range extender or for long-haul trucks). Employed in vehicles, PEM fuel cell must be able to withstand thousands of operating hours under changing load conditions. Power loss over the lifetime is mainly caused by the loss of the electrochemically active surface (ECSA) of the cathode catalyst layer. The catalyst layer typically consists of agglomerates of platinum nanoparticles on a carbon support. A solid electrolyte is blended with the catalyst to carry protons to the Pt surface. Under operating conditions, platinum is electrochemically unstable. Due to the Gibbs-Thompson effect, dissolved platinum tends to re-deposit on large particles, leading to permanent particle coarsening and hence ECSA loss.

To investigate cathode aging, we developed a theoretical framework of Pt behavior in the catalyst that predicts the coarsening of the nanoparticles over long-term cycling. Existing models of Ostwald ripening cannot capture the complexity of the cathode catalyst microstructure, and the network of capillary water that forms the transport pathways for Pt-ions. A key feature of the proposed mesoscale approach is the explicit representation of the local environment around each particle. This includes modeling Pt-ions transport within the microstructure and the dissolution/redeposition processes caused by voltage cycling.

Through numerical tests, the scaling of coarsening kinetics is predicted as function of voltage. The effect of voltage cycling, and initial particle size distribution are also probed. The power-law exponents for the mean square radius vs. time are affected by the reduced dimensionality of inter-particle diffusion (constrained by the carbon support and the surface wetting). This theoretical framework can be used to understand how material design influences the degradation pathways that are responsible for platinum surface area loss.

SESSION EF04: Ceramic Membrane Reactors I

Session Chairs: Georgios Dimitrakopoulos and Ahmed Ghoniem

Monday Afternoon, July 18, 2022

Lobby Level, Avenue 34, Studio 1

2:00 PM **EF04.01

Proton-Conducting Electroceramics for Electricity Generation, Energy Storage and Fuels Synthesis [Neal Sullivan](#)¹, Long Q. Le², Carolina Herradon¹, Charlie Meisel¹, Youdong Kim¹, Jake Huang¹ and Ryan O'Hayre¹; ¹Colorado School of Mines, United States; ²Pacific Northwest National Laboratory, United States

In this presentation, we review our recent progress in harnessing proton-conducting ceramic materials for next-generation energy technologies. This includes fuel cells for high-efficiency electricity generation, electrolyzers for intermittent energy storage, and membrane reactors for fuels synthesis. Proton-conducting ceramics are developing into a promising class of electrochemical materials. These materials provide high proton conductivity at intermediate temperatures (~ 500 C), enabling efficient operation at substantially lower temperatures than used in more-conventional oxygen-ion conducting ceramics. Materials development continues for discovery of protonic ceramics with improved electrochemical properties. We have observed lower ohmic resistance and higher device durability with the BaCe_{0.4}Zr_{0.4}Y_{0.1}Yb_{0.1}O_{3-δ} (BCZYYb4411 or BCZYYb) perovskite material.

Adopting architectures similar to those of solid-oxide devices, we utilize the BCZYYb material to fabricate tubular and planar membrane-electrode assemblies (MEAs) for electricity and chemicals production. MEAs utilize a composite Ni–BZCYYb fuel electrode (negatrode), a BCZYYb electrolyte, and a BaCo_{0.4}Fe_{0.4}Zr_{0.1}Y_{0.1}O_{3-δ} air-steam electrode (positrode). The fuel electrode and electrolyte layers are co-sintered using solid-state reactive sintering (SSRS), an attractive MEA-fabrication method that reduces the number of time-consuming high-temperature sintering processes. During SSRS, the single-phase BCZYYb is formed from parent oxides during high-temperature co-sintering of the negatrode-electrolyte layers. This is in contrast to more-traditional processing, in which the desired electrolyte is first calcined from parent oxides, and the MEA is formed in follow-on high-temperature sintering steps.

The ~ 1-mm-thick negatrode serves as the mechanical support for the MEA, and defines the cell architecture. We dry press the negatrode support for our planar devices, while using high-pressure extrusion to fabricate tubular electrode supports. Recent fabrication advances include atomistic-spray deposition of the electrochemically active layers, including the BCZYYb electrolyte, and positrode and negatrode functional layers. The process control realized through spray atomization has improved the morphology and the electrochemical performance of both our planar and tubular devices.

We develop tubular protonic ceramics for portable military fuel-cell applications. Our planar devices are witnessing wider interest as electrolyzers and membrane reactors. Device sealing is critical in such applications. To this end, the planar MEA is packaged within a “picture-frame” stack design with ferritic steel interconnects, metallic current collectors, vermiculite sealing gaskets, and glass sealants. The protonic-ceramic unit-cell stack has demonstrated remarkable stability in electrolysis mode, with voltage degradation below 1% per thousand hours of operation at 0.5 A cm⁻² of driving current

(550 C). Through careful balancing of gas pressures across the delicate MEA, we have demonstrated protonic-ceramic electrolyzer operation to 18 bar. We are extending protonic ceramics beyond fuel cells and electrolyzers to applications in CO₂ utilization, CH₄ upgrading, and NH₃ synthesis. The unique processing conditions brought by each application can have tremendous impact on the electrochemical performance of the protonic ceramic device. The oxidizing conditions presented by CO₂ upgrading can produce significant electronic conduction in the electrolyte, potentially reducing efficiency by more than 50%. Carbon deposition is expected during methane dehydroaromatization, bringing cell deactivation. High operating pressures are central to achieving practical ammonia synthesis rates, while sealing of electroceramics has proven challenging at atmospheric conditions. While many challenges remain, the unique properties of proton-conducting ceramics can be harnessed to in-part address our evolving energy needs.

2:30 PM **EF04.02

Circular Materials for the Green Energy Transition [Anke Weidenkaff](#); Fraunhofer IWKS and Technical University of Darmstadt, Germany

Green energy conversion technologies require green materials. The development of recyclable materials and the sustainable large scale production from secondary raw materials has to be based on sustainability and performance criteria defined by a holistic life cycle assessment. The implementation of intelligent green chemistry for synthesis and scalable production processes of substitution materials from waste will be based on profound knowledge on composition-structure-property relationship. An efficient circularity of the energy converters with a programmable lifetime and regeneration will be introduced as a suitable approach in this talk. The design of circular high performance materials is based on theoretical predictions and the criticality analysis of applied elements to improve the cycle life of future energy converters such as batteries, fuel cells, electric motors, generators and solar cells.

3:00 PM *EF04.03

Tubular Oxygen Transport Membranes for Energy [Ralf Kriegel](#) and [Olga Ravkina](#); Fraunhofer-Institut für Keramische Technologien und Systeme IKTS - Standort Hermsdorf, Germany

Energy production by fuel combustion dominates CO₂ emissions worldwide. Oxygen – O₂ - intensifies combustion and can save up to 50 % of primary fuel, especially at high process temperatures [1]. Advanced oxy-fuel power plants based on internal combustion with O₂ like Graz cycle or Allam-Fetved cycle [2] are much more efficient than conventional power plants. Since concentrated CO₂ is formed, oxy-fuel is the most efficient route for CO₂ separation from combustion [3].

The economic benefit of oxy-fuel combustion is always affected by the additional costs for oxygen supply. Mature O₂ technologies like ASU (cryogenic Air Separation Unit) are only competitive at very high O₂ throughputs. Customers with smaller O₂ demand are provided with LOx (Liquid Oxygen) or compressed gas entailed by O₂ costs growing steeply with decreasing O₂ demand. Scalable PSA (Pressure Swing Adsorption) and VPSA (Vacuum PSA) delivers O₂ with a purity of appr. 95% only. The residual gases N₂ and Ar are also contained in the CO₂ produced and affect its usability.

Since 2009, Fraunhofer IKTS is developing membrane plants for local production of O₂. Separation principle is always based on a patented vacuum process using MIEC membranes (Mixed Ionic Electronic Conductor). Last MIEC membrane plant has already realized a total energy demand of 0.72 kWh/m³(STP) O₂ (Standard Pressure and Temperature, 0,0 °C, 1.01325 bar) at a small production rate of appr. 9.6 m³(STP) O₂/h [4]. If a combustion of fuels or high temperature waste heat is used for balancing of thermal losses, the remaining electricity demand amounts to 0.20 kWh/m³(STP) O₂ only. Compared to an optimized ASU with 0.46 kWh/m³(STP) O₂ [5] or a delivery of LOx with at least 0.86 kWh/m³(STP) O₂ [6], a large part of expensive electricity and CO₂ emissions entailed could be saved. Accordingly, much lower OPEX (Operational Expenditures) will be possible entailed by a larger economic benefit for oxy-fuel combustion processes.

Advanced power plant processes could profit significantly on an O₂ membrane supply. The high combustion temperature enables an easy and efficient thermal integration. The remaining propulsion power for the vacuum pump system is less than a half of an optimized ASU decreasing the net efficiency already by 8 – 9% -points [2]. Accordingly, its total efficiency could be enhanced from 55% to appr. 59% to 60%.

Oxy-fuel operation of internal combustion engines (ICE) opens a simple route for local energy production together with CO₂ capture and utilization. Oxyfuel operation of ICE enables an increase of Carnot's efficiency together with CO₂ capture and elimination of NO_x emissions. Because of the low energy demand of MIEC membrane separation process, Oxyfuel ICE would be able to produce more energy from the same amount of fuel.

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3:20 PM *EF04.04

Inorganic Proton Conducting Membranes for Use in the Petrochemical Industry [Arian Nijmeijer](#)^{1,2}; ¹Shell Global Solutions International BV, Netherlands; ²Universiteit Twente Faculteit Technische Natuurwetenschappen, Netherlands

Inorganic ion conducting membranes have been under development for many years, unfortunately with limited to no commercial applications. However, it looks like change is coming. There are highly interesting developments in the field of these inorganic ion conducting membranes. Especially proton (hydrogen) conducting membranes are of interest in view of the anticipated electrification of the chemical industry.

Inorganic proton pumps enable electrical driven reactors to produce useful products (e.g. olefins or aromatics from natural gas or dehydrogenation of hydrocarbons such as alkanes to alkenes). Another application could be the production of high pressure hydrogen in (small, forecourt, scale) integrated steam reformers for hydrogen mobility. And last but not least similar ceramic proton pumps can also be used for efficient water electrolysis as well as co-electrolysis of water and carbon dioxide to syngas (and further to higher hydrocarbons).

The presentation will provide an overview of the various developments in this space within Shell.

3:40 PM BREAK

4:00 PM **EF04.05

Ionic Conducting Ceramic Membranes for Membrane Reactors—Potential Applications—Microstructures, Performance and Components Wilhelm A. Meulenber¹, Stefan Baumann¹, Wendelin Deibert¹, Nikolaos Margaritis², Remzi Can Samsun², Ralf Peters² and Olivier Guillon¹; ¹Forschungszentrum Julich Institut für Energie- und Klimaforschung, Germany; ²Forschungszentrum Julich GmbH, Germany

Ceramic mixed ionic-electronic conducting membranes can be used for the separation of single gases (e.g. hydrogen or oxygen) from gas mixtures or in membrane reactors. Ceramic membrane reactors (CMR) offer an opportunity to combine separation processes directly with chemical reactions, leading to process intensification and, hence, benefits with regard to efficiency. This integral coupling of both processes, separation and reaction, generates synergies between them. Current research activities focus on membrane reactors due to their high intrinsic efficiency and great potential for the production of a large variety of commodity chemicals, energy carriers, and synthetic fuels. This includes the reduction of CO₂ emissions and the utilisation/valorisation of CO₂. The development of ceramic membrane materials for such devices is focussed on performance and stability (chemical and thermal) in application relevant environments. The operating temperature is between 400-850°C. To reach a high performance, thin film membranes, active surface layers and thermochemical and -mechanical stable supports with designed porosity and microstructure are required. The lecture covers a literature study of all possible applications of mixed conductors and the manufacturing challenges from lab scale 15 mm diameter to relevant size (7cm×10cm) including characterisation of the membrane structures. The manufacturing is shown using sequential tape casting and lamination as well as freeze casting for different ion conductors. Finally, the construction of a Proof of concept of a membrane reactor will be shown. Furthermore, this concept is analysed for different operation modes with the help of computational fluid dynamics simulations for a selected application case. The lecture concludes with an outlook on future development directions.

4:30 PM **EF04.06

Catalytic Ionic-Membrane Reactors for Energy Storage and Synthetic Chemistry Jose M. Serra; Instituto de Tecnologia Quimica, Spain

Electrochemical solid-electrolyte cells enable the design of catalytic reactor processes that shift chemical equilibria favorably and facilitate the separation of reaction products. Ionic membrane reactors allow the intensification of equilibrium-limited reactions where H₂O or H₂ are produced. This contribution introduces the concept of electrochemically-driven catalytic reactors, enabling process intensification through integration of the catalytic reactions and separation in a single step. The role of the type of ion transport through the ceramic membrane electrolyte and the electrocatalysts' nature are presented and put in context for different catalytic reactions of interest. In addition, the membrane reactor operation was simulated and optimized by computational fluid dynamics (CFD) modeling, evaluating gas diffusion, heat transfer, and electrochemistry. We show how methane dehydro-aromatization (MDA), steam methane reforming (SMR) or direct CO₂ conversion into hydrocarbon processes, limited by equilibrium and coking, can be improved by integrating an ionic membrane achieving high catalyst stability and product yield beyond equilibrium limits. In particular, integrating a catalytic CO₂ reduction in an electrochemical catalytic membrane reactor allows to couple the thermo-chemical processes ascribed to: i) H₂O electrolysis and H₂ production using renewable electricity, and ii) CO₂ reduction to CO via RGWS followed by CO hydrogenation to valuable hydrocarbons. These results illustrate the promising use of ionic cells in industrial plants and electrification of chemical processes with high energy efficiency while mitigating CO₂ emissions.

5:00 PM *EF04.07

Protonic Ceramics in Intermediate-Temperature Membrane Reactors Robert Kee, Huayang Zhu and Sandrine Ricote; Colorado School of Mines, United States

Protonic ceramics (typically doped barium cerates and zirconates with perovskite structure), together with appropriate electrodes, enable a range of electrochemical reactor technologies. Because the proton conduction is highly activated, practical proton mobility is achieved at temperatures above 500 C. Thus, applications must involve chemical processes that benefit from elevated temperature. Although proton conduction is central to the desired membrane performance, the materials are mixed ionic-electronic conductors (MIEC) in which oxygen vacancies and small polarons are also mobile defects. Because practical reactor design and operation is significantly influenced by the MIEC behaviors, a predictive understanding is valuable to technology development.

Chemical transformations via heterogeneous catalysis often involve equilibrium-limited mole-producing chemistries. For example, with suitable catalysts methane dehydroaromatization (MDA) produces benzene from methane (i.e., $6 \text{CH}_4 = 9 \text{H}_2 + \text{C}_6\text{H}_6$). Removing the H₂ via a membrane beneficially shifts the equilibrium toward increased C₆H₆ yield and separates H₂ as a valuable co-product. High-temperature steam electrolysis using protonic ceramics (PCEC) is emerging as a valuable technology that supports the production of green hydrogen. There are significant advantages compared to solid-oxide electrolysis cells (SOEC) that use oxygen-ion-conducting membranes. One important advantage of PCEC is that it can deliver nearly dry H₂ directly, eliminating a subsequent separation process. These applications depend on electrochemical polarization to drive the protons through the membrane. Thus, external electrical energy (ideally from renewable sources) must be supplied to the reactor.

Although technology applications can be very different, there are important common elements in the protonic-ceramic membrane physics and chemistry. This presentation focuses on understanding and predicting the chemical, electrochemical, and transport processes that are responsible for desired membrane performance. Broadly speaking, the physics-based modeling is formulated as a Nernst-Planck problem. Compared to single-defect-conducting membrane materials (e.g., yttria stabilized zirconia, YSZ), the theory to predict defect transport within protonic ceramics is substantially more complex. The presentation will also discuss the impacts of defect (e.g., proton) introduction into, and removal from, the membrane via thermal defect-incorporation reactions and electrochemical charge-transfer reactions. Discussion of the underpinning theory and model implementation will be augmented with technology examples that illustrate salient aspects of the protonic-ceramic membrane performance.

5:20 PM *EF04.08

Nanoengineered Electrocatalysts Through Exsolution in Solid Electrolyte Membrane Reactors Towards Efficient Power-To-Chemical Transformations Vasileios Kyriakou; Rijksuniversiteit Groningen, Netherlands

Chemical energy storage is the transformation of electrical power into chemical energy carriers, allowing grid flexibility by backing up intermittent renewable sources. Once the excess renewable energy is stored into chemical bonds several pathways are opened for both re-electrification and mobility. For such type of storage, the electrosynthesis of chemical fuels from abundant molecules is key for a sustainable and secure energy future of our society. To commercialize, however, research efforts should result in a substantial increase in the efficiency of the existing processes through the development of selective and catalytically active mixed ion-electron conducting (MIEC) materials. In this context, the introduction of metal nanoparticles onto the MIECs, such perovskite oxides is instrumental in activating the inert molecules involved. Redox exsolution is a unique approach for introducing nanophases whereby the catalyst is substituted into the crystal lattice of the MIEC and is released as metallic nanoparticles at the surface upon reduction (reducing gas, applied bias, plasma) at temperature. Compared to the conventional deposition methods, exsolved particles are uniformly dispersed and anchored at the MIEC. These partly immersed, and hence confined nanoarchitectures, attribute stability and versatility to the system whilst providing access to enhanced catalytic properties. Here, the application of exsolution triggered by different agents towards increasing the performance and stability of renewable energy-

fuelled solid electrolyte membrane reactors is discussed. Different reaction systems are explored including solid oxide electrolysis of H₂O, CO₂ or both, as well as the fuel assisted operation, in which the endothermic electrolysis is combined with exothermic oxidations of renewable fuels to enhance the electrical efficiency of the process.

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5:40 PM EF04.09

Membrane Separation Reactor—Challenges and Steps Towards Hydrogen Mobility Xanthi Georgolamprou¹, Stéven Pirou¹, Sandrine Ricote², Wolff-Ragnar Kiebach¹ and Peter V. Hendriksen¹; ¹Danmarks Tekniske Universitet, Denmark; ²Colorado School of Mines, United States

The aim of the presented work is to develop a membrane reactor for hydrogen separation from carbon-based fuels. Such a membrane reactor can be used in mobile applications, where it can directly supply high-purity hydrogen to Proton Exchange Membrane Fuel Cell (PEMFC) stacks.

The membrane reactor consists of planar, symmetrical Proton Conducting Ceramic Cells (PCCCs). As fuel is supplied to one side of the membrane, a hydrogen-rich gas is formed via in-situ steam reforming. The hydrogen is then electro-chemically pumped to the other side of the cell through the electrolyte (consisting of BaCe_{0.4}Zr_{0.4}Y_{0.1}Yb_{0.1}O_{3-δ} (BCZYb4411)), and high-purity hydrogen is obtained. This concept is a promising alternative to the state-of-the-art hydrocarbon steam reforming, as it is completed in one step/one unit, is a less energy-intensive and costly process, while the performance is comparable [1]–[8].

This contribution will discuss some of the main challenges that arose during the development of such a membrane reactor. The focus will be on the cell development, the complexity of the sealing process in such a multi-layer device, and finally, the design implementation based on the unique characteristics of the symmetrical membranes.

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SESSION EF05: Poster Session I: Energy and Fuels Conversion I

Session Chair: Georgios Dimitrakopoulos

Monday Afternoon, July 18, 2022

6:00 PM - 8:00 PM

Mezzanine Level, Second Floor, Stadler

EF05.01

Ruthenium Doped LSCF Based Cathode for Enhanced Performance of Solid Oxide Fuel Cells Abid Ullah^{1,2}, Basharat Hussain¹ and Sayed Sajid Hussain³; ¹Korea Advanced Institute of Science and Technology, Korea (the Republic of); ²University of Science and Technology South Korea, Korea (the Republic of); ³Chungnam National University, Korea (the Republic of)

Recently, a tremendous upsurge in the research of Solid oxide fuel cells (SOFCs) has been documented due to cheap electricity production and without harming the environment. The development of efficient SOFCs requires more robust cathode for oxygen reduction. Until yet a copious amount of research has been done on varieties of materials including LSCF. In this work, Ruthenium is doped on the LSCF forming nanostructured Ru-LSCF with various Ru stoichiometric quantities. The Ru-LSCF catalyst is prepared via simplistic technique “Glycine combustion process”, producing evenly embedded Ru in LSCF perovskite materials leading to increased oxygen reduction reaction (ORR). The nanostructured Ru-LSCF cathode showed polarization resistance of approximately 0.031 Ωm² at 750 °C. The peak powers of approximately 1760.5, 1480.1, 893.3 mW/cm² were recorded at 750, 700, and 650 °C, respectively. Ru LSCF was quantitatively optimized for enhanced power production with high precision calculation. The results show that the Ru-LSCF optimum fabricated nanostructured cathode is promising catalyst for the reduction of oxygen at the cathode side for highly durable SOFCs.

EF05.02

Fabrication of PrBa_{0.5}Sr_{0.5}Co_{1.5}Fe_{0.5}O_{5+δ} Cathode for High Performance Proton Ceramic Fuel Cells Using a Piezoelectric Inkjet Printer Joon Hyung Shim¹, Wanhyuk Chang¹, Eun Heui Kang¹, Gwon Deok Han², Heon Jun Jeong¹ and Dong Hwan Kim¹; ¹Korea University, Korea (the Republic of); ²Stanford University, United States

Ceramic fuel cells have been actively studied and are in the commercialization stage due to economic and efficiency advantages including no use of precious metal catalyst including Pt, fuel flexibility and high efficiency. The most typical type of ceramic fuel cell is solid oxide fuel cells (SOFCs) that conduct oxide ions. However, the operating temperature of SOFCs is typically relatively high (>700 °C) because of high activation energy for the ion conduction. Prolonged operation at the high temperature can cause chemical and mechanical degradation in materials and peripheral parts discouraging use as a long-time stationary generator that is the main target market of SOFCs. For these reasons, expectations and interest in proton ceramic fuel cells (PCFCs) that have recently exhibited excellent power and durability at intermediate temperatures (<600 °C) have been increasing. In particular, according to recent reports, the durability of PCFC is superior to SOFC even in use of methane fuel or city gas. Cathode reaction accounts for the highest resistance in PCFC operation. Therefore, developing a high-performance cathode will be the biggest factor for PCFC success. In order to develop a high-performance cathode, the following factors must be optimized: 1) surface and interface shapes and components that can maximize the charge transfer reaction, 2) porous microstructure that can effectively deliver oxygen gas to the reaction sites, 3) electrolyte-electrode adhesion at the interface. The potential of inkjet printing (IJP) as a fabrication technology capable of optimizing these structures and components has recently been confirmed by our group. The IJP thin film process is a commercial technology that is economical and capable of large area processing. In addition, IJP can fabricate patterns freely without masking or complicated lithography. In this study, a porous $\text{PrBa}_{0.5}\text{Sr}_{0.5}\text{Co}_{1.5}\text{Fe}_{0.5}\text{O}_{5+\delta}$ (PBSCF) cathode was successfully fabricated using a commercial piezoelectric inkjet printer (P-IJP). We confirmed that the performance of the material produced with P-IJP is superior to the material synthesized with the conventional thermal IJP. The microstructure i.e. porosity and thickness of the PBSCF cathode was successfully controlled by managing the printing cycle and color level of the printing software. As a result, PCFC with PBSCF cathode made by the P-IJP achieved a high power of >0.5 W/cm² at 500 °C, which is one of the highest levels ever reported. In this presentation, we will discuss in more detail the correlation between the P-IJP process conditions and fuel cell performance.

EF05.03

Energetics of Formation of High Entropy Proton Conductors Aleksandra Mielewczyk-Gryn¹, Daniel Jaworski¹, Arkadiusz Dawczak¹, Wojciech Skubida¹, Iga Szpunar¹, Tamilarasan Subramani², Tadeusz Miruszewski¹, Kristina Lilova², Alexandra Navrotsky² and Maria Gazda¹; ¹Politechnika Gdanska, Poland; ²Arizona State University, United States

The so-called High Entropy Oxides (HEOs) constitute a new group of materials consisting of a minimum of five elements randomly occupying one position in the crystal structure and by this stabilize compound by configurational entropy [1]. Recently we reported that for some perovskite HEO the protonic contribution to conductivity has been identified [2]. To follow up we decided to synthesize and analyze the wider group of high entropy proton conductors belonging to two groups: perovskite HEO based on barium zirconate and fergusonite/scheelite HEO based on lanthanum orthoniobate. For such structures, the energetics of formation can be exceptionally interesting especially in comparison to low entropy equivalents. Therefore, we decided to employ high-temperature drop solution calorimetry [3] for the determination of values of enthalpies of formation of these oxides. The phase purity of the materials has been evaluated by the means of both XRD and SR-XRD.

Acknowledgments

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EF05.04

Electrophoretic Deposition of $\text{Cu}_{1.35}\text{Mn}_{1.65}\text{O}_4$ Spinel Powders for Interconnector Protective Coatings in SOFC Seong-Uk Oh, Dokyung Kim, Chan-Sik Choi, Woo Seop Shin, Sumi Kim, Eunji Kim, Seung Hyan Kim, Jung-A Lee, Young-Woo Heo and Joon-Hyung Lee; Kyungpook National University, Korea (the Republic of)

As the operating temperature of SOFC decreases to intermediate temperature ranges below 800 °C, interconnect materials have been replaced from ceramics to Cr-containing stainless steel alloys. However, the formation of a high resistance Cr_2O_3 oxide film and Cr poisoning deteriorates the performance of cells. To protect the chromium poisoning phenomenon and to improve the electrical conductivity of interconnectors with high area-specific resistance (ASR), researches on the anti-oxidation protective coatings on stainless steel have been conducted.

In this study, spinel structured $\text{Cu}_{1.35}\text{Mn}_{1.65}\text{O}_4$ powders were coated on 460FC stainless steel by electrophoretic deposition (EPD) method. Unlike other previous studies, the powder used in this study was formulated commercial grade, which was prepared by the general solid state reaction method. A suitable amount of iodine was dissolved in ethanol for the EPD process to make the $\text{Cu}_{1.35}\text{Mn}_{1.65}\text{O}_4$ powder charged with the highest zeta potential. The samples of the 460FC were immersed in the slurry, and a DC voltage of 20-60 V was applied for 30-120 s. The amount of the coated powders increased linearly as the coating time increased. The coated samples were heat-treated at 800 °C for 2 h in a 5% H_2 /95% N_2 atmosphere then oxidized at 700 °C for 50 h in air. The phase identification and microstructure observation of the coated films were conducted, and the ASR at 700 °C over 1000 h was evaluated. Among the various coating conditions, the sample coated at 40V for 60 s revealed a resistivity of ~15 mΩcm² after 1000 h at 700 °C.

EF05.05

Synthesis and Characterization of Nanocrystalline Ceria $\text{Ce}_{1-x}\text{M}_x\text{O}_2$ (M = Mn, Fe, Co, Ni, Cu, x = 0.1, 0.15, 0.2) Agata Ducka¹, Patryk Blaszczyk¹, Adrian Mizera² and Beata M. Bochentyn¹; ¹Politechnika Gdanska, Poland; ²Akademia Gornicza-Hutnicza imienia Stanisława Staszica w Krakowie, Poland

The exhaustibility of fossil fuels has led to the transition toward the so-called green sources of energy. One of them are Solid Oxide Fuel Cells (SOFC), which work the most efficiently when fed with pure hydrogen. Feeding with other fuels, such as biogas, leads to cell degradation. Thus, great effort has been put in the development of materials for SOFCs that work with alternative fuels. Among the anode materials that are intensively investigated for this purpose, ceria-based compounds can be found. They are considered good catalysts for biogas reforming and, additionally, they are able to improve long-term stability of the fuel cell by coking prevention [1]. Ceria (CeO_2) is known for its exceptional oxygen storage performance, due to its ability to easily shift between different oxidation states ($\text{Ce}^{3+} \leftrightarrow \text{Ce}^{4+}$) and high mobility of the ions [2]. Doping ceria with metals with lower oxidation states affects redox properties and enhances the formation of oxygen vacancies [3]. While a significant differences in the catalytic properties and operation of DIR-SOFC with ceria additive was observed depending on the type and amount of the introduced dopant, their origin has not been explained and understood so far. In this work a sample series of ceria doped with transition metals $\text{Ce}_{1-x}\text{M}_x\text{O}_2$ (TM = Mn, Fe, Co, Ni, Cu, x = 0.1, 0.15, 0.2) and an undoped reference sample have been synthesized by the reverse microemulsion method, which is reported elsewhere [1]. X-ray diffraction was performed on as-synthesized materials, which revealed that all samples were nanocrystalline (because of the broadening of the peaks). All XRD peaks corresponded to the CeO_2 phase, and no additional phases were observed in the case of as-synthesized oxides. The samples were then subjected to further annealing at higher temperature, in which recrystallization took place. After this step, the secondary phases of respective oxides were found in the materials. SEM imaging of the as-synthesized oxides confirmed the high nanocrystallinity. The average size of the crystallites did not exceed 100 nm, which was consistent with XRD studies.

However, the tendency to agglomerate was also observed for these materials. The EDS analysis coupled with SEM imaging proved that the composition of oxides was close to the nominal one. Other studies have been carried out with FTIR, which did not show any clear evidence of the presence of transition metals in the materials. Only vibrations corresponding to CeO_2 were visible. Additionally, to determine the behavior of the catalysts during activation and the reducibility of the metal oxides, H_2 -TPR measurements were performed. The search for a proper explanation of the structural properties of synthesized oxides led us to encourage the usage of more advanced characterization techniques involving synchrotron radiation. A series of X-ray Absorption Spectroscopy (XAS) measurements were performed at SOLARIS National Synchrotron Radiation Centre, Kraków, Poland. The XAS measurements revealed that in the case of all introduced dopants, transition metals were present in the form of oxides.

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EF05.06

Minimising Sr Precipitation on LSCF Electrodes—Chemical Surface Modifications Can Enhance Electrode Activity and Stability Filip Grajkowski, Sophie C. Coppeters, t Wallant, Bill Liu and Bilge Yildiz; Massachusetts Institute of Technology, United States

The development of next-generation solid oxide fuel cells (SOFCs) relies on the introduction of novel materials into these systems. Lanthanum strontium cobalt ferrite (LSCF) has been lauded for these applications due to its fast oxygen ion and electron conduction, along with its ability to promote high oxygen reduction activity. Such materials are promising for reducing the operating temperatures of SOFCs from ~800-1000°C down to ~400-800°C. However, the use of LSCF has been plagued by stability issues caused by Sr precipitation at the surface, yielding passivating layers of SrO, and poisoning by Cr-containing species, forming SrCrO_4 at the surface. Herein, we present a study of chemical surface modifications and their influence on the stability of LSCF electrodes. We have previously^{1,2} shown that the introduction of more oxidizable cations (such as Hf, Zr, Ti or Nb) at the electrode surface can effectively improve both the stability and the oxygen exchange kinetics of the electrodes. Motivated by this, here we make use of both a conventional solution infiltration method and a “surface sol-gel” deposition method;³ the latter involves the use of solubilized metal alkoxides and their subsequent reaction at the electrode surface to yield conformal coatings with precise thickness control, analogous to atomic layer deposition. The influence of these surface coatings on the electrode activity is characterized using electrochemical impedance spectroscopy and long-term performance studies. The physicochemical reasons behind the observed activity and stability changes are rationalized by a combination of x-ray photoelectron spectroscopy, electron microscopy and diffraction studies. Our results elucidate the morphology of the combined coating-electrode systems before and after operational cycling and highlight effective methods for optimizing the electrode surface chemistry as a means of minimizing Sr segregation at *in operando* conditions.

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EF05.07

Identification of Morphological Changes of Mixed Conducting Oxides Upon Anodic Polarization by an Electrochemical Method Martin Krammer¹, Alexander Schmid¹, Matthäus Siebenhofer^{1,2}, Christopher Herzig¹, Andreas Limbeck¹, Markus Kubicek¹ and Juergen Fleig¹; ¹Technische Universität Wien, Austria; ²Centre for Electrochemical Surface Technology GmbH, Austria

Microstructural and morphological changes at highly polarized oxygen electrodes (anodes) are a common issue of solid oxide electrolysis cells (SOECs). Post-test analyses with electron microscopy techniques reported in Refs. [1-3] revealed pore and crack formation in the electrode or electrolyte material or at the electrode/electrolyte interface as well as delamination of the anode from the electrolyte or the barrier layer. However, in order to identify such degradation processes at an early stage, it is desirable to use online electrochemical methods.

In this study, we use electrochemical impedance spectroscopy to identify microstructural changes of the mixed conducting oxide $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_{3-\delta}$ (LSC) upon anodic polarization. Dense LSC films were deposited on yttria-stabilized zirconia (YSZ) single crystals with and without a gadolinia doped ceria (GDC) interlayer by pulsed laser deposition, yielding polycrystalline and oriented films, respectively.

Chemical capacitance values of the electrodes were deduced from the obtained spectra. After the application of high anodic DC voltages up to 1 V, the chemical capacitance exhibits an unusual and irreversible increase upon anodic polarization. It turned out that this increase is stronger for the polycrystalline films. Moreover, correlations of this capacitive effect with oxygen exchange kinetics were analyzed. We found that the increase of the chemical capacitance is accompanied by morphological changes of the electrode. Our working hypothesis is that material segregating to the surface or interfaces under polarization leads to formation or enlargement of nanopores in the electrode or at the electrode/electrolyte interface. Hence, by analyzing the chemical capacitance of mixed conducting oxides upon anodic polarization it is possible to non-destructively identify morphological changes under operating conditions via an electrochemical method.

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EF05.08

Relationship Between Performance and Hydrogen Production Efficiency in Different Thickness of Cathode Materials for Solid Oxide Electrolyzer Cells Wei Cheng Chin, Hang Wen Wei and Yi Hsuan Lee; National Taipei University of Technology, Taiwan

In this study, $\text{La}_{0.9}\text{Sr}_{0.1}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{3-\delta}$ (LSGM) was applied as the electrolyte. Ni-SDC and $\text{SrFe}_{1.5}\text{Mo}_{0.5}\text{O}_{6-\delta}$ (SFM) were applied as cathode materials for solid oxide electrolyzer cells (SOECs). The different thicknesses of cathode materials were utilized to observe cell performances under 20% H_2O -80% N_2 atmosphere at 800 °C. The correlations between cell performance and cathodic thickness were observed. According to I-V curve results, in the case of Ni-SDC samples, cell performance increased with increasing cathodic thickness. It is indicated that triple boundary phases (TPBs) increased with the thicker cathode. However, the faradaic efficiency of hydrogen production became lower from 81% (10 μm) to 59% (20 μm) at the same current density. It is indicated that a part of supplied electrons may react with SDC especially in the thicker cathode. For this reason, the faradaic efficiency of hydrogen production is reduced. In the case of SFM cathode, cell performance maintained approximately the same values whether cathodic thickness. It is suggested

that TPBs did not change with increasing thickness. Also, the faradaic efficiency of hydrogen production maintained around 80% whether cathodic thickness. It is indicated that supplied electrons could transport smoothly in SFM cathode whether thickness.

EF05.09

Design of Anode Functional Layers for Protonic Solid Oxide Electrolysis Cells [Chunmei Tang](#), Sho Kitano, Hiroki Habazaki and Yoshitaka Aoki; Hokkaido University, Japan

Protonic solid oxide electrolysis cells (P-SOECs) are considered as one of the most efficient and cost-effective devices for hydrogen production from renewable electricity. P-SOECs based on proton-conducting perovskites, i.e., $\text{Ba}(\text{Ce}, \text{Zr}, \text{M})\text{O}_{3-\delta}$ ($\text{M} = \text{Y}, \text{Yb}$, etc.) enable an intermediate operating temperature region (400–600 °C) due to the low activation energy required for proton conduction (0.3–0.6 eV). One of issues in P-SOECs is a lack of suitable anode materials to promote anode reaction with oxygen evolution, thereby increasing the conversion efficiency. Many $\text{H}^+/\text{O}^{2-}/\text{e}^-$ triple conducting oxides, such as $\text{BaCo}_{0.4}\text{Fe}_{0.4}\text{Zr}_{0.1}\text{Y}_{0.1}\text{O}_{3-\delta}$ (BCFZY), $\text{PrNi}_{0.5}\text{Co}_{0.5}\text{O}_{3-\delta}$ (PNC), $\text{PrBa}_{0.5}\text{Sr}_{0.5}\text{Co}_{2-x}\text{Fe}_x\text{O}_{5+\delta}$ (PBSCF), $\text{NdBa}_{0.5}\text{Sr}_{0.5}\text{Co}_{1.5}\text{Fe}_{0.5}\text{O}_{5+\delta}$ (NBSCF) and $\text{PrBa}_{0.8}\text{Ca}_{0.2}\text{Co}_2\text{O}_{5+\delta}$ (PBCC) have been explored to spatially expand reaction zone to the whole anode particles. The triple conductivity of the anode materials has been found to be important to encourage the charge transfer to reactant and alternatively to suppress the hole injection to electrolyte. Herein, we demonstrate that both the steam electrolysis performances and efficiency of P-SOECs with $\text{BaZr}_{0.6}\text{Ce}_{0.2}\text{Y}_{0.1}\text{Yb}_{0.1}\text{O}_{3-\delta}$ (BZCYYb6211) electrolyte can be drastically improved by a use of $\text{H}^+/\text{O}^{2-}/\text{e}^-$ triple conducting $\text{Ba}_{0.95}\text{La}_{0.05}\text{Fe}_{0.8}\text{Zn}_{0.2}\text{O}_{3-\delta}$ (BLFZ) thin film (~140 nm) as anode functional layer (AFL) at the interface of electrolyte and conventional $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ (LSCF) anode. The electrochemical analysis clarifies that BLFZ AFL can significantly promote interfacial proton transfer at anode-electrolyte interfaces, resulting in low interfacial resistivity, and provide the reaction zones extended overall the surfaces of AFL and thus promote the anodic reaction without long range diffusion of oxygen species from gas-anode-electrolyte triple phase boundary (TPB) to LSCF anode surfaces. Hence, the BLFZ cell yields high electrolysis current of 570 mA cm^{-2} at 1.3 V under 600 °C benefiting from the minimal ohmic and polarization resistances (0.58 and 0.46 $\Omega \text{ cm}^2$), and an increased efficiency from 46% to 75% in comparison to the cell without BLFZ AFL at 500 °C. These results reveal that effective AFL can boost anodic reaction and optimize efficiency of P-SOECs.

EF05.10

Highly Active Non-Precious Metal Oxide and Carbon Nanopstructure Composite for Sea Water Reduction [Seung Hyun Hur](#), Jayasmita Jana and Tran Van Phuc; University of Ulsan, Korea (the Republic of)

Sea water, being abundant at earth surface, can become a promising energy source for generation of hydrogen fuel during electrolysis. However, the limitations including evolution of toxic chlorine gas as counter reaction of hydrogen evolution, catalyst poisoning, catalyst stability, and corrosion of electrodes are to be surmounted during electrocatalysis of seawater. Hence, along with mechanical methods for suppressing of chlorine evolution and designing of stable as well as efficient catalysts are needed as well. Recently, different nonprecious metal functionalities are being engineered in search of a stable, low cost, and efficient electrode material. It has been observed that the presence of carbon support on the metal oxide composite increased the electroactive surface area and catalytic activity. In this regard, an amorphous carbon nanosphere supported $\text{CuO}/\text{Co}_3\text{O}_4$ composite has been synthesized through heat treatment (CCuU). The synergism within spinel Co_3O_4 and monoclinic CuO boosted the electrocatalytic activity. CCuU was used as cathode material towards alkaline seawater a system. showed overpotential of 73 mV to attain the current density of 10 mA cm^{-2} , Tafel slope of 47 mV dec^{-1} , which are one of the lowest values among ever reported. In addition, the composite was stable enough and showed almost unaltered activity and morphology over long time chronopotentiometric study. Such amorphous carbon nanoparticle supported nonprecious metal oxide composites being first time reported for alkaline seawater electrolysis, would pave the way of designing different mesoporous nonprecious metal based electrocatalysts towards seawater electrocatalysis.

EF05.11

Non-Toxic (HF-Free) Synthesis of MXene and There Optimization for H₂ Evolution Activity and Stability [Ranjit D. Mohili](#), Monika Patel and Nitin K. Chaudhari; Pandit Deendayal Energy University School of Technology, India

MXenes are highly conductive, temperature resistant, chemically stable, and possess good cocatalytic property; and denoted by a general formula $\text{M}_{(n+1)}\text{X}_n\text{T}_x$ (M , X , and T stand for transition metal, carbon/nitrogen, and surface terminations such as OH, O, Cl, F, and etc. respectively and $n = 1-3$). In general, MXenes can be synthesized using hazardous HF by selectively etching out A layer from MAX (where A= 13-16 group element) phase precursors. In this work, we report MXene synthesized by non-toxic (HF-free) novel etching route. The resulting MXene has appreciably high conductivity, numerous hydrophilic functionalities (-Cl, -OH and =O) on its surface, and enhanced electrocatalytic performance. The MXene synthesized by this unique and non-toxic approach shows almost complete and successful etching of 13-16 group element and shows improved electrocatalytic H₂ evolution performance. To obtain layered structure of MXene, detailed study into the delamination of MXene is carried out in suitable solvent followed by SEM-EDX, TEM and X-Ray Diffraction study. Electrochemical water splitting test of this uniquely prepared MXene is also obtained.

Keywords: MXene, Two-Dimensional (2D), MAX, HF-free, Water splitting, Hydrogen evolution reaction

EF05.12

Effects of Irradiation Conditions on LDPE-Based Anion Exchange Membranes Properties—Performance and Stability [Andrey S. Barbosa¹](#), [Ana Laura G. Biancolli¹](#), [Alexandre Jose C. Lanfredi²](#), [Orlando Rodrigues Jr¹](#), [Fabio Fonseca¹](#) and [Elisabete I. Santiago¹](#); ¹Instituto de Pesquisas Energeticas e Nucleares, Brazil; ²Universidade Federal do ABC, Brazil

Anion exchange membranes (AEM) are polymeric solid electrolytes used in solid electrolyte-based electrochemical devices, such as fuel cells. This type of material has gained great emphasis in recent decades due to its high versatility and low cost when compared to well-established proton exchange membranes (PEM). Radiation-induced grafting (RIG) is a technique used in the preparation of polymeric AEMs. In this technique, the base polymer is copolymerized (grafting) with monomers derived from styrene by using radiation sources, such as electron beam and gamma rays, and followed by functionalized with quaternary ammonium groups (QA), whose are responsible for anion conduction properties. The properties of AEMs are highly influenced by the characteristics of the functional group, but also by the structure of the former polymer. The irradiation conditions, such as atmosphere (inert and/or oxidizing), temperature and absorbed dose during the irradiation of the base-polymer have been poorly explored in the literature but have shown to be fundamental in the understanding of AEM properties as well as the obtaining membranes with enhanced performance and stability. In this context, this work presents a systematic study of the influence of the irradiation conditions of low-density polyethylene (LDPE) films on the physical chemistry properties of the LDPE-grafted AEMs. The results show that the degree of grafting, degree of crosslinking, OH⁻ conductivity, stability and performance of AEMs in fuel cell are directly influenced by the irradiation. Impedance spectroscopy results showed that LDPE film irradiated at room temperature and air atmosphere achieves AEM conductivity of 120 mS cm^{-1} , while LDPE film irradiated at low temperature (-10 °C) the AEM conductivity increases up to 210 mS cm^{-1} . Such a result is highly related to fuel cell performance that, in this case, lead to an increase in power density from 800 mW cm^{-2} to 1100 mW cm^{-2} . Herein, it was also shown that the stability of membranes can be improved by more than 50% when the LDPE film is irradiated at low temperature. Thus, the conclusions of this study will help to understand and choose the best irradiation conditions for the preparation of anion exchange membranes for application in electrochemical devices.

EF05.13

Bio-Synthesis of Nanoscaled Er₂O₃ Using Egyptian *H.Thebaica* Plant Extract—Physical Properties & Photocatalytic Activity Hamza Mohamed^{1,2}; ¹UNESCO-UNISA Africa Chair in Nanoscience and Nanotechnology College of Graduates Studies, University of South Africa, South Africa; ²Nanosciences African Network (NANOAFNET), iThemba LABS-National Research Foundation, South Africa

In present study, pure Erbium oxide nanoparticles (Er₂O₃) have been synthesized by using the green syntheses approach through the use of *Hyphaene thebaica* fruit extract. XRD pattern confirms the formation of Er₂O₃ NPs with high crystallinity of the green synthesized nanoparticles. FTIR spectrum obtained confirms the Er-O spectrum at 573 cm⁻¹. HR-TEM of the nanoparticles confirm the quasi-spherical morphology of the Er₂O₃ with particle size in the range of 4nm to 9nm. Raman shift has been observed at 260 cm⁻¹, 650cm⁻¹ and 1500 cm⁻¹. The results also reveal the efficient photocatalytic properties of the newly synthesized Er₂O₃ through green synthesis approach.

EF05.15

Design of Highly Dispersed Metal Alloy Catalysts on Exsolved Nano-Socket in Supports for Hydrogen Production Hyung Jun Kim, Dongjae Shin, Tae Yong Kim and Jeong Woo Han; Pohang University of Science and Technology, Korea (the Republic of)

For decades, over use of carbon for human convenience has resulted in numerous forms of environmental pollution, including global warming. The move toward decarbonized energy sources, therefore, has been rising as a cutting-edge technology for sustaining a life of humankind. In this regard, hydrogen has been attracted because it is a renewable and energy-efficient resource without any hazardous byproducts. The production of hydrogen, however, requires energy-intensive process and/or utilization of petroleum-derived feedstocks. This situation indicates that a development of a highly active catalyst is required to realize hydrogen economy. Pt has a high level of activity in a variety of hydrogen production reactions. However, due to the high cost and scarcity of Pt, its use is limited. Atomically dispersed single atom catalysts have been actively investigated in order to utilize Pt more efficiently. Despite the efficient use of Pt, the loss of active sites due to insufficient stability creates a significant hurdle to commercialization and application in a variety of reactions. Meanwhile, designing a stable catalyst is also a critical issue to extend the interval of catalyst replacement or regeneration.

In this study, we overcame the limitations of conventional single atoms with low thermal stability and loss of active sites in these reactions by isolating Pt single atom on the isolated nano-socket site. We developed a highly stable and active catalyst by selectively dispersing Pt single atoms or ensembles on transition metal nanoparticles that are exsolved from the CeO₂ support. We first created exsolved nano-sockets (i.e., half-embedded nanoparticles) by doping a transition metal ions into the CeO₂ support and followed by treating under reducing atmosphere. The exsolved nano-sockets were strongly bound on the support surface, preventing them from the agglomeration. In addition, these nano-sockets work as strong binding sites for Pt metals. This binding property, in turn, was used to selectively disperse the single (or ensemble of) Pt atoms on the transition metal nano-socket by a rational synthetic protocol controlling surface charge. The isolated Pt on the immobile nano-socket physically prevents agglomeration between Pt atoms, and the strong bonding strength with the exsolved nano-socket inhibits the mobility of Pt even on this nano-socket surface, resulting in a high thermal resistance. This catalyst retains higher activity than conventionally loaded Pt single atoms on the CeO₂ due to the strong bonding strength between the exsolved nanoparticles and Pt single atom in reactions involving high temperature and water such as water-gas shift, dry reforming of methane, and wet CO oxidation. This approach will shed light on the design of single atom catalysts with high stability for a wide range of catalytic reactions.

EF05.16

Nucleation and Growth of Cu₂O—Effect of pH, Potential and Substrate Akhilender J. Singh, Garima Aggarwal, Sushobhita Chawla, Chandan Das and K. R. Balasubramaniam; Indian Institute of Technology Bombay, India

Nucleation and growth mechanism studies of functional oxide films are essential to gain an understanding of their deposition and thereby control their morphologies. Towards this, we study the effect of solution pH and deposition potential on the nucleation and growth of the technologically important material Cu₂O electrodeposited as a thin film on polycrystalline metal oxide and metal substrates. The Cu₂O films are deposited on FTO & Au substrates at three different overpotential values and in electrolytes of pH 9 & 12. The films deposited on both the substrates in a pH 9 electrolyte exhibit 3-D nucleation consisting of both instantaneous and progressive types. The growth of these nuclei is controlled by the diffusion of electroactive species as determined by the modeling of chronoamperometric data. The microstructural analysis shows that preferred orientation is dependent on overpotential instead of the substrate type. At low overpotentials, the Cu₂O films are 100 oriented at both the substrates, which starts to shift to 111 at higher overpotentials. The grain size of Cu₂O decreases from 4 μm to 0.5 μm within an increment of ~100 mV in overpotential on FTO substrates, whereas it increases from 100 nm to 500 nm on Au substrates. It is hypothesized that the number of sites available for nucleation is much higher on Au than FTO. An induction period of more than 60 secs is observed on Au at a low overpotential of -120 mV, where no nucleation occurs till the end of this period. However, such a long induction period is not observed on FTO, indicating that the difference in surface energies of sites available for nucleation is much less on Au than on FTO substrate. As a result, Au substrates are quickly covered with a very thin layer of Cu₂O. At a low overpotential of -120 mV, the growth of already existing nuclei takes place, whereas, at slightly higher overpotentials of -160 mV & -200 mV, homogeneous nucleation starts on an already existing thin layer of Cu₂O which gives rise to large size Cu₂O grains. When Cu₂O is electrodeposited in pH 12 media, the nucleation is still both 3-D instantaneous and progressive type. However, growth is now both diffusion and charge transfer controlled. In addition, the induction period as long as 450 secs are observed on Au substrates at low overpotentials. Such a long induction period in the pH 12 electrolyte compared to pH 9 indicates a change in electrolyte chemistry by the addition of hydroxide ions and its effect on electrochemical reaction for the deposition of Cu₂O. This study highlights the effect of changing overpotential and electrolyte pH on morphology and preferred orientation of Cu₂O thin films from modeling of chronoamperometric data and microstructural analysis.

EF05.17

Gadolinia Doped Ceria Infiltration into Ni-(Y₂O₃)_{0.08}(ZrO₂)_{0.92} Fuel Electrodes—Effects on Reversible Solid Oxide Cell Stability Jerren J. Grimes, Junsung Hong and Scott Barnett; Northwestern University, United States

Gadolinium doped ceria (GDC) nanoparticle infiltration into the Ni-(Y₂O₃)_{0.08}(ZrO₂)_{0.92} (Ni-YSZ) fuel electrodes of solid oxide cells (SOCs) has shown to significantly improve electrolysis performance and stability. However, the effects of GDC infiltration on SOC operated reversibly between fuel cell and electrolysis modes has not been reported previously. Here we report reversible SOC life test (~ 1000 h) results for different GDC infiltration loadings into Ni-YSZ electrodes of fuel electrode supported full cells with (SrTi_{0.3}Fe_{0.7}O_{3-δ}) STF air electrodes. Cell voltage measured versus time at current densities of +/- 0.5 A cm⁻² at 800 °C showed that the degradation rate is approximately halved going from an un-infiltrated cell to a cell infiltrated with the 0.5 or 1.0M infiltration solutions. Electrochemical impedance spectroscopy (EIS) revealed a lower initial cell area specific resistance (ASR); this, combined with the lower degradation rate with infiltration, led to an ASR reduction of 28% for a 0.5M GDC infiltrated solution and by 48% with a 1M GDC solution after 500 hours. Even after ~1000 h reversible operation, the infiltrated GDC retains considerable activity, even though the GDC nanoparticles coarsen considerably. Equivalent circuit modeling combined with distribution of relaxation analyses times suggests that the infiltrated nanoparticles lower charge transfer and O²⁻ ion resistances within the fuel electrode significantly compared to an un-infiltrated fuel electrode.

SESSION EF06: Proton Conducting Electrolysis Cells I

Session Chairs: Jong-Ho Lee and Zongping Shao

Tuesday Morning, July 19, 2022

Lobby Level, Avenue 34, Studio 1

9:10 AM **EF06.01**Process Intensified Flexible Chemical and Fuel Production Using Protonic Ceramic Electrochemical Cells at Intermediate Temperatures** Dong Ding; Idaho National Laboratory, United States

Protonic ceramic electrochemical cells (PCECs) are solid-state devices using the proton-conducting oxide as the electrolyte. Besides power generation as fuel cells, PCECs is an emerging technology that could be employed for flexible chemical manufacturing by using a range of feedstocks. Economically competitive PCEC systems have distinct advantages over conventional oxygen-ion conducting ceramic electrochemical cells, but further technology development and widespread market acceptance will require continuous innovation of materials and structures in order to improve cell performance, enhance system lifetime and reduce cost. Herein, we report the advancement of PCEC with new electrode component, catalyst integration, unique electrode structures as well as deep investigation on the state-of-the-art electrolyte materials to enable high-performance and robust operation for chemical and fuel production when sustainable feedstocks (e.g. steam, carbon dioxide and nitrogen) are used. Special emphasis is placed how the operating temperature is pushed down to lower region (e.g. 350-500°C), which shows huge potentials of PCEC as process intensified and decarbonization technologies compared with those industrial mature processes. At the end, we will also highlight the INL's effort on advanced manufacturing and scaleup of PCEC.

9:40 AM *EF06.02**Advanced Manufacturing of High-Performance Protonic Ceramic Electrochemical Cells and Stacks** Jianhua (Joshua) Tong; Clemson University, United States

Protonic ceramic electrochemical devices (PCEDs) such as fuel cells, electrolysis cells, reversible fuel cells, electrochemical hydrogen compressors, and electrocatalytic membrane reactors for ammonia synthesis, carbon dioxide upcycling, and fuel processing can operate at intermediate temperatures (400-700°C) because of the low proton transport activation energy, which allows the significant improvement of durability, materials cost, and efficiency of energy conversion and storage. In recent ten years, a significant amount of high-performance PCEDs have been achieved, based on small-area button cells (<0.5cm²) fabricated using spin coating, drop coating, manual brushing, and screen printing of electrolyte on the dry-pressed anode supports followed by co-firing. However, there are challenges to transferring the excellent microstructures and materials chemistries/properties to large-area cells and stacks. Furthermore, the decrease of cell component layer thickness for high volumetric cell performance and the requirement of more efficient, faster, and more cost-effective manufacturing motivated the advanced manufacturing of PCED cells and stacks. This talk gives a brief overview of what has been done about the advanced manufacturing of PCEDs in recent ten years from open literature. After that, we focus on the laser 3D printing (L3DP) of PCEDs performed at Clemson University in recent five years. The integration of 3D printing based on microextrusion and ultrasonic spraying and laser processing (sintering, drying, and cutting) allows manufacturing PCED components, single cells, and stacks with the desired microstructures and geometries. We demonstrated that the L3DP could rapidly and cost-effectively manufacture PCEDs without using conventional long-term furnace processing. The processing speed could be 1-2 orders of magnitude faster than the conventional tape-casting and furnace co-firing method. The achieved cells and stacks showed excellent fuel cell performance and less dependence on the effective area. This L3DP provided a new advanced manufacturing method for manufacturing the desired PCEDs, targeting the commercial applications, which can be expanded to manufacturing other ceramic-based energy conversion and storage devices.

10:00 AM EF06.03**High-Performance Reversible Protonic Ceramic Fuel Cells** Francesco Ciucci; The Hong Kong University of Science and Technology, Hong Kong

Reversible protonic ceramic cells (RePCCs) are promising energy storage and conversion devices that can accelerate the global transition to renewable energy sources.[1] However, the commercialization of RePCCs is limited by several factors, including high cost, poor stability, and insufficient electrode activity towards fuel oxidization/generation and oxygen reduction/evolution reactions (ORR/OER).[2, 3] Herein, we introduce Sr_{0.9}Ce_{0.1}Fe_{0.8}Ni_{0.2}O_{3-δ} (SCFN) perovskite-based nanocomposite and Ni-Fe alloy support as RePCCs air and fuel electrode, respectively, to address these issues. First, for air electrodes, we rationally design and develop a SCFN nanocomposite, composed of tetragonal and Ruddlesden-Popper perovskite with surface-enriched CeO₂ and NiO nanoparticles. Experiments and calculations suggest that RP phase promotes hydration and proton transfer, while NiO and CeO₂ nanoparticles facilitate O₂ surface exchange and O²⁻ transfer from the surface to the major perovskite phases. Hence, SCFN nanocomposite possesses high H⁺/O²/e⁻ triple conduction, thereby contributing to good ORR/OER activity.[4] Second, for the fuel electrodes, we further introduce a Ni-Fe metal-supporter, which possesses good mechanical strength and thermal compatibility with cermet-based electrodes/electrolytes, ensuring a facile cell fabrication and robust durability. Calculations suggest that the interface of the Ni-Fe support/fuel electrode and the diffusion of Fe towards the fuel electrode functional layer provide additional and more active sites for the hydrogen evolution reaction, further promoting H₂ production. The as-fabricated RePCCs at 700 °C achieved an excellent peak power density of 586 mW cm⁻² and an electrolysis current of -428 mA cm⁻² (at 1.3 V). Furthermore, the cell was exceptionally stable, as evidenced by 930 h of fuel cell operation with ultra-low degradation (~0.78 %/kh) and much better than an analogous anode-supported cell (~17.78 %/kh).[4] In addition, the cell was stable during 50 h of reversible fuel cell/electrolysis cycling further proving the potential of this type of cell. These research works propose a simple, new, highly active, and durable RePCC, thereby accelerating the commercialization possibilities of this technology.

Keywords: Reversible protonic ceramic cells, Nanocomposite, Metal-supporter, Energy storage and conversion**References**

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10:15 AM EF06.04

A Universal Bifunctional Air-Electrode for Oxygen-Ion- and Proton-Conducting Solid Oxide Cells with Exceptional Activity and Stability Jun Hyuk Kim, Dongyeon Kim, Sejong Ahn, Kang Taek Lee and WooChul Jung; Korea Advanced Institute of Science and Technology, Korea (the Republic of)

Solid oxide cells (SOCs) represent facile and sustainable routes to convert chemical fuels into electric power and vice versa on demand, thus are heralded as one of the key technologies to address current energy-storage-and-conversion challenge. However, the sluggish kinetics at air-electrode is the major barrier impeding the realization of high-performance SOC. Here, we present Ta stabilized barium cobalt perovskite oxides ($\text{BaCo}_{1-x}\text{Ta}_x\text{O}_{3-\delta}$) as highly active and durable bifunctional electrocatalysts that can be universally adopted on both oxygen-ion- and proton-conducting SOC. Doping strategy of pentavalent ion (i.e., Ta^{5+}) effectively stabilizes the hexagonal barium cobaltite to form cubic perovskite structure, resulting in highly boosted oxygen-electrocatalytic activity. Thereupon, with an optimum doping concentration, exceptional power densities (e.g., ~ 1.03 and $\sim 1.07 \text{ W cm}^{-2}$ at 550°C with $\text{Gd}_{0.2}\text{Ce}_{0.8}\text{O}_{2-\delta}$ (GDC)- and $\text{BaZr}_{0.4}\text{Ce}_{0.4}\text{Y}_{0.1}\text{Yb}_{0.1}\text{O}_{3-\delta}$ (BZCYYb)- based cell, respectively), outstanding water electrolysis current densities (e.g., 1.1 A cm^{-2} at 1.3 V , 550°C with BZCYYb-based cell) and remarkable stability (e.g., fuel cell mode > 700 hours, electrolysis mode > 500 hours, 100 hours of reversible operations, 10 rapid thermal cycles) were demonstrated, which are among the best values ever reported. This work also points toward the renaissance in the investigation of stabilized barium cobaltite as next-generation air-electrodes.

10:30 AM BREAK**11:00 AM EF06.05**

Exploring the Impact of $\text{Ba}(\text{ZrYPr})\text{O}_{3-\delta}$ Overlayers on Water Splitting Kinetics with $\text{Pr}_2\text{NiO}_{4+\delta}$ Anodes in Proton-Conducting Electrolysis Cells Mayuri M. Kushare¹, Sandrine Ricote¹, Jesse Fosheim¹, Su Jeong Heo², Andriy Zakutayev² and Gregory Jackson¹; ¹Colorado School of Mines, United States; ²National Renewable Energy Laboratory, United States

Proton-conducting oxide materials such as $\text{BaCe}_{0.8-x}\text{Zr}_x\text{Y}_{0.1}\text{Yb}_{0.1}\text{O}_{3-\delta}$ (BCZYYb) present a pathway for efficient water electrolysis between 500 and 700°C . High protonic conductivity of BCZYYb compositions (defined by different values of x) in proton-conducting electrolysis cells (PCECs) can lower operating temperature relative to solid oxide electrolysis cells. PCECs require alternative anode materials to reduce overpotentials associated with water-splitting kinetics and proton incorporation. $\text{Pr}_2\text{NiO}_{4+\delta}$ (PNO) have emerged as effective water-splitting anode electrocatalyst, but their low electronic and ionic conductivities limit charge transfer reactions near to three-phase boundaries, which increase anode overpotentials. Our collaborators at West Virginia University have proposed deposition of conformal overlayers of triple conducting $\text{BaZr}_{0.7}\text{Y}_{0.3-y}\text{Pr}_y\text{O}_{3-d}$ (BZYP) overlayers onto the PNO anode to enhance surface conductivity and thus, active surface area. To explore the impact of BZYP overlayers on PNO anodes, our team has developed electrolyte-supported PCECs using thin-film PNO anodes with and without BZYP overlayers to provide well-characterized geometries for electrochemical testing and in operando X-ray photoelectron spectroscopy (XPS) in relevant steam environments. This study presents some investigations into the changes in cell performance and surface chemistry on the PNO anodes with the BZYP overlayers.

To fabricate PCECs with thin-film anodes, BCZYYb ($\text{BaCe}_{0.4}\text{Zr}_{0.4}\text{Y}_{0.1}\text{Yb}_{0.1}\text{O}_{3-\delta}$) electrolytes and Ni/BCZYYb cathodes were prepared by solid-state reactive sintering. Patterned 300-nm -thick PNO films were deposited on a 1.0-mm -thick BCZYYb electrolyte via pulsed-laser deposition and annealed at 1200°C to form films with a porous structure. Some PNO films were coated with $>30\text{-nm}$ -thick BZYP ($\text{BaZr}_{0.7}\text{Y}_{0.15}\text{Pr}_{0.15}\text{O}_{3-\delta}$) overlayers. Thin Au current collectors were deposited over a narrow region of the thin-film electrodes. Electron microscopy showed columnar PNO film structures that create significant three-phase boundaries between the electrolytes and thin-film anodes.

Electrochemical characterization was performed on pre-hydrated cells between 550 and 700°C at constant anode flow H_2O mole fraction $X_{\text{H}_2\text{O}} = 37\%$. Measured open circuit values are below thermodynamic values by only 1.2% at 550°C , but this drop increases to 3.6% at 700°C due to increased electronic leakage. Measured $V-I$ curves with the thin-film anodes and electrochemical impedance spectroscopy (EIS) measurements show that BZYP overlayers reduce area-specific resistance of the PNO anode by $50\% \pm 4\%$ over the full temperature range. The EIS showed that the BZYP overlayers predominantly lowered the bulk resistance of the thin-film electrodes, which is consistent with the hypothesis that the BZYP increases surface conductivity and electrochemical active area of the thin-film electrode. The BZYP did not significantly reduce polarization resistance suggesting that the overpotential to drive the charge-transfer current did not change.

Environmental XPS at 500 to 600°C in 1.5-mbar H_2O pressure and in UHV on thin-film PNO (uncoated and BZYP-coated) electrodes were performed with a Scienta-Omicron HIPP Lab system. Comparison of the O $1s$ peaks between 528 and 535eV indicated that BZYP overlayers significantly reduced the extent of OH in the electrode's near surface region, which suggests a reduction in activity for H_2O splitting that offsets the expanded reaction area.

Accelerated surface electron transport would expand charge transfer reaction in water-splitting kinetics beyond the triple-phase boundaries. Analysis of the Pr $3d$ spectra quantified the Pr oxidation state with $\text{Pr}^{4+}/\text{Pr}^{3+} = 2.1\text{-}2.3$ at no bias, and this ratio did not vary with steam content or temperature. Biasing the cell with 0.6 V increased the Pr oxidation state with $\text{Pr}^{4+}/\text{Pr}^{3+}$ rising to $2.4\text{-}2.7$. Further E-XPS and electrochemical studies are providing insights to validate water-splitting mechanisms on PNO and BZYP.

11:15 AM EF06.06

A Proton Conducting Electrolyte with Improved Conductivity for Solid Oxide Electrolysis Cells Hanping Ding, Clarita Regalado Vera and Dong Ding; Idaho National Laboratory, United States

Hydrogen production via proton-conducting solid oxide electrolysis cells (SOECs) has been regarded as a promising approach to utilize the clean renewable energies and nuclear heat. To deliver fast water splitting reaction during intermediate-to-low temperature ($400\text{-}600^\circ\text{C}$) operation, an efficient electrolyte as one of key components is needed to achieve high electrolysis current density. With considerations on performance, chemical stability, and reliability, the barium-zirconate based electrolyte is selected as good parent composition for flexible adjust on structure and properties related to proton conduction. In this work, we present a new dopant (Scandium) that can enhance hydration ability to increase proton concentration and consequently improve conductivity. The relevant characterizations are performed to study the hydration behavior, proton conductivity, transference number, and chemical stability in the realistic conditions, and the underlying mechanism is also investigated. High electrolysis performances are demonstrated to show the great potential of this new composition for SOECs.

11:30 AM EF06.07

A Novel High-Entropy Perovskite Oxide Electrolyte for Reversible Protonic Ceramic Electrochemical Cells Minda Zou, Hua Huang, Hua Huang and Jianhua (Joshua) Tong; Clemson University, United States

Reversible protonic ceramic electrochemical cells (R-PCECs) based on proton conducting ceramics offer great potential for the cost-effective and efficient production of fuels and electricity for energy conversion and storage. However, it is difficult to achieve both high performance and excellent long-term stability due to the low ionic conductivity or the poor chemical stability of the available protonic ceramic electrolytes. In this work, a new type of protonic

electrolytes based on high-entropy perovskite oxides has been explored to achieve high ionic conductivity and excellent chemical stability against carbon dioxide and water. The conductivities and proton concentrations under different atmospheres are evaluated to understand the materials' electrical properties. The crystal structure stability and the electrical conductivities under the carbon dioxide and water-containing atmospheres are studied to assess the long-term stability under operating conditions. The electrochemical performance under fuel cell and electrolysis cell modes is also analyzed to demonstrate that high-entropy perovskite oxides can be promising candidates for R-PCECs.

11:45 AM EF06.08

Utilizing Mixed Ionic and Electronic Conducting Materials to Enhance Performance of Proton-Conducting Ceramic Electrochemical Devices [Charlie Meisel](#)¹, Long Q. Le², Carolina Herradon¹, Jake Huang¹, Youdong Kim¹, Ryan O'Hayre¹ and Neal Sullivan¹; ¹Colorado School of Mines, United States; ²Pacific Northwest National Laboratory, United States

Proton-conducting ceramic electrochemical devices (PCEDs) are a promising new technology for clean energy generation and green fuels production. PCEDs show favorable performance operating as fuel cells, but still lag behind their higher-temperature solid-oxide fuel cell (SOFC) predecessors. PCEDs display great promise in generating pure dry hydrogen while operating as electrolyzers, but more work is needed to increase electrolysis performance. This work sets out to tailor the positrode-electrolyte interface in PCEDs by increasing the oxygen reduction reaction (ORR) activity and oxygen transference to bolster electrochemical performance and durability.

The positrode-electrolyte interface is a major source of voltage loss during fuel cell operation and is also suspected to be a primary contributor to cell-level degradation. Both oxygen reduction (ORR) and H₂O formation must be simultaneously facilitated in the PCED positrode. This contrasts with SOFC positrodes, where only oxygen reduction is required since water formation occurs separately at the anode. The dual reaction processes occurring in a PCED positrode can lead to competitive interference between water adsorption/desorption and ORR activity. We hypothesize that placing materials with high ORR activity and oxygen-ion conduction at the positrode-electrolyte interface may help alleviate polarization loss.

To explore this hypothesis, we incorporate Er_{0.4}Bi_{1.6}O₃ (ESB), Dy_{0.08}W_{0.04}Bi_{0.88}O_{1.56} (DWSB), Gd_{0.1}Ce_{0.9}O_{1.95} (GDC10) and SmCoO₃ were fabricated into the positrode functional layers (PFLs) in this study. As the addition of an interlayer to the positrode-electrolyte interface can inadvertently affect the morphology (e.g. roughness, porosity) and mechanical integrity of the interface, control cells with a porous BaCe_{0.4}Zr_{0.4}Yb_{0.1}O_{3-δ} (BCZYYb) positrode functional layer were also fabricated and tested. PFLs were fabricated through ultrasonic spray coating of thin layers of the PFL material onto a precursor BCZYYb electrolyte and co-fired with the negatode support. The positrode is then brush painted onto the resulting half-cell and sintered to complete a full electrochemical cell. To further parse out effects of the interlayer materials and morphological changes, positrodes were also fabricated with each interlayer material homogeneously mixed into the bulk. The impact of PFL's was studied through microstructural and morphological characterizations, and AC and DC electrochemical performance measurements.

12:00 PM EF06.09

Effect of Partial Conductivities on the Polarisation Resistance of Positrodes for Proton Ceramic Fuel Cells and Electrolysers [Kalpana Singh](#), Truls Norby and Ragnar Strandbakke; Universitetet i Oslo Det Matematisk-naturvitenskapelige Fakultet, Norway

The lower activation energy for proton conduction when compared to oxide ion conduction enables operation of Proton Ceramic Electrochemical Cells (PCECs) – comprising Fuel Cells (PCFCs) and Electrolysers (PCEs) – at intermediate temperatures (400-700 °C).^[1-6] One of the main challenges of intermediate temperature operation is the limitations on positrode kinetics, i.e., oxygen reduction in fuel cell mode and steam oxidation in electrolysis mode. Conventional mixed oxide ionic and electronic conducting oxides do not exhibit acceptable PCEC electrode performance, as the protonic reaction sites are then restricted to the triple-phase boundary region. Literature has shown only a few materials with triple conducting properties (proton, oxide, and electron holes), but even fewer – if any – have shown the quantitative impact of the selective transport of the various charge carriers over electrode and electrolyte. To design high-performing PCEC positrodes, it is important to understand how partial conductivities affect the polarisation resistance (*R_p*) under anodic and cathodic biases. In the present work, we therefore study the effect of partial conductivities on the respective partial *R_p*'s under anodic, cathodic, and reversible operation, present a theoretical model for total resistance at direct current (DC), and discuss experimental challenges and interpretations of the obtained results. The results display trends highlighting the rate-limiting reactions occurring at a specific operating condition (temperature, DC bias, *pO₂*, and *pH₂O*) for positrode and electrolyte systems with a defined geometry, and specific partial electrical conductivities. Ultimately displaying the effect of partial DC resistances for protons and oxide ions on the solid oxide electrolyser (SOE)/PCE operation.

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12:15 PM EF06.10

Improving performance of Layered Cobaltite Cathode Materials for Reversible Protonic Ceramic Cells [Park Kwangho](#), Minkyong Jo, Gwangmin Park and Jun-young Park; Sejong University, Korea (the Republic of)

These days, global issues such as climate change and greenhouse effect are driving the search the clean next generation energy system. Among various energy production systems, solid oxide fuel cells (SOFCs) have shown several advantages such as high efficiency, negligible pollutant emissions, and great fuel flexibility [1]. However, some technical issues related to the high-temperature operation, such as chemical compatibility and thermal mismatch of components, cause irreversible performance degradations during operation of SOFCs [2]. For these reasons, the current research of SOFCs is mainly focused on lowering operating temperatures while maintaining high performances [3]. Further, as the alternative to high-temperature SOFCs, protonic ceramic fuel cells (PCFCs) are rising as a strong candidate because of high performances at reduced operating temperatures. However, PCFCs have a difficulty to apply the conventional SOFC's cathode materials because of their low proton conductivity. Hence, we try to develop novel layered cobaltite structure cathode materials for PCFCs with the triple-conducting (H⁺/O²⁻/e⁻) property.

Cobaltite materials are known to show good catalytic properties for oxygen reduction reactions (ORRs), but unfortunately, these materials usually have high

thermal expansion coefficient (TEC) values at operating temperature for PCFCs [4]. To solve this problem, we use the layered cobaltite material for the cathode of PCFCs because their a low TEC of $9\sim 10\times 10^{-6} \text{ K}^{-1}$ despite containing cobalt elements [5]. This value is suitable to a $\text{BaZr}_{0.1}\text{Ce}_{0.7}\text{Y}_{0.1}\text{Yb}_{0.1}\text{O}_{3-\delta}$ -based electrolyte. In addition, an alkali metal is doped into the layered cobaltite material to improve the ORR property at intermediate temperatures. Alkali-doped layered cobaltites are synthesized by the combined combustion-hydrothermal method and characterized by X-ray diffraction spectroscopy and secondary electron microscopy. The electrical conductivity is measured in the symmetrical cell configuration using an electrochemical impedance spectroscopy. Furthermore, the developed cathode materials are applied to the anode-support cell and their power density is also measured at 450-800°C.

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12:30 PM EF06.11

Performance Evaluation and Modelling of Electrocatalytic CO₂ Reduction in a Tubular Protonic Membrane Reactor Imanol Quina¹, David Catalan-Martinez¹, Sonia Escolástico¹, Laura Almar¹, Amir Masoud Dayaghi², Camilla Vigan³ and Jose M. Serra¹; ¹Instituto de Tecnología Química, Spain; ²Universitetet i Oslo, Norway; ³CoorsTek Membrane Sciences AS, Norway

Integration of membranes into reactors creates the opportunity to increase the conversion and yield for CO₂ reactions as well as the potential to increase energy efficiency for the production of carbon-neutral synthetic liquid fuels. In this work towards further process intensification via the direct electrochemical synthesis of long-chain hydrocarbons, also the CO₂ reduction into methane was studied in a tubular protonic membrane reactor composed of (i) $\text{BaZr}_{0.8}\text{Ce}_{0.1}\text{Y}_{0.1}\text{O}_3$ as electrolyte and (ii) $\text{Ni}+\text{BaZr}_{0.7}\text{Ce}_{0.2}\text{Y}_{0.1}\text{O}_3$ as electrodes, that allows the proton injection in the reaction chamber. Hydrogen production, CO₂ conversion, CO and CH₄ selectivity, impedance spectroscopy, and voltage distributions were studied as a function of the applied current density and the operational conditions (from 400 °C to 600 °C and pressures ranging from 1 to 30 bar). Total pressure plays a key role in both CO₂ conversion and CH₄ selectivity that strongly rises when pressure is increased above 20 bar, as demonstrated experimentally. Additionally, computational fluid dynamics (CFD) simulations were employed to optimize the reactor performance and to validate the experimental data with the modeling. These results provide critical knowledge about the thermodynamics, transport phenomena, and electrochemical performance of membrane reactors for electrocatalytic CO₂ reduction.

Acknowledgment: This study has received European Union's Horizon 2020 Research and Innovation funding under grant agreement No 838077.

SESSION EF07: Solar Cells II
Session Chairs: David Ginger and Nitin Padture
Tuesday Morning, July 19, 2022
Lobby Level, Avenue 34, Studio 2

9:10 AM **EF07.01

Recent Progress of Organic and Perovskite PV at UCLA Yang Yang; University of California Los Angeles, United States

In this presentation, I will firstly introduce the basic principle of photovoltaic (PV) materials and devices. Once the fundamental aspects have been laid out, I will follow with a detail discussion of organic photovoltaics (OPV) and perovskite (PVSK) PV technologies.

OPV technology, utilized organic and polymer materials as the active elements, which has emerged as one of the promising photovoltaic technologies. One of the features of using organic compounds as active materials is the narrow absorption. Compared to the early stage of OPV development when only wide-band-gap organic semiconductors were employed, the efficiency has been boosted from less than 5% to 19% in the past two decades through the design and synthesis of near-infrared organic conjugated molecules. The concept of near-infrared donors/acceptors was introduced by our group and became a turning point in the OPV field. I will summarize our work beginning in 2008 on the design and synthesis of near-infrared polymer donors/non-fullerene acceptors. Especially, we highlight our work on the first report on the near-infrared acceptor Y1, which pioneered the future development and usage of acceptors belonging to the Y1 family (or series).

On the other hand, perovskite solar cell is another major research in my group. Being solution-processed at relatively low temperatures, it is inevitable that crystallographic defects are formed in abundance during fabrication. Such defects may cause undesirable energy losses by non-radiative recombination to limit the performance of PSCs. More importantly, it has become apparent that defect activity is fundamentally responsible for the operational instability issues hindering the commercialization readiness of PSCs. In this presentation, the strategies and the in-depth mechanisms of preventing the formation of specific detrimental defects accumulated at grain boundaries or the surface will be reported, including by designing various passivation molecules with certain functional groups, such as carbonyl groups, amine groups, or sulfonic groups. I will also discuss our discovery on reconfiguring the band-edge states of photovoltaic perovskites by conjugated organic cations and the surface reconstruction behavior during post-treatments in perovskite process.

9:40 AM **EF07.02

Self-Healing in Solar Cells, Starring CIGS and Halide Perovskites David Cahen^{1,2}; ¹Weizmann Institute of Science, Israel; ²Bar-Ilan University, Israel

Self-healing, as distinct from repair or self-repair, implies that a material (or device or system) does not require any external factor to reconstitute itself after damage is inflicted. We'll start with the ability of Si solar cells to repair themselves, and of Si: Li detectors to self-heal. Then we move to the secret to CIGS' supposed radiation-hardness, which is not the static type (hard to damage) that we know from materials like InP, but a dynamic one, due to ion migration at operating temperatures. The Halide Perovskites, though, are quite a different kettle of fish, even if often described as fast ion (halide) conductors. All evidence points to their lattice dynamics as the cause of their ability to self-heal. While often misinterpreted for defect tolerance, that option can be eliminated as the root cause, by logic. The results of materials that I will present are badly needed to have a chance to understand what happens with complete devices, for which a wealth of experimental data is available for solar cells and for radiation and particle detectors, some of which will be discussed. Time permitting, guidelines for self-healing will be extracted from the data available for the materials that we and others have studied and continue to be surprised by.

10:10 AM **EF07.03

Controlling Charge, Spin and Light in Lead-Halide Inspired Hybrid Semiconductors and Semiconductor Nanocrystals Matthew C. Beard; National Renewable Energy Laboratory, United States

Hybrid organic/metal-halide inorganic semiconductors offer tremendous opportunities to control fundamental properties that underpin energy technologies. Inherent in these unique hybrid systems is the dichotomy between organic/molecular moieties and inorganic/extended systems. As a result, they exhibit properties that are not solely a juxtaposition of the inorganic and organic sub-units, but instead exhibit emergent or synergistic phenomena, with the concomitant ability to control and design new properties by judicious *choice* of the inorganic and organic components.

In this presentation, I will discuss a few studies of controlling the charge carrier dynamics, light/matter interactions, and spin populations. With respect to controlling spins we have studied and developed a novel class of chiral hybrid semiconductors based upon layered metal-halide perovskite 2D Ruddlesden-Popper type structures. These systems exhibit chiral induced spin selectivity (CISS) whereby only one spin sense can transport across the film and the other spin sense is blocked. We have demonstrated >80% spin-current polarization and high spin-injection efficiency from the chiral layer into a nanocrystal layer. To demonstrate our control, we developed novel spin-based light emitting diodes (LEDs) using non-chiral nanocrystals as the light emitting layer. The spin-LEDs emit circularly polarized light (CPL) with 2.5% discrimination at room temperature without the use of magnetic fields. We also demonstrate spin-PV systems, half-spin valves, and the circular photogalvanic effect (CPGE).

We are investigating carrier transport at various 2D/3D interfaces. For these layered systems we are interested in controlling both in-plane and out-of-plane transport. Two systems highlight our studies of how to increase the out-of-plane charge transport while maintaining the advantage of the 2D layers. One system consists of using the organic components to template a more favorable arrangement of the inorganic layers and thus increase out-of-plane transport. The other system contains a quasi-2D layer with attributes of both 3D and 2D. In another effort, some 2D layered systems exhibit a broadband emission that is more intense than the free-exciton emission.

Finally, we are studying NCs of metal-halide perovskite semiconductors as photocatalysts for light-driven chemical transformations. Recently we are taking advantage of the ease of cation substitution at the surface of the NCs to develop a photocatalyst that undergoes multiple sequential inner-sphere photo-oxidation events. A diamine substrate is bound to surface Cu^{+1} cations, which attract holes from the valence band of the NCs and promotes sequential oxidation of the bound diamine to form a N-N heterocycle.

10:40 AM BREAK

11:00 AM *EF07.04

Build a Direct Relationship Between Ultrafast Carrier Dynamics and Quantum Devices Jianbo Gao; Clemson University, United States

The understanding of ultrafast carrier dynamics has profound implications in basic fields in photophysics, photochemistry, and photosynthesis, and applied fields in photonics, optoelectronics, optical quantum communication, quantum computing, etc. Despite that classic time-resolved approaches such as time-resolved photoluminescence and pump-probe have revealed the interaction among the excited states carriers with phonon, spin, and other carriers, those all-optical approaches are limited by the carrier diffusion dynamics, and leave a significant gap between the dynamics and device applications.

In this talk, I will highlight we use an ultrafast photocurrent spectroscopy with the state-of-the-art time resolution to explore ultrafast carrier dynamics when devices are at work. Aim to break the limitations of solar cell efficiency and superconductor critical temperature, I will focus on low dimensional materials including perovskite nanocrystals (quantum dots) and 2D layer transition metal dichalcogenide (TMDC). Because of their unique electronic and phonon band structure, leading to the novel phenomena such as hot carrier and exciton quantum phase transition, the understanding of ultrafast dynamics may lead to next generation hot carrier solar cells and room temperature superconductors.

11:20 AM *EF07.05

Materials Engineering Approaches for Interface and Bulk for Perovskite Solar Cells Nikolai Tsvetkov; Korea Advanced Institute of Science and Technology, Korea (the Republic of)

Nowadays, in the face of global climate change, renewable energy has attracted a lot of attention in the scientific community. The conversion of sunlight into electricity is one of the most promising ways to satisfy the increased energy consumption without the detrimental impact of on the global climate. Perovskite solar cells (PSCs) have rapidly increased in power conversion efficiency within the past several years and attracted significant attention as low-cost alternative to silicon-based solar cells. However, for commercialization of PSCs, it is of primary importance to enhance the perovskite material stability and charge transfer efficiency at the PSC interfaces.

First, I will talk about hybrid organic/inorganic light absorber material, methylammonium lead iodide (MAPbI_3), when it is in contact with different, organic or inorganic, charge transfer layers for solar cells applications. The performance of perovskite solar cells based on MAPbI_3 is limited by surface recombination at Electron Transfer Layer (ETL)/ MAPbI_3 and MAPbI_3 /Hole Transfer Layer (HTL) interfaces [1-3]. The defects at the interfaces with charge extraction layers slow down the charge extraction rate leading to increased loss of photo-generated carriers. For efficient hole extraction from perovskites, the CdSe Quantum Dots (QDs) of various sizes were used as charge transfer mediators between MAPbI_3 and Spiro-MeOTAD HTL. Moreover, the application of the QDs yields an increase in the light-harvesting efficiency of solar cells in both visible and near-IR ranges of the solar spectrum. Time correlated single photon counting measurements confirmed the Förster resonance energy transfer from small-sized, 2 nm, QDs to MAPbI_3 leading to the raise of photocurrent response under visible light. QDs of larger size, 4 nm, improved near-IR light absorption due to light backscattering at the MAPbI_3 /QD interface. From the side of the ETL, the major challenge is in realizing the full potential for the charge transfer at the perovskite/ETL interface [2,3]. It was shown that the metallic layer could be formed at the interface TiO_2 /perovskite when TiO_2 is covered with a PbO monolayer [2]. As the atomistic origin of the emergent two-dimensional interfacial metallicity, first-principles calculations performed on the representative MAPbI_3 /PbO/ TiO_2 interface identify the interfacial strain. Direct and indirect experimental evidence for the presence of interfacial metallic states are provided, and a nonconventional defect-passivating nature of the strained interdigitated perovskite/ETL interface is emphasized.

The final part of the presentation is on the improvement of the stability and charge transfer within the perovskite layer itself. Here, I would like to present an effective strategy to modulate moisture using a hygroscopic copper(II) benzene-1,3,5-tricarboxylate metal-organic framework (Cu-BTC MOF) hybridized with a light-absorbing perovskite layer for PSCs. Metal-organic frameworks (MOFs), crystalline porous materials that consist of inorganic metal nodes and organic linkers, have a high degree of synthetic tunability. The introduction of Cu-BTC MOF enlarged the perovskite crystal grains and enhanced its moisture resistance. Besides, this MOF offers additional pathways for electron extraction in the light-absorbing layer, thus facilitating the transfer of photo-excited electrons. As a result, the PSCs with perovskite-MOF hybrid delivered enhanced power conversion efficiency and ambient stability.

References

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11:40 AM EF07.06

Supported Bimetallic Nanostructures Through Galvanic Restructuring of Exsolved Nanoparticles for Catalytic Versatility [Xiaolan Kang](#); Universitetet i Oslo, Norway

There is a growing need to develop new ways of controlling and tuning nanoparticles to increase their stability and effectiveness, especially for photo- and electrochemical energy conversion applications. Exsolved particles have been shown to be well anchored and can be re-shaped without changing their initial location and structural arrangement. However, this usually involves lengthy treatments (20–40 hours) and the use of toxic gasses (CO). Here we use the galvanic replacement/deposition method which is simpler, safer, and leads to a wealth of new nanostructures with a higher degree of tailorability. The produced NiAu bimetallic nanostructures supporting on SrTiO₃ display exceptional activity in plasmon-assisted photoelectrochemical water oxidation reactions. *In situ* transmission electron microscopy is used to visualize the structural evolution of the plasmonic bimetallic structures, while theoretical simulations provide mechanistic insight and correlate the surface plasmon resonance effects with the structural features, and enhanced PEC performance. We demonstrate the versatility of this concept in shifting catalytic modes to the hydrogen evolution reaction by preparing NiPt nanoparticles on highly reduced SrTiO₃ supports. This methodology enables the design of supported bimetallic nanomaterials with tunable morphology and catalytic functionalities.

11:55 AM EF07.07

Photocatalytic Oxygen Evolution Reaction for Bismuth Ferrite Loaded with IrO₂ [Wegdan Ramadan](#)¹ and Detlef Bahnemann^{2,3}; ¹Alexandria University Faculty of Science, Egypt; ²Institut für Technische Chemie, Leibniz Universität Hannover, Callinstr. 3, D-30167, Germany; ³Saint-Petersburg State University, Laboratory “Photoactive Nanocomposite Materials”, 198504, Russian Federation

Here we report on the photocatalytic OER, of BiFeO₃ nanoparticles synthesized by sol gel. Oxygen evolution reaction is challenging because production of one molecule of gaseous oxygen, O₂, requires four holes and occurs on a time scale approximately 5 orders of magnitude slower than that required for H₂ evolution. There are two important issues to address when photocatalysis intended for water redox reaction to takes place; sacrificial agents to be used and the co-catalyst to be loaded on surface. For the former and in case of OER a sacrificial agent acts as an electron acceptor. Although many choices of sacrificial electron donor are available for water reduction to produce H₂, the choices are narrowing down to only few for sacrificial electron acceptors used for water oxidation to produce O₂. Silver, Ag⁺, and ferric, Fe³⁺ ions are commonly used for this purpose and to a lower extend sodium persulfate, Na₂S₂O₈, is sometimes used. The redox potential of Ag⁺, Fe³⁺ and S₂O₈ at pH zero are 0.8 V, 0.77 V and 2.05 V, respectively. The redox potential of Ag⁺ and Fe³⁺ are much closer to the conduction band of BFO and their values are less than that of S₂O₈. It is reported that both the quantum efficiency and the stability of the colloidal nanocrystals in solution improve with increasing redox potential of the scavenger. The higher redox potential leads to faster scavenging, which in turn increases quantum efficiency and stability of the catalyst. This finding is important for choosing hole/electron scavengers and for comparing efficiencies and stabilities for different photocatalytic nano systems. Hence the resolve to Na₂S₂O₈ as electron scavenger. Mott Schottky measurements and the UV-Vis spectroscopy showed that the band positions of BFO, the conduction band and valence band lie at 0.46V and 2.69 V with respect to NHE, respectively. To enhance BFO photocatalytic OER, IrO₂ nanoparticles as a co-catalyst were loaded on the surface using impregnation method. OER showed two folds enhancement upon loading with 2wt% IrO₂. IrO₂ is one of the best catalysts for OER, unfortunately it is also one of the most expensive rare elements, so their applicability is limited by the high cost. Reducing IrO₂ content onto the system should be an option to make its application feasible and cost effective and loading on IrO₂ nanoparticles on the surface could be feasible solution. Scanning the loaded IrO₂ content on BFO from 0.5 wt% up to 4 wt% showed a maximum of the evolved oxygen at 2wt % followed by a decrease in activity. XPS showed the 4f peaks of Ir, it shows symmetric two peaks at binding energies 64.9 and 61.87 eV corresponding to the 4f 5/2 and 4f 7/2 of Ir (IV) respectively. TEM indicated non uniform distribution of it on the surface. Charge carrier lifetime and dynamics for pure BFO and IrO₂ loaded BFO have been studied by means of laser transient absorption spectroscopy, TAS. Absorption peak was observed around 560 nm and suffered significant reduction in its intensity after introducing N₂-methanol atmosphere. This in turn indicates that this signal could be assigned to holes. And to further elucidate this result, transient absorption as function of time was recorded for pure BFO powder at 560 nm in three different atmospheres; N₂, N₂-methanol and O₂, which acts as an electron scavenger. As the holes react rapidly with the methanol, the whole transient absorption spectrum in the methanol environment shows remarkably lower absorption, around 80% less, compared to N₂ atmosphere. On the other hand, a slight change in the case of O₂ atmosphere was observed. This clearly indicates that holes and not electrons are the dominant photogenerated charge carriers around the 560 nm. To the best of our knowledge, there is no reports about TAS of BFO dealing with the identification of absorption spectra of the photogenerated charge carriers, holes and/or electrons, hence it was important to address this point in this work.

12:10 PM EF07.08

Unraveling the Structural Properties of Ba₂CuWO₆ Thin Films [Olivia Wenzel](#), Moritz Braun, Heike Stoermer, Michael Hoffmann and Dagmar Gerthsen; Karlsruher Institut für Technologie, Germany

This work focuses on the structural, chemical, and optoelectronic properties of Ba₂CuWO₆ thin films synthesized by pulsed laser deposition for future ferroelectric solar-cell absorber layers. We want to use laterally polarized ferroelectric domains and their electric fields to drive the photogenerated charge carrier towards the domain walls, along which they can be extracted into the electrodes. Early results on the efficacy of this idea were achieved with methylammonium lead halide (MAPb) perovskites [1]. However, we strive for a non-toxic ceramic-based material with similar properties. A possible material system with desirable properties and suitable bandgap energy is Ba₂CuWO₆ (BCW), where Ba²⁺ occupies the A site with alternating Cu²⁺ and W⁶⁺ on the B site in the ABO₃ double perovskite structure. In this contribution, the material properties are investigated in detail by different electron microscopic techniques on the nanoscale to understand the bulk material's optoelectronic properties and improve material synthesis. BCW films were deposited by pulsed laser deposition (PLD) on a fluorine-doped tin oxide (FTO) layer. We used several analytical scanning/transmission electron microscopy (S/TEM) techniques for comprehensive characterization, such as quantitative energy-dispersive X-ray spectroscopy (STEM-EDXS), electron energy loss spectroscopy (STEM-EELS), selected area electron diffraction (SAED), and other imaging modes. X-ray diffractometry (XRD) was additionally applied.

The presented BCW thin films are polycrystalline with a thickness of 340 nm. Bright-field S/TEM images reveal a columnar microstructure with 30–50 nm small grains at the FTO substrate interface that grow to 170 nm width at the BCW surface. Crystal structure analysis of the thin films demonstrates the dominant phase to be tetragonal Ba₂CuWO₆ with a tetragonal distortion of 9.7%. We find ferroelectric domains in bright-field TEM images in large grains with domain sizes below 10 nm, which points toward BCW having ferroelectric properties as previously observed by [3].

An average composition of Ba(Cu_{0.7}W_{0.6})O_{3.3} was obtained by quantitative EDXS, which is close to the target composition. However, in addition to BCW, one sample shows numerous needle-shaped CuO precipitates within the BCW film. This copper oxide phase is frequently observed at the FTO-BCW interface. CuO precipitates are frequently oriented diagonally within the BCW thin film. In-depth STEM-EELS investigations of the fine structure of the oxygen-K edge confirm the presence of monoclinic CuO, which can be differentiated from the distinct K edge of oxygen of the BCW perovskite. Further, a broadening of the O-K edge fine-structure of BCW points towards a more pronounced structural disorder of this BCW thin film at the surface. We relate these structural features to the PLD conditions, and adjustment of the synthesis conditions resulted in marked improvement in chemical heterogeneity and a reduction of copper oxide secondary phases. Both the presence of the CuO phase and the structural disorder at the surface of the thin films can explain the

measured UV-Vis and photoluminescence spectra where deviations from the expected properties can be observed for this particular sample. This study shows that BCW thin films were successfully synthesized by tuning the PLD synthesis conditions based on the comprehensive electron microscopic analysis. Looking ahead, we are aiming to fine-tune the ferroelectric domain structure and move from PLD to spin coating due to the lower production cost.

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12:25 PM EF07.09

Ionic Effect on Space Charges at Interfaces Between MAPbI₃ and Contact Materials Mina Jung, Gee Yeong Kim, Alessandro Senocrate, Davide Moia and Joachim Maier; Max-Planck-Institute Stuttgart, Germany

Most hybrid perovskite solar cells (PSC) consist of a stacked structure with a perovskite thin film layer and charge carrier transporting layers (CTLs).[1] Among the main challenges in the optimization of this class of devices, non-radiative recombination at the contact interfaces is a key factor which can significantly reduce the open circuit voltage of PSCs. Therefore, understanding and modifying interfacial effects in PSCs is critical to improve their photo-conversion efficiency. Indeed, several studies showed improvement in PSC performance through engineering of the interfaces between halide perovskites and CTLs.[2,3]

CH₃NH₃PbI₃ (MAPI) is the most intensively studied material in the field of PSCs. MAPI is a mixed ionic electronic conductor, where iodide vacancies are the majority ionic mobile carriers, with minor contribution to ion conduction from Pb²⁺ and MA⁺ defects.[4] Ion conduction is expected to have significant influence on the interfacial properties of PSCs, however its role on the performance of these devices is largely unexplored.

In this study, we discuss experimental evidence of ionic effects on space charges at the interfaces between MAPI and various contact materials, such as insulating oxide Al₂O₃, electron transporting oxide TiO₂, and hole transporting oxide NiO. We used zeta potential measurements performed on nanoparticles of these materials in electrolyte containing lead-based salts, for investigating the surface charge of the oxides. The results indicate the tendency of all these materials to strongly interact with positive charged ions, which are expected to adsorb on their surface. When oxide particles embedded in perovskite thin films, these particles can induce the depletion of positive charge carriers and accumulation of negative charge carriers in proximity of their surface. To verify this hypothesis, we investigated the ionic and electronic conductivity of MAPI:oxides composite films using AC impedance and DC polarization as a function of the oxide nanoparticles concentration. The results show that, for TiO₂ and Al₂O₃, a space charge zone is formed in MAPI, confirming the interaction of positive ions with the oxide surface. This finding indicates that the local conductivity due to ionic and electronic charge carriers at the perovskite/oxide interfaces can have a dominant contribution on the overall film conductivity compared with MAPI film. For the case of NiO, we observe a different behavior, which seems to suggest accumulation of positive charges at the interface of MAPI with this oxide. We discuss possible interpretations of this effect based on the NiO contribution to the total conductivity and the possible contribution of electronic equilibration. To show that interfacial ionic effects are relevant also for “flat” interfaces, as it is the case for common solar cell structures, we show conductance measurements performed on horizontal architectures of MAPI films with different thicknesses deposited on Al₂O₃ substrates. The results once again confirm the trend observed for the composite films, indicating the formation of an ionically induced space charge at the interface, despite the redox-inactive nature of the oxide used.

This study shows that ionic charge carrier redistribution at the interface between halide perovskite and oxides is a critical factor affecting electronic charge carrier behavior and space charges at interfaces relevant to solar cell devices.

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SESSION EF08: Oxygen-Ion Conducting Electrolysis Cells I
 Session Chairs: Georgios Dimitrakopoulos and Poul Moses
 Tuesday Afternoon, July 19, 2022
 Lobby Level, Avenue 34, Studio 1

2:00 PM **EF08.01

The Puzzling Interplay Between Operating Conditions, Overpotentials and Degradation Mechanisms Anne Hauch, Ming Chen, Henrik Lund Frandsen, Anke Hagen, Peter V. Hendriksen, Soren H. Jensen, Rainer Küngas, Theis Skafte, Mogens Mogensen, Xiufu Sun and Marie L. Trulsen; Danmarks Tekniske Universitet, Denmark

With the integration of increased share of energy from renewable, but fluctuating, energy sources there will be an increased demand for large-scale flexible conversion of electrical energy into easy storable chemical fuels. Electrolysis will be a part of the future energy conversion and storage solutions and studies show that e.g. a region like Europe will need electrolysis capacity in the range of 1600 GW simply to de-carbonize heavy-duty transport [1]. The solid oxide cells (SOC) can provide the most efficient electrolysis technology [2]. Furthermore, the solid oxide electrolysis cell (SOEC) technology has improved tremendously in terms of initial performance, long-term durability and up-scaling of cell and stack sizes; and with respect to commissioning and operation of SOEC plants [3]. Nevertheless, it is evident that further improvement of electrochemical performance and especially long-term durability is crucial for the coming up-scaled and integrated SOEC systems as part of our energy grid. This calls for research in thorough mapping of degradation mechanisms, determination of thresholds for onset of irreversible degradation processes, degradation wise safe operating conditions and means to mitigate known degradation processes etc. However, degradation is not a simple singular property and most often there is a puzzling interplay between parameters such as chosen electro-catalysts, manufacturing of cell components, the obtained microstructures, resulting initial electrochemical performance, operating conditions and the nature and extend of different degradation processes.

In this keynote speak we will therefore present an overview of the puzzling interplay between initial electrochemical performance and long-term durability and provide examples of multiple and complementary characterization techniques applied for the analyses of these features and processes (e.g. SEM, TEM, Raman spectroscopy and electrochemical impedance spectroscopy). Furthermore, we will present strategies to mitigate and/or limit specific degradation processes and insight into data required to establish degradation wise safe operating conditions. Among the performance characteristics and degradation processes that will be touch upon in this presentation are: 1) TPB and critical micro/nano-structural parameters of the porous Ni/YSZ electrode; 2) the perception of electrode overpotential and why this parameter is more important than the set current density or operating cell/stack voltage, 3) effect of

impurities, 4) the interplay between impurities and carbon deposition and 5) last but not least the degradation caused by Ni migration and actions to mitigate this degradation process. The focus in this presentation will be on results obtained from test and characterization of technological and commercially relevant SOECs which in turn means typically employing a Ni/YSZ based fuel electrode, YSZ electrolyte and commonly applied oxygen electrodes such as LSFC/CGO and LSC/CGO.

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2:30 PM **EF08.02

Degradation Processes in Solid Oxide Electrolysis Cells Scott Barnett, Qian Zhang, Jerren Grimes, Dalton Cox, Junsung Hong, Beom-Kyeong Park, tianrang Yang and Peter Voorhees; Northwestern Univ, United States

Solid oxide cells (SOCs) should operate at useful current densities with degradation rates that are low enough to allow operation over useful time frames. Thus, it is important to understand degradation mechanisms and to reduce degradation rates to economically viable operating lifetimes. This presentation will discuss experimental and theoretical analysis of processes that cause electrochemical performance degradation of SOCs operated in electrolysis or reversible modes. Experimental results on oxygen electrode delamination are explained using a model to predict the oxygen partial pressure at or near the electrode/electrolyte interface, and comparing this with the materials' fracture strength. The magnitude of the oxygen pressure reached depends strongly on the electrode overpotential, explaining why high-performance MIEC electrodes achieve much better stability than LSM-based electrodes. Experimental results indicate that Ni-YSZ fuel electrodes can degrade during high-current-density electrolysis via Ni migration away from the electrolyte under high-steam conditions, or zirconia reduction under low-steam conditions. Phase-field modeling of Ni migration will be described and compared with experimental observations. Recent work on SOC electrolyzers, making use of electrode infiltration to provide good stability, is described. Finally, results on degradation during SOC reversing-current cycling are described and compared with that during electrolysis.

3:00 PM *EF08.03

Exsolution of Nanoparticles on Ni Doped (La,Sr)FeO₃—Its Effect on Co-Electrolysis of CO₂ and H₂O for Syngas Production Umit Ozkan¹, Jaesung Kim¹, Dhruva Deka¹, Matt Ferree¹, Seval Gunduz¹, Jean-Marc Millet² and Anne Co¹; ¹The Ohio State University, The Ohio State University, Columbus, OH, US, academic, United States; ² Institut de Recherche sur la Catalyse et l'Environnement de Lyon, France

A promising strategy to reduce the atmospheric CO₂ levels is to convert CO₂ into valuable chemicals and fuels. Nowadays the electrocatalytic conversion of CO₂ has received significant attention due to the fact that the high-temperature electrolysis of CO₂ and co-electrolysis of CO₂ and H₂O for syngas production processes offer higher conversion and enhanced reaction kinetics since the system can be operated at elevated temperatures.

In the scope of this study, A-site deficient Sr and Ni-doped lanthanum ferrite type perovskite oxides (LSNF) were synthesized as SOEC cathode materials. The exsolution of nanoparticles on LSNF cathode induced by reduction and its effect on the co-electrolysis of CO₂ and H₂O for syngas production were investigated using various *ex-situ/in-situ* characterization techniques. The TPR, ETEM and *in-situ* XRD results revealed that LSNF material experiences the exsolution of B-site metals and Ruddlesden-Popper (RP) phase under a reducing environment at 500–800°C. The *ex-situ* XRD pattern of the reduced LSNF (Red-LSNF) showed that Red-LSNF was composed of hetero-phases including La₂NiO₄ (RP-phase), zerovalent Ni and La₂O₃ with a uniform size distribution (4.2–9.2 nm) and dispersion (1.31–0.61 particle μm²). The electrocatalytic activity results showed that Red-LSNF has significantly higher activity for the co-electrolysis of CO₂ and H₂O due to the presence of reduced oxidation states of B-site ions, as evidenced by XPS and XANES results, better accessibility of the active sites via exsolution of active nanoparticles to the electrode surface, and formation of oxygen vacancies that serve as adsorption sites for CO₂ and H₂O.

3:20 PM *EF08.04

Solid Oxide Cells—Theory and Stability of Oxygen Electrodes Xiao-Dong Zhou; University of Louisiana at Lafayette, United States

In this talk, I will describe the fabrication of high performance solid oxide cells with a thin electrolyte based on doped zirconia. Electrochemical performance for both fuel cells and electrolyzers will be discussed. I will focus this talk on the discussion of the development of accelerated test protocols and improvement of durability of solid oxide cells. Theoretical analysis and modeling will be described to calculate and model the electrode local environment during operation. The electronic conduction of the interlayer will be incorporated in the model to illustrate its role on the electrolysis performance and performance stability.

3:40 PM BREAK

4:00 PM EF08.05

Pr- and Co-Substituted Rare Earth Nickelates as Air Electrodes for Solid Oxide Electrolysis Cells Werner Sitte, Sarah Eisbacher-Lubensky, Kathrin Sampl, Andreas Egger and Edith Bucher; Montanuniversitat Leoben, Austria

Compounds of the mixed conducting first-order (n=1) Ruddlesden-Popper-type nickelates Ln_{n+1}B_nO_{3n+1} with Ln=La, Nd, Pr and B=Ni are promising (alkaline earth free) materials for application as air electrodes in solid oxide cells. They show fast oxygen transport, high catalytic activity for the oxygen reduction reaction, as well as good electronic and ionic conductivities. It could be demonstrated that partial substitution of Ni by 10% of Co increases the oxygen surface exchange rates of Pr₂NiO_{4+δ} (PNO) [1]. Interestingly, long-term stability tests with Pr₂NiO_{4+δ} electrodes also indicated an increased resistance against Cr-poisoning in the SOEC mode compared to La₂NiO_{4+δ} [2].

Within this work, the properties of La₂NiO_{4+δ}-based electrode materials with A-site substitution by Pr and B-site substitution by different amounts of Co have been investigated in order to improve the oxygen surface exchange kinetics. Results will be given for La_{1.8}Pr_{0.2}Ni_{0.9}Co_{0.1}O_{4+δ} (LPNCO18291) and La_{1.8}Pr_{0.2}Ni_{0.8}Co_{0.2}O_{4+δ} (LPNCO18282), compared with Pr-free La₂Ni_{0.9}Co_{0.1}O_{4+δ} (LNCO291) and La₂Ni_{0.8}Co_{0.2}O_{4+δ} (LNCO282). Chemical diffusion and surface exchange coefficients of oxygen as well as electronic conductivities were available from conductivity relaxation measurements on dense samples in the temperature range of T = 600 - 800°C and oxygen partial pressure range pO₂ = 0,001 – 0,1 bar. The oxygen non-stoichiometry was obtained by thermogravimetric analyses in the same temperature and pO₂ ranges.

Additionally, the results from performance tests with LPNCO18291 and LPNCO18282 air electrodes will be reported. The tests were conducted on full cells at 800°C in SOEC operation mode in humid atmospheres with current densities up to 1000 mA/cm².

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4:15 PM EF08.06

Tailoring Nano-Catalysts Exsolution with *In Situ* Ion Irradiation Towards Enhanced H₂O Splitting Jiayue Wang¹, Kevin B. Woller¹, Abinash Kumar¹, Iradwikanari Waluyo², Adrian Hunt², Zhan Zhang³, Hua Zhou³, James LeBeau¹ and Bilge Yildiz^{1,1}; ¹Massachusetts Institute of Technology, United States; ²Brookhaven National Laboratory, United States; ³Argonne National Laboratory, United States

A central theme in renewable energy technologies today is to design nanostructured catalysts at the solid/gas and solid/liquid interfaces towards desired reactions. A recent advance in materials for electrochemical energy and fuels conversion is to synthesize metal nanoparticle catalysts anchored onto the oxide surface in a process termed “exsolution”. Exsolution generates stable and catalytically active metal nanoparticles via phase precipitation out of a host oxide. Unlike traditional nanoparticle infiltration techniques, the nanoparticle catalysts from exsolution are anchored in the parent oxide. This strong metal-oxide interaction makes the exsolved nanoparticles more resistant against particle agglomeration as compared to the infiltrated ones. In addition, the exsolved particles also open up the possibility of regeneration of catalysts. To date, the concept of exsolution has been successfully applied to a number of applications including solid oxide electrochemical cells, ceramic membrane reactors, chemical looping combustion, and (electro)catalysis.

As the exsolution process starts with a solid solution that contains the to-be-exsolved transition metal ions, this method is often limited by the intrinsic solubility limit of the host oxide. Here, we propose that ion beam irradiation be a unique tool to promote exsolution as it can introduce defects and dopants into the host oxides and at concentrations higher than thermodynamic limits. Moreover, due to the surface sputtering effect, ion beam irradiation can modulate the surface morphology, creating novel nanostructures. To demonstrate this approach, we chose thin-film SrTi_{0.65}Fe_{0.35}O₃ (STF), a promising electrode material in solid oxide fuel/electrolysis cells, as a model system and examined its exsolution behavior under *in-situ* Ni⁺ beam irradiation at 800 °C. As a result, we found that Ni irradiation not only reduced the size of the exsolved nanoparticles, but also changed the nanoparticle composition from unitary metallic iron to Fe-Ni alloy. Moreover, we showed that the Ni irradiated STF exhibited enhanced oxygen evolution reaction (OER) activity compared to the conventional thermally exsolved STF. These observations suggest that ion beam irradiation can be a robust and generalizable method to promote and tailor exsolution-synthesized nano-catalysts, which can benefit a wide range of applications in clean energy storage and conversion.

4:30 PM EF08.08

Controlling the Dispersion of Pt Catalyst Through Heteroatom Doping of CeO₂ Support Seunghyun Kim¹, Gunjoo Kim¹, Kyeounghak Kim², Sangwoo Kim¹, Yong Beom Kim¹, Jeong Woo Han², Hyunjoo Lee¹ and WooChul Jung¹; ¹Korea Advanced Institute of Science and Technology, Korea (the Republic of); ²Pohang University of Science and Technology, Korea (the Republic of)

The size and dispersion of reactive metal particles on oxide support is an important factor for the reactivity of heterogeneous catalysts. Atomically dispersed single atom catalysts are recognized for their maximum metal efficiency however, at the same time, their catalytic activity and selectivity are still under debate. For certain reactions, metal ensemble sites of the highly dispersed nanoclusters are desired however, for others, selectivity driven from the homogeneous active site of single atoms is more beneficial. Therefore, a specific strategy to control the dispersion state of the active metal species on the atomic scale is required to design highly active catalysts depending on their target reaction.

Here, we present a model catalyst of highly dispersed Pt on CeO₂ based oxide and investigate the effect of heteroatom (Sm) doping on the dispersion of Pt catalyst. Through the combination of various atomic resolution analyses and density functional theory (DFT) calculation, we reveal that Sm atoms on the surface can work as a clustering site for Pt atoms and result in highly dispersed Pt clusters compared to the fully dispersed single atoms on bare CeO₂ support. For the demonstration of the catalytic activities of the dispersion-controlled model catalysts, CO oxidation, thermochemical catalysis, and oxygen reduction reaction, an electrochemical catalytic test is performed. This heteroatom doping technique can feature an easy way to control the structural catalyst design for the metal supported catalysts.

4:45 PM EF08.09

Chemical Capacitance Peaks of La_{0.6}Sr_{0.4}CoO_{3-δ} Electrodes Upon Anodic Polarization Caused by Extremely High Oxygen Gas Pressures in Pores Martin Krammer¹, Alexander Schmid¹, Matthäus Siebenhofer^{1,2}, Christopher Herzig¹, Andreas Nennung¹, Andreas Limbeck¹, Christoph Rameshan¹, Markus Kubicek¹ and Juergen Fleig¹; ¹Technische Universität Wien, Austria; ²Centre for Electrochemical Surface Technology GmbH, Austria

Mixed conducting oxides are promising for the application as air electrode (anode) in solid oxide electrolysis cells (SOECs). Particularly perovskite-type La_{1-x}Sr_xCo₃Fe_{1-y}O_{3-δ} (LSCF) is interesting due to its good oxygen diffusivity and catalytic activity for the oxygen evolution reaction. However, undesired degradation processes may occur under operation conditions including formation of detrimental secondary phases at the anode/electrolyte interface and anode delamination from the electrolyte. High oxygen chemical potential (or high equivalent oxygen partial pressure) together with porosity seem to be key factors for these degradation phenomena. Hence, further clarification of the role of pressure build-up and closed pores at the oxygen electrode upon SOEC conditions is desirable.

In this work, the chemical capacitance of porous La_{0.6}Sr_{0.4}CoO_{3-δ} (LSC) thin film model electrodes is used to observe and quantify oxygen partial pressure build-up in closed pores upon anodic polarization (corresponding to the SOEC mode). For this purpose, closed porosity was enforced by a dense capping layer on a porous thin film, all prepared via pulsed laser deposition. These electrodes exhibit extremely high capacitance peaks with values of more than 8000 F/cm³ at anodic overpotentials higher than 100 mV. However, in contrast to chemical capacitances in mixed conductors under cathodic or less anodic conditions, we do not face a point defect related phenomenon. Rather, the huge capacitance increase can be traced back to gaseous oxygen in the pores of our electrode. This oxygen is present under conditions far beyond the applicability of the ideal gas law.

We demonstrate that the measured capacitance increase agrees very well with calculated chemical capacitances deduced from a real gas equation. Thus, our electrochemical measurements can quantify this novel capacitive effect at anodic polarization as well as determine simultaneously pressure and fugacity (up to gas pressures of >10⁴ bar and fugacities of >10⁷ bar) in few nanometers wide closed pores.

5:00 PM EF08.10

Synthesizing Functional Ceramic Materials for Solid Oxide Cells in Minutes Through Thermal Shock Weiwei Fan¹, Zhichu Ren¹, Zhu Sun², Xiahui Yao¹, Bilge Yildiz¹ and Ju Li¹; ¹Massachusetts Institute of Technology, United States; ²Xi'an Jiaotong University, China

Ceramic fuel/electrolysis cells are key energy/material conversion devices. Here, we report that by thermal shock, mixed ionic and electronic conducting electrode materials with perovskite structure can be successfully synthesized within 2 min, while it needs two-step calcination and almost 40 h by using the conventional furnace. This benefits from the large driving force supplied to the system, greatly enhancing the reaction kinetics among the raw materials. Moreover, typical electrolyte materials with fluorite structure, such as YSZ and SDC, are also synthesized in several minutes through thermal shock, which significantly reduces the fabrication time of a solid oxide cell. Also, one can easily prepare multiple samples at one time via tailoring the carbon support to the desired size. The availability of fast synthesis of the thermal shock technique enables the development of new functional ceramic materials for SOCs in a high-throughput and economic manner.

5:15 PM EF08.11

***In Situ* Optical Studies of Operando Generated Ni-Based Alloy Nanomaterials as Fuel Electrodes in Solid Oxide Electrochemical Cells** Syed N. Qadri¹ and Xiangling Yue²; ¹U.S. Naval Research Laboratory, United States; ²University of St. Andrews, United Kingdom

Recent effort in material development for solid oxide fuel cells has been focused on developing nanostructure through exsolution, which has been demonstrated as an effective approach to producing electrode materials with superior performance and stability, primarily due to the excellent catalytic properties offered by the well-embedded nanoparticles that are exsolved from a supporting oxide. Here, we focus on investigating titanate perovskites with exsolved Ni-Co alloy nanocatalysts as fuel electrodes for SOCs, particularly on operando generation of these nanomaterials by applying a potential bias in CO₂ electrolysis operating conditions.

Previously, the ability to understand the underlying mechanisms for electrolysis of CO₂ and co-electrolysis of CO₂ and steam has been hindered due to a lack of experimental methods that can probe intermediate species and materials directly during operation. Although there have been studies on using Ni-YSZ and ceria based cathodes for electrode materials in high temperature solid oxide electrolysis cells (SOECs), these have mainly utilized post-mortem and *in situ* electrochemical analyses. Here, we present an *in situ* duplex technique that combines near infrared thermal imaging (NIRTI) and Fourier-transform infrared emission spectroscopy (FTIRES) to monitor processes for electrolysis of CO₂ and co-electrolysis on operating SOECs. The results are correlated with traditional electrochemical measurements to identify any polarization dependence on species during the course of reactions under a range of conditions. These studies serve as benchmark data for better understanding the processes during CO₂ electrolysis in real working conditions for exsolution-based electrode materials.

5:30 PM EF08.12

Steam/Carbon Dioxide Co-Electrolysis and Methanation in SOEC Modified by Transition Metals Nanoparticles Patryk Blaszczyk¹, Sea-Fue Wang², Marcin Zajac³, Beata M. Bochentyn¹ and Piotr Jasinski⁴; ¹Politechnika Gdanska Wydział Fizyki Technicznej i Matematyki Stosowanej, Poland; ²National Taipei University of Technology, Taiwan; ³National Synchrotron Radiation Center SOLARIS, Poland; ⁴Politechnika Gdanska Wydział Elektroniki Telekomunikacji i Informatyki, Poland

Recently, the problem of air pollution has increased the demand for research in the field of green energy provision and storage. Although energy can be easily generated from renewable sources, such as wind or solar farms, the problem of storage of excess energy still exists. The conversion of this energy into chemical fuels is of high interest because it can stabilize the grid at the time when a renewable source might not generate enough power. Furthermore, the recirculation of CO₂, the most infamous greenhouse gas, produced by power plants should be highly efficient in reducing its emission into the atmosphere. The one good way to reuse the CO₂ gas is through electrolysis or coelectrolysis. The Solid Oxide Electrolysis Cell (SOEC) possesses two major advantages over other electrolysis techniques, that makes it much more interesting solution to the aforementioned problems. First, high operation temperature favors fast kinetics and lowers the electrical energy input for water electrolysis. On the other hand, SOECs can simultaneously split H₂O and CO₂, generating higher output of reactive CO molecules that can be further utilized. Two parallel processes of CO₂/H₂O splitting and Reverse Water-Gas Shift (RWGS) reaction take place in SOEC fuel electrode chamber. This can lead to enhanced overall process efficiency. Furthermore, the heat from SOEC setup and operation can also be transferred to a hydrogenation reactor for the synthesis of e.g., methane, ethane, methanol, dimethyl ether, or ammonia, which are easy to store and transfer [1]. The proper catalysts should allow for an increase in the overall efficiency of the coelectrolysis process by altering the electrochemical reactions occurring at the fuel electrode of SOEC.

In this study, a novel method of SOEC modification was developed by βCD-assisted wet impregnation of the fuel electrode with transition metal nanoparticles. Conventional Ni-YSZ cermet electrodes of SOEC were enriched with Co-, Cu-, Fe-, Mn-, and Fe-oxide nanoparticles, which were further reduced during the SOEC start-up procedure. Modified cells were tested towards performing H₂O/CO₂ coelectrolysis process. The addition of native cyclodextrin to the precursor solution affected the nanoobject formation step and resulted in nanoparticles of high dispersity and homogeneity throughout the whole electrode material. The impregnation route allowed us to easily introduce various amounts of metals into Ni-YSZ after repeated cycles of deposition. The nanoparticles and their interface with the Ni and YSZ grains were characterised by the means of XRD, SEM, XPS, and H₂-TPR/O₂-TPO techniques. It was observed that the addition of secondary can lower the reduction temperature and increase the resistance to reoxidation. XAS measurements were performed for the most interesting samples to reveal the dependence between the chemical surrounding/electronic structure and the overall performance increase. The formation of mixed Ni valence (e.g. spinel phase compounds) is a most possible source of the performance enhancement. As an example, SOEC impregnated twice with Co precursor solution presented an increase in the CO₂ conversion rate by over 20% at a voltage of 1.3 V. At the same time, the electrical efficiency was also higher or remained the same as for the unmodified sample. Furthermore, the long-term tests revealed nearly no degradation of the Co-impregnated cell at 1.3 V. The new approach to SOEC modification can lead to the development of onsite H₂/CO delivery systems.

References

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SESSION EF09: Solar Fuels I
Session Chairs: Sean Bishop and Avner Rothschild
Tuesday Afternoon, July 19, 2022
Lobby Level, Avenue 34, Studio 2

2:00 PM **EF09.01

Thermochemical Properties of Non-Stoichiometric Perovskite and Related Oxides for Solar Fuel Generation Sossina Haile; Northwestern University, United States

Solar-driven thermochemical production of chemical fuels using redox active oxides has emerged as an attractive means for storing solar energy for subsequent use on demand. In this process a reactive oxide is cyclically exposed at high temperatures to an inert gas, which induces partial reduction of the oxide, and to an oxidizing gas of either H₂O or CO₂, which oxidizes the oxide, releasing H₂ or CO. The capacity for fuel production is dictated by the thermodynamic properties of the oxide, specifically the enthalpy and entropy of reduction. Less appreciated is the fact that the fuel production rate is also highly dependent on the thermodynamic properties. Here we review progress made in measuring the thermodynamic functions for a range of materials and in identifying suitable thermodynamic values for efficient fuel production.

2:30 PM **EF09.02

Sustainable Transportation Fuels from Sunlight and Air Remo Schäppi and Aldo Steinfeld; Eidgenössische Technische Hochschule Zurich, Switzerland

Developing solar technologies for producing carbon-neutral transportation fuels has become a global energy challenge, especially for the long-haul aviation sector. A promising solution are drop-in fuels – synthetic alternatives for petroleum-derived liquid hydrocarbons such as kerosene, gasoline or diesel, which are compatible with the worldwide existing infrastructures for fuel distribution, storage, and utilization. Among the many possible approaches for solar-driven processes, the thermochemical path using concentrated solar radiation as the source of high-temperature process heat utilizes the entire solar spectrum and thus offers potentially high production rates and efficiencies. It can deliver truly carbon-neutral fuels if the required CO₂ is obtained directly from atmospheric air. If H₂O is also co-extracted from air, feedstock sourcing and fuel production can be co-located in desert regions with high solar irradiation and limited access to water resources. While individual steps of such a scheme have been implemented, we now demonstrate the stable operation under real field conditions of the entire thermochemical solar fuel production chain to drop-in fuels from concentrated sunlight and ambient air. Crucial to this accomplished milestone is the serial integration of three thermochemical conversion processes, namely: 1) the co-extraction of CO₂ and H₂O directly from air via an amine-based adsorption-desorption cycle; 2) the solar co-splitting of CO₂ and H₂O to produce a tailored syngas mixture via a ceria-based redox cycle; and 3) the conversion of syngas to liquid hydrocarbons via Fischer-Tropsch or methanol synthesis. We further identify the R&D needs aimed at process optimization and upscaling, and describe the roadmap towards the long-term decarbonization of the aviation sector.

3:00 PM *EF09.03

Solar Fuels—From Lab to Market Christian Sattler, Martin Roeb, Freidemann Call and Josua Vieten; Deutsches Zentrum für Luft- und Raumfahrt eV, Germany

In a time of massive transitions in the energy economy promising research needs to be developed into applications. Solar fuels has been a research topic for over twenty years. However, because of the missing economical and political conditions the way into application was nearly impossible. This started to change after the Paris Agreement signed at COP 21 in 2015. Today, the application can't be fast enough to contribute to the defined climate goals. Therefore, materials designed to convert solar energy efficiently into fuels need to be available in large quantities. Numerous of such materials are described on a research level and are continuously improved on targets like stability and reactivity. Additional targets need to get in the focus even more like the use of abundant materials, and the possibility for mass production. The talk will discuss specifically solar thermochemical processes and the reactive materials necessary to carry out solar fuel production in an industrial scale. And it will give a view on the strategy how to implement the technologies on a global scale.

3:20 PM *EF09.04

Efficient Plasma-Assisted Dry Methane Reforming Mruthunjaya Uddi, Chien-Hua Chen, Yue Xiao, Josh Kintzer and Joshua Przyjemski; Advanced Cooling Technologies Inc, United States

Endothermic Dry Methane Reforming (DMR) consumes two greenhouse gases-methane and carbon dioxide-to produce syngas, a valuable product to prepare various chemicals such as liquid transportation fuels through Gas-to-Liquid (GTL) Fischer-Tropsch (FT) processes, methanol, acetyls (acetic acid), formaldehyde, formic acid, and dimethyl ether, etc. While thermal-catalytic DMR is conducted at high temperature (seven hundred to nine hundred C) with fossil fuel supply, Plasma assisted DMR (pDMR) can be conducted at lower temperatures (three hundred to five hundred C) using waste heat and renewable energy to produce syngas while performing carbon capture. Dielectric Barrier Discharge (DBD) plasma has been extensively investigated for its convenient scaled-up design for industrialization.

However, the energy efficiency and conversion of DBD-based pDMR are still low, and considerations for potential industrial process flow integration are lacking. In recent years, we further investigated on improvements in the efficiency of pDMR, including an innovative reactor design that eliminates the detrimental surface discharge and with adoption of Ni-based perovskite catalysts. The study of these various configurations, power supply, and catalysts on DMR efficiency and conversion levels will be presented. The effect of plasma-catalysis synergy will also be discussed. As a result, we have achieved a maximum conversion of methane of more than 95% and carbon dioxide conversion of 20% using plasma DMR, in a 1:9 mixture ratio of methane to carbon dioxide. The high methane conversion is designed to eliminate the separation process in a potential industrial process integration. In this case, the specific energy input of less than 11 eV/molecule was achieved. We continue to develop more efficient DMR processes.

3:40 PM BREAK

4:00 PM **EF09.05

Prospecting for Green Hydrogen Using Complex Perovskites and Concentrated Sunlight Anthony H. McDaniel; Sandia National Laboratories California, United States

Green hydrogen is a carbon-free energy carrier that is considered one of the best ways to not only decarbonize the energy supply system, but address the zero-emission challenges specific to large-carbon emitting industries that are difficult to separate from fossil fuels (e.g., heavy-duty trucking, load-following electricity; iron, steel, ammonia, and cement manufacture). Therefore, developing technologies to produce renewable and sustainable green hydrogen from sunlight is widely seen as a global imperative, and there is significant interest in utilizing high-temperature thermochemical water splitting cycles powered by concentrated solar energy to achieve these objectives.

Here we offer a perspective on solar thermochemical hydrogen production (STCH) processes that utilize concentrated thermal energy from the sun to drive chemical reactions to split water into hydrogen and oxygen. This talk will focus on a STCH process based upon a deceptively simple two-step redox cycle. In step one, a concentrated solar resource heats a non-stoichiometric oxide to spontaneously create O₂ and oxygen-atom defects within the solid while depositing the solar energy directly into the reduced oxide, much like charging a battery. Once "charged," the reduced oxide is exposed to water in a second step under conditions that result in spontaneous gas splitting, yielding molecular hydrogen. Essentially, the oxygen atom is stripped from the water molecule to re-oxidize the solid, create H₂, and close the redox cycle.

Effective and efficient redox-active materials are key to the commercial success of STCH technologies, and material discovery efforts at laboratories around the globe are currently underway. This talk will discuss the use of hexagonal perovskites BaX_{0.25}Mn_{0.75}O₃ (X = Ce, Nb, Pr) to accomplish the redox cycle chemistry and describe our efforts to explore the fundamental underpinnings of important relationships between oxide composition, electronic structure, and functionality. Heretofore layered perovskites have not been considered for STCH applications. We recently discovered a complex layered perovskite that is a B-site, Mn-based compound (BaCe_{0.25}Mn_{0.75}O₃, or BCM) which outperforms all known perovskites tested for STCH functionality. BCM is a line compound where Ce substitutes for Mn in a perfectly ordered intergrowth of cubic and hexagonal layers that transitions to a stoichiometric but more disordered polytype when thermally reduced. In addition, the polytypes accessible to BCM are distinguished by the complexity of the Mn-O oligomer arrangements within the layered structures. Replacing Ce with Pr or Nb in BCM does not alter the stoichiometry or ground state crystal structure

but dramatically changes the observed water splitting behavior, as well as the crystallographic transitions induced by oxygen deficiency. The significant chemical variants in the BXM family provide an opportunity through comparison to explore the relationship between hydrogen production capability and the different local environments of the metal-oxygen bonds, resulting from the chemical modification.

Lastly, we will review progress made by the HydroGEN Advanced Water Splitting Materials Consortium (h2awsm.org), which is a research community brought together and funded by the US DOE as an Energy Materials Network initiative in late 2017 and tasked with using high throughput computational material science approaches to discovering STCH-active oxides. We will also review challenges and opportunities for discovering new redox cycle chemistries within the context of achieving high solar-to-fuel conversion efficiency in engineerable and appropriately designed solar reactors.

4:30 PM **EF09.06

Efficient Redox Reactor Train System and Materials for Solar Hydrogen Production [Ahmed F. Ghoniem](#); Massachusetts Institute of Technology, United States

Efficient production of hydrogen and other renewable fuels will pave the way for decarbonization of long-haul transportation and industries that need high temperature heat, among other sectors. Water electrolysis is a mature technology that can be used for this purpose, but round the clock production is challenged by the high cost of electricity storage. Concentrated solar heat coupled with high temperature redox cycles offer an attractive alternative, but their demonstrated efficiency has been low and not economically competitive. We have used comprehensive thermochemical modeling to uncover processes that contribute to the low efficiency, and we are working on the design of a *reactor train system* that employs regenerative solids heating, gas heat recovery, efficient vacuum pumping and waste heat utilization to achieve up to 5X improvement over existing designs. Redox material selection to optimize the reactor system design by maximizing hydrogen productivity without compromising the efficiency is critical, and we are exploring the use of composites, e.g., metal doped ferrite-ceria, for balancing different requirements but with enhanced stability. Work done with Aniket Patankar, Xiaoyu Wu, Wonjae Choi and Harry Tuller.

5:00 PM *EF09.07

Materials Discovery, Characterization and Development for Lower Temperature Thermochemical H₂ Production [Jonathan Scheffe](#), Dylan McCord, Elizabeth Gager, Ximeng Wang, Juan Nino and Simon Phillpot; University of Florida, United States

Materials discovery and development related to thermochemical materials for H₂ production has historically been focused on materials that have large entropy changes and moderate enthalpies, in order that temperature swings between reduction and oxidation steps are minimized and thermal reduction temperatures are reduced below 1400 °C. Isothermal or near-isothermal cycling has been proposed as a means to decrease sensible heating requirements to the solid phase, but theoretical and experimental work has yielded mixed predictions and results. Based on our recent theoretical and experimental work, we postulate that the prior mixed results reported in literature stem from a combination of materials and conditions for isothermal operation (e.g., CeO_{2-δ} at pO₂ ~ 10⁻⁴ atm and 1400°C-1500 °C), that has been far from those desired for optimal performance. In this work, we implement a materials design concept that identifies and investigates new material classes, compositions, and operating conditions that are ideal for isothermal thermochemical H₂ production. Starting from La-Sr-Mn perovskites, which have been theoretically and experimentally identified as having more favorable properties than ceria, we are utilizing high throughput screening coupled to direct DFT computations of down-selected materials for key performance properties such as oxide formation energies and oxygen vacancy formation and migration energies. DFT computation and screening is coupled closely with experimental synthesis of powdered, replica and direct foam compositions that afford enhanced heat and mass transfer properties. In this talk we will focus on thermodynamic and kinetic analysis of identified candidate materials that are characterized through thermogravimetric analysis and relaxation experiments, using powdered and dense body forms.

5:20 PM *EF09.08

Bridging Photoelectrochemical and Thermochemical Approaches for Solar Fuel Processing [Sophia Haussener](#); Ecole Polytechnique Federale de Lausanne, Switzerland

Solar radiation is the most abundant renewable energy source available but it is distributed and intermittent, thereby necessitating its storage via conversion to a fuel or chemical commodity (e.g. hydrogen or carbohydrates) for practical use. Solar thermo-chemical and photo-electro-chemical approaches (and combinations thereof) provide viable, non-biological routes for the direct synthesis of solar fuels and chemical commodities. While solar thermochemical approaches utilize heat at high temperature to support an endothermic reaction, photoelectrochemical approaches utilize the photons (with sufficient energy) to drive the endothermic reactions. The latter are usually limited in the utilization of the full solar spectrum and thermal integration has the potential to increase their performance [1]. Furthermore, the large kinetic, ohmic and transport overpotentials limit the current density and therefore the power density of these approaches. I will explore approaches for close thermal integration and high current density operation. Specifically, I will discuss the development of a modeling framework that assesses the possibility of high-temperature operation (temperatures > 400 K) of the photoelectrochemical approach in a solid state equivalent design [2]. Such devices would utilize ceramic electrolytes, earth abundant catalysts with small overpotentials, and high-temperature solar cells utilizing the thermionic emission principle. I will discuss requirements on materials (solid electrolyte, catalysts, semiconductor absorber and barriers, etc.), operating conditions and design for such approaches to be feasible and explore limiting efficiencies.

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5:40 PM *EF09.09

Strategies to Improve CeO₂ Performance for Solar-Driven Chemical Looping Syngas Production and CO₂ Splitting [Alfonso J. Carrillo](#); Instituto de Tecnologia Quimica, Spain

Production of synthetic fuels, such as syngas, through solar-driven thermochemical cycles, represents a promising route for enabling the storage of solar energy into chemicals, alleviating the inherent intermittence of this renewable source and mitigating CO₂ emissions. Conventionally, this technology uses concentrated solar power to drive the thermal reduction of a metal oxide at high temperatures (1200-1500 °C). Alternatively, it is possible to use methane to chemically reduce the oxide. Solar-driven reforming of methane by chemical looping consists of two steps: in the first step, solar energy drives the reduction of a metal oxide, e.g. CeO₂ with methane, producing syngas. In the second step, CO₂ reacts with the reduced oxide, CeO_{2-δ} generating CO, and closing the chemical loop. The use of CH₄, which could come from a renewable source such as biogas, as a reducing agent allows decreasing the reduction temperature down to ca. 900 °C, which will lower radiation heat losses, improve materials stability and increase the oxide reduction extent. This latter fact results in higher fuel yields for the CO₂ (or H₂O) conversion, increasing the overall solar-to-fuel efficiency of the process. However, CeO₂ presents slow methane partial oxidation (MPO) kinetics if compared to perovskite oxides [1], mainly limited by the number of available active sites for the activation of

CH₄. In order to overcome this issue, several strategies are being considered to improve the MPO kinetics and increase the syngas yield and selectivity. Namely, research has been focused on four main approaches: changes in textural properties, metal cation doping [2], combinations of ceria and perovskite oxides to form dual-phase composites [3], and incorporation of a metallic catalyst [4]. In this talk, I will cover examples of the above with a special focus on the latter. Traditionally, metal nanocatalysts such as Ni are commonly deposited over the oxide surface to improve syngas production rates. However, the high temperatures at which this process takes place (ca. 900 °C) can degrade the catalytic phase via nanoparticle sintering causing the loss of its activity over cycling. An alternative for the creation of metallic nanoparticles is the exsolution method, which consists of the migration of certain cations incorporated in the oxide crystal lattice as dopants that under reductive atmospheres nucleate in the oxide surface, remaining anchored to the oxide. Here, I will introduce the concept of nanoparticle exsolution as an efficient route for the creation of metallic nanoparticles well attached to CeO₂ and its application in solar-driven chemical looping reforming of methane. I will show that exsolved Ru nanoparticles exhibit high stability over prolonged cycling, increasing the syngas production rates, methane conversion, and CO selectivity.

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- 4 A. J. Carrillo, L. Navarrete, M. Laqdiem, M. Balaguer and J. M. Serra, *Mater. Adv.*, 2021, 2, 2924–2934.

SESSION EF10: Poster Session II: Energy and Fuels Conversion II
 Session Chair: Georgios Dimitrakopoulos
 Tuesday Afternoon, July 19, 2022
 6:00 PM - 8:00 PM
 Mezzanine Level, Second Floor, Stadler

EF10.01

Leveraging Experiment and DFT to Tune Exsolution of Ni Nanoparticles from SrTiO₃ Willis O'Leary¹, Livia Giordano^{1,2}, Yang Shao-Horn^{1,1} and Jennifer Rupp^{3,1}; ¹Massachusetts Institute of Technology, United States; ²University of Milano-Bicocca, Italy; ³Technische Universitat Munchen, Germany

Exsolution of metallic nanoparticles from perovskites is a promising route to highly active and stable catalysts for solid oxide fuel cells, thermochemical cycling, and other energy and chemical conversion applications. In exsolution, a perovskite is reduced, typically with hydrogen gas at high temperatures, which drives oxygen from the lattice and leads to the formation of metallic nanoparticles on the perovskite surface. These nanoparticles have good catalytic activity and are strongly anchored in the perovskite backbone. Although strategies to tune the exsolution process have come a long way (for SrTiO₃ and LaTiO₃ solid solutions in particular), there remains a shortage of principles for designing perovskite solid solutions that exsolve nanoparticles with targeted properties. Development of more universal and reliable design principles would make exsolution perovskites much more commercially attractive.

Towards this end, we have developed a framework for tuning exsolution through modification of perovskite chemical composition. First, we worked with Ni-doped SrTiO₃ solid solutions to investigate how introduction of Sr deficiency, as well as tailored concentrations of Ca, Ba, and La doping on the Sr site, influence Ni nanoparticle surface density after reduction at fixed conditions. We then correlated density functional theory (DFT) calculations to the observed trends. The result is a first-principles-based model to predict exsolution nanoparticle density for arbitrary perovskite compositions. Our model provides insights into the exsolution mechanism and can hopefully serve as a practical tool for designing exsolution perovskites.

EF10.02

Equivalent Circuit Analysis of Gas/Solid Phase Reaction in Proton Ceramic Fuel Cells Soichiro Ebata¹, Keiji Yashiro¹, Masami Sato^{2,3}, Reika Nomura⁴, Mayu Muramatsu⁵, Kenjiro Terada⁴ and Tatsuya Kawada¹; ¹Graduate School of Environmental Studies, Tohoku University, 6-6-01, Aoba, Aramaki, Aoba-ku, Japan; ²Mechanical Design & Analysis Corporation AXIS Chofu 2F, 1-40-2 Fuda, Japan; ³Graduate School of Engineering, Tohoku University 468-1-S403, Aoba, Aramaki, Aoba-ku, Japan; ⁴International Research Institute of Disaster Science, Tohoku University, 468-1-S403, Aoba, Aramaki, Aoba-ku, Japan; ⁵Department of Mechanical Engineering, Keio University, Hiyoshi 3-14-1, Kohoku-ku, Japan

An equivalent circuit of a triple carrier system of protons, electrons, and oxide ions was created to find effects of gas/solid exchange reactions on the electrochemical responses of a PCFC. The ac responses of the circuit were calculated using a general-purpose electric circuit simulator, LTspice®. Systematic variation of gas/solid exchange parameters were tested to find the major contributor to the electrochemical impedance of a PCFC.

The circuit used in this simulation consists of three parallel conducting paths for charge carriers, "proton", "oxygen vacancy", and "hole" in the proton conductor, and potential-dependent bulk transport resistances of each carrier are placed in each path. The local potential of each path in the equivalent circuit is represented by $\eta_i/(z_i F)$, which corresponds to the local electrochemical potential η_i of carrier i , where z_i is the valence of carrier i and F is Faraday's constant. This implies that a potential difference between two lines represents a chemical potential of oxygen, hydrogen, or water, according to the local equilibrium. The three conducting paths in the equivalent circuit are connected to each other by capacitances on which the charge changes in response to local potential difference between the paths. This means that the "chemical capacitance" represents the exchange among the three carriers, corresponding to the local change in the chemical potential of the three carriers. The boundary condition of the sample was given by the chemical potential of the gas phase on the electrode surface, which is given as the voltage source located between the three lines in the equivalent circuit. The gas-solid exchange reactions are represented by the resistances in series with the voltage source. Here, three types of reactions are considered between the carriers and gas phase, i.e. hydrogenation, hydration, and oxidation for which the reaction resistances are given as R_H , R_W , and R_O , respectively.

Using this equivalent circuit, the electrochemical potential distribution, and the carrier concentration distribution in the thickness direction of the sample were calculated first, and impedance analysis simulations were then performed. Calculations were made by varying the gas/solid exchange resistances systematically to investigate the effect of electrode reaction components on the impedance response. In the calculation, either the cathodic or anodic interface reactions were ignored to simplify the conditions. It was suggested that, in both cases, the resistance R_H of the surface reaction contributed most to the magnitude of the polarization resistance of the impedance response. In the case where the cathodic interface reaction was ignored, the resistance R_O of the surface reaction was suggested to contribute to the inductance behavior at the low frequency side of the impedance response. A surrogate model was constructed based on a proper orthogonal decomposition algorithm for a rapid estimation of the impedance responses with various combinations of exchange resistances.

EF10.03

In Situ Growth of Palladium Nanoparticles on A-Site Layered Double Perovskite PrBaMn₂O_{5+δ} [Ritika Vastani](#), Eleonora Cali, Sivaprakash Sengodan and Stephen J. Skinner; Imperial College London, United Kingdom

The process of exsolution, in which there is *in-situ* growth of nanoparticles by phase separation under reducing conditions from an oxide lattice, has become an efficient technique to allow for the commercial use of noble metals. In addition, exsolution overcomes the drawbacks from conventional deposition techniques due to the formation of embedded nanoparticles in the host lattice. For this reason, exsolution has been used in the last decade as a technique to address the drawbacks of solid oxide fuel cell (SOFC) electrode materials. The exsolution of active metals such as Ni, Co, Ru and Pd from perovskite oxides has led to an increase in the electrochemical performance of SOFC anode materials, as they provide a catalytic site for electrochemical reactions. A-site layered double perovskites, namely PrBaMn₂O_{5+δ} (PBMO) consist of alternate layered PrO_x and BaO along the c-axis with a stacking sequence of BaO|MnO₂|PrO_x|MnO₂ [1]. Such ordered structures show remarkable mixed conductivity of up to 8.16 S cm⁻¹ in 5% H₂ and stability in carbon and sulfur containing fuels [1]. The electrochemical performance and catalytic activity of PBMO towards fuel oxidation has been further increased up to 1.8-fold through the exsolution of Ni and Co metal nanoparticles [1,2]. However, there has been little to no research focused on the exsolution of noble metals from A-site layered double perovskites, given noble metals such as Pd have shown to significantly enhance the catalytic activity of SOFC anode materials [3].

Here, we report 0.5wt% Pd incorporated into A-site layered PBMO and the exsolution of Pd nanoparticles by reduction. The palladium doped material was synthesised through a two-step method, first in air to produce the disordered single perovskite and then under reducing conditions to form the double perovskite and facilitate exsolution. The crystal structure of the material was characterised by X-ray diffraction (XRD) showing the formation of a tetragonal double perovskite with the appearance of metallic palladium. These results were supported through thermogravimetric analysis (TGA) under 5% H₂ to observe the phase change to the double perovskite. The presence of exsolved palladium nanoparticles was confirmed through transmission electron microscopy (TEM) and scanning transmission electron microscopy-energy dispersive X-ray spectroscopy (STEM-EDX) mapping. The oxidation states were characterised by X-ray photoelectron spectroscopy (XPS) which revealed a change in oxidation state from cationic palladium before reduction to metallic palladium upon exsolution. Further investigations aim to understand the catalytic effect of palladium exsolution on the electrochemical performance due to its promising properties as an anode material for SOFCs.

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EF10.04

Introducing A-Site Deficiency to Enhance the Properties of Intermediate Temperature Solid Oxide Fuel Cells Cathodes—A Case Study on (Ba_{0.95}La_{0.05})_{1-x}FeO_{3-δ} [Alessio Belotti](#) and Francesco Ciucci; The Hong Kong University of Science and Technology, Hong Kong

Reducing the working temperature of solid oxide fuel cells (SOFC) has the potential to greatly benefit their durability, ease of operation, and manufacturing cost reduction. The key to do so is developing and optimizing cathodes capable of working at an intermediate temperature (IT) range of 500-700 °C, as BaFeO_{3-δ} (BFO)-based perovskites. These materials rely on their highly oxygen vacant structure and on their holes to conduct both oxygen ions and electronic charges, respectively. Thus, maximizing the concentrations of oxygen vacancy and holes can further enhance oxygen reduction reaction (ORR) catalysis. Using (Ba_{0.95}La_{0.05})_{1-x}FeO_{3-δ} as a case study, this work shows that A-site deficient compositions introduce additional negative charges into the perovskite crystal. Therefore, these compositions trigger the formation of more oxygen vacancies and holes for charge compensation. The A-site deficient materials showed improved electrochemical performance, including smaller polarization resistance, higher electrical conductivity and faster electrical conductivity relaxation. For the above reasons, A-site deficiency could be regarded as a simple and effective method to enhance the performance of mixed ionic electronic conductors, such as BFO-based cathodes, and its application should be taken into account as a standard parameter during cathode development and optimization.

EF10.05

Effect of Ca Concentration on the Electrochemical and Crystallographic Properties of La_{0.2}Sr_{0.7-x}Ca_xTi_{0.95}Fe_{0.05}O_{3-δ} Fuel Electrode at Solid Oxide Fuel Cell Conditions [Sara Paydar](#), Kuno Kooser, Priti Möller, Enn Lust and Gunnar Nurk; Tartu Ulikool, Estonia

Improvement of the activity and stability of ceramic hydrogen electrodes is one important challenge for developing solid oxide fuel cells (SOFC). In this research, set of cubic perovskite type La/Ca/Fe doped strontium titanates, La_{0.2}Sr_{0.7-x}Ca_xTi_{0.95}Fe_{0.05}O_{3-δ} (LSCTF) is synthesized using glycine-nitrate synthesis method. The crystal structure and microstructure have been studied using X-ray diffraction and SEM before and after long term electrochemical stability tests in reducing atmosphere, respectively to confirm the phase purity and visualize the microstructure of studied electrode layers. The electrochemical activity and performance stability of the fuel electrodes in the symmetrical cell test in reducing atmosphere was evaluated. It was confirmed by the results that the electrochemical activity and stability of the LSCTF electrodes are significantly dependent of Ca concentration in A-site. In the case of an optimal composition of La_{0.2}Sr_{0.35}Ca_{0.35}Ti_{0.95}Fe_{0.05}O_{3-δ} fuel electrode the polarization resistance value 0.44 Ω cm² was obtained after 100 hours of stabilization at 800 °C in 98.3% H₂ + 1.7% H₂O atmosphere.

EF10.06

Optimization of the Deposition of a Micrometric Dense Layer of Er_{0.5}Bi_{1.5}O₃ on CGO by Spin Coating [Soukaina Mountadir](#)^{1,2,3}, Victor Duffort^{1,3} and Rose-Noëlle Vannier^{2,3}; ¹Centre National de la Recherche Scientifique, France; ²Centrale Lille Institut, France; ³Unite de Catalyse et Chimie du Solide, France

Solid oxide fuel cells have unique advantages over the traditional power generation technologies. They convert the chemical energy contained in a fuel/oxidizer pair, generally H₂/O₂, into electrical energy with high electrical efficiency (60 %), durability, low cost and flexibility in the choice of fuel. The main specificity in these cells is a high operating temperature between 800 and 1000 °C that allow an activation of the reactions at the electrodes without the need of noble metal catalyst¹. These high operating temperatures are usually a consequence of the use of yttria stabilized zirconia (YSZ) as the electrolyte material. However, these operating conditions impose strong constraints on the chemical and mechanical compatibilities of the different components, driving the search for lower temperature systems.

Bi-layer electrolytes formed by association of a stabilized bismuth oxide layer and stabilized ceria layer is one of the way to achieve a significant decrease of the operating temperature.² Such systems have already achieved impressive specific power density of ~2 W.cm⁻² at 650 °C.³ In order to pursue the search

for new cathode materials operating at even lower temperatures, we considered the development of a two-layer electrolyte $\text{Gd}_{0.1}\text{Ce}_{0.9}\text{O}_{1.95}/\text{Er}_{0.5}\text{Bi}_{1.5}\text{O}_3$ (GDC/ESB) by spin-coating.

This study focuses on the fabrication and deposition of thin and dense layer of ESB on GDC pellets. In order to minimize the grain size of the ESB powder, the latter was synthesized at temperature as low as ~ 500 °C using citrate route yielding a more reactive powder than the traditional wet chemical co-precipitation route. Two ink systems, ethanol-based and terpeneol-based, were evaluated to achieve dense and crack free layers with a controlled thickness of a few micron by optimizing the sintering temperature, component percentage in the ink composition and by controlling the spin coater parameters. The optimization of the ink composition will be presented and explained based on microstructural data obtained by Scanning Electron Microscopy (SEM) and Energy-Dispersive X-ray spectroscopy (EDX).

Acknowledgements

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EF10.07

Electron Microscopic Characterization of Solid State Electrolyzer Cells (SOEC) After Long-Term Operation Tibor Lehnert¹, Florian Wankmueller¹, Cedric Großelindemann¹, Chen-Yu Tsai², Dagmar Gerthsen¹, Andre Weber¹ and Heike Stoermer¹; ¹Karlsruher Institut für Technologie, Germany; ²Sunfire GmbH, Germany

High-temperature solid oxide electrolyzer cells (SOEC) are promising candidates for the production of hydrogen. To implement hydrogen production on an industrial scale, degradation processes and, structural changes on a microscopic level have to be identified and understood.^[1]

We use transmission electron microscopy (TEM) and electron diffraction (ED) to investigate the microstructure on electrolyte supported cells (ESC). The microstructural aging of an SOEC, which was operated for ~ 6500 h in the electrolyzer mode was compared with an as-sintered reference cell. Systematic changes of the structure along the gas flow direction of the Ni/GDC (Gd doped CeO_2) fuel electrode, and of the $\text{La}_{1-x}\text{Sr}_x\text{Co}_{1-y}\text{Fe}_y\text{O}_{3-\delta}$ (LSCF)/GDC air electrode are analyzed. The electrodes are connected via a GDC barrier with an yttria-stabilized zirconia (YSZ) electrolyte. Energy-dispersive X-ray spectroscopy (EDXS) was performed with high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) to investigate the chemical composition at the GDC/YSZ interfaces to determine position-dependent cation interdiffusion.

Furthermore, different aging effects are studied, e.g., poisoning from the inlet gas, formation of different phases such as the secondary SrZrO_3 phases at the air electrode as well as structural changes on the atomic scale. We were able to identify strong structural differences between the gas inlet and gas outlet of the SOEC, which we explain via poisoning at the active sites.^[2, 3]

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EF10.08

Raw Material Availability—How Scalable are Compositions and Designs for Solid-State Ionics-Based Devices? George Harrington^{1,2,3}, Dino Klotz^{2,3} and Israel Mendonça dos Santos⁴; ¹Rheinisch-Westfälische Technische Hochschule Aachen, Germany; ²Kyushu Daigaku, Japan; ³Massachusetts Institute of Technology, United States; ⁴Kumamoto Daigaku, Japan

Materials with the ability to transport ions, electrons, or a combination of the two form the basis of a range of energy conversion and storage technologies such as solid oxide fuel cells (SOFCs), solid oxide electrolyzer cells (SOECs), and solid-state batteries (SSBs). Some or all of these technologies will be crucial for global decarbonization efforts currently taking place and expected to expand over the coming decades. Therefore, improving the performance of these materials and devices, such as the conductivity, durability, and power or energy density, is a primary focus of the solid state ionics community. The various national targets set in line with the Paris Agreement establish a timeline for the large-scale roll-out of many of these technologies. For example, clean hydrogen production at scale must be in place in the 2040s, to decarbonize steel, cement, and fertilizer manufacturing, with SOECs being a primary candidate to fill this role. Additionally, global battery production is expected to reach between 0.5 and 4 TWh by 2040. Given the urgent time constraint for decarbonization and the scale at which the energy transition must take place, it is imperative that new energy conversion/storage devices need to be technologically proven, commercially viable, but also scalable in terms of raw material and mineral supply.

Issues of raw material supply are becoming increasingly concerning. Institutions such as the EU Commission and the US Department of Energy (DOE) publish lists of elements that have been identified as ‘critical raw materials’, based on factors of economic importance and susceptibility of supply risk. Part of the problem is the inability for mining and mineral processing to react quickly to demand for particular elements, with 10-20 years being the typically timeframe for new mining operations to become operational. These issues present an alarming discrepancy between material production and expected demand over the coming decades. It may be particularly problematic for multi-component ceramic-based devices, such as solid oxide cells and solid-state batteries, with complex multi-step and highly optimized fabrication procedures, where time-to-market can be a decade or longer the substitution of one material for another can be highly non-trivial.

Considering the tight time constraints for decarbonization, raw material supply may particularly problematic and face a real barrier for meeting climate targets. While lists of critical raw materials published by the EU Commission and US-DOE are useful for spreading awareness among the development community, these lists have limited use for researchers, such as those in the solid state ionics community, in deciding what are acceptable usage amounts when developing new material compositions, or design decisions for devices.

In this work, we have developed a simple, yet effective framework for evaluating the raw material requirements, and therefore scalability, of compositions, components, and architectures of solid-state devices for energy applications. By calculating the amount of raw materials and minerals required for components and devices and comparing to annual global production, it can be easily assessed whether devices can be manufactured at a scale to meet

projections or targets for decarbonization. Our analysis framework has been integrated into an easy-to-use software tool for researchers based on parameters they have to hand, such as compositions, densities, and device performance. It is our hope that, through a growing awareness of materials scalability issues and from the use of tools such as the one presented, materials criticality will become an increasing important parameter within the solid state ionics community for materials developments in energy conversion and storage technologies.

EF10.09

Highly Efficient and Flexible High Temperature CO₂-H₂O Co-Electrolysis Over Nanoengineered Perovskite Electrocatalysts Roelf Maring and Vasileios Kyriakou; Rijksuniversiteit Groningen, Netherlands

The change of the existing liquid hydrocarbon infrastructure to a hydrogen-based one is till today economically not viable. The production of synthetic fuels from renewable energy could be a more efficient solution for a sustainable future without the need of huge investments for modifications in the existing infrastructure [1]. The raw material for synthetic fuels, syngas (H₂, CO and some CO₂) is mainly produced from the reforming of fossil fuels. The solid oxide co-electrolysis of carbon dioxide and steam is an emerging route to produce syngas and thus store renewable electricity in the form of chemical bonds [1]. The commonly employed materials for fuel electrodes (cathode) are Ni based cermet, which exhibit high ionic-electronic conductivity and electrocatalytic activity. Nevertheless, Ni cermet suffer from coarsening under redox conditions and coking under carbon rich environments [2]. To circumvent coarsening, a reducing agent, such as hydrogen has to be introduced with CO₂-H₂O in order to keep Ni in a reducing state [1]. Perovskite oxide ceramics (ABO₃) are the most promising alternative fuel electrodes. Perovskites exhibit mixed ionic-electronic conductivity as single phases and can accommodate several kind of defects under redox conditions, allowing them to adapt to various external conditions and therefore maintain stability and functionality under redox environments [3]. By controlling deficiency of the A-site, transition metal nanoparticles may be exsolved to the surface from the perovskite oxide backbone under reducing environments. The grown particles are uniformly dispersed as well as anchored to the perovskite scaffold, thus rendering them more catalytically active and chemically stable compared to the oxide supported counterparts prepared by infiltration [4,5]. Along these lines, here we report on the electrochemical performance of several perovskite fuel electrodes for high temperature CO₂-H₂O co-electrolysis. The cells are characterized and tested at 700–850 °C under different operating conditions, such as feed mixtures, applied voltages and time on stream.

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EF10.10

Manganese Dioxide Nanotubes Catalyst for Oxygen Reduction Reaction at Cathode Side of PEMFC Abid Ullah^{1,2}, Basharat Hussain¹ and Sayed Sajid Hussain³; ¹University of Science and Technology South Korea, Korea (the Republic of); ²Korea Advanced Institute of Science and Technology, Korea (the Republic of); ³Chungnam National University, Korea (the Republic of)

Alkaline fuel cell is an electrochemical cell which undergoes oxygen reduction reaction at cathode side to produce energy. Platinum (Pt) metal has been used for catalysis since its inception but expensiveness is the major obstacle in commercialization of fuel cell. Herein a non-precious group metal is employed instead of Pt metal to reduce the cost of AFC. Manganese dioxide nanorods (MnO₂) is a catalyst having excellent electrochemical properties and offers a better alternative to the Platinum based PEMFC. The catalyst is synthesized by impregnating the transition metal on large surface carbonaceous CNTs by hydrothermal synthesis techniques. To enhance the catalytic activity and increase the volumetric current density, the sample was pyrolyzed at 800 °C temperature under nitrogen atmosphere. During pyrolysis, the nitrogen was doped in the framework of CNTs. The material is then treated with acid for removing the unreacted metals and adding oxygen functional group to the CNT framework. This process ameliorates the catalytic activity of the manganese based catalyst. The catalyst has been characterized by scanning electron microscope (SEM), X-ray diffraction (XRD) and the catalyst activity has been examined by Rotating Disc Electrode (RDE) experiment. The catalyst was strong enough to withstand austere alkaline environment in experimental conditions and had high electro catalytic activity for oxygen reduction reaction (ORR). Linear Sweep Voltammetry (LSV) depicts an excellent current density of -4.0 mA/cm² and an over potential of -0.3V vs. Standard Calomel Electrode (SCE) in 0.1M KOH electrolyte. Rotating Disk Electrode (RDE) was conducted at 400, 800, 1200, and 1600 rpm. The catalyst exhibited a higher methanol tolerance and long term durability with respect to commercial Pt/C. The results of MnO₂/CNT show that the low cost catalyst will supplant the expensive Pt/C catalyst in the fuel cell.

EF10.11

Electrochemical Reduction of Methane to Value-Added Products Using Bifunctional CeO₂/ZrO₂ Catalysts Nicole B. Patricio¹, Juliano C. Cardoso¹, Marcia T. Escote², Alexandre Jose C. Lanfredi² and Elisabete I. Santiago¹; ¹Instituto de Pesquisas Energeticas e Nucleares, Brazil; ²Universidade Federal do ABC, Brazil

Methane (CH₄) is the main component of natural gas (70 to 90%), the fossil fuel, whose consumption has grown the most in the world. The International Energy Outlook 2019 projects that global consumption of natural gas will increase by 40% from 2018 to 2050, reaching 200 quadrillion btu. Methane is usually flared into carbon dioxide for damage reduction, implying in the transformation of a potential feedstock into polluting waste. In order to save energy and become it installable on remotely located reserves, the conversion of methane to methanol under moderate conditions is the ideal approach. Electro-oxidation of this compound can occur at low temperatures *via* direct method and the increase in the conversion rate to methanol can be achieved with the development of new efficient catalysts.

When used as catalysts, some oxides are capable of producing alcohols, such as methanol. Among them, ceria (CeO₂) has been confirmed as a promising CH₄ electrocatalyst. In the context of bifunctional catalysts, zirconia (ZrO₂) is often used as a component of mixed oxides, improving the redox properties of pure ceria due to the increase on methane adsorption.

In this work, the synthesis of CeO₂/ZrO₂-based bifunctional electrocatalysts was evaluated using the hydrothermal process assisted by microwave, varying the proportions in the ratios of 1:2, 2:1 and 1:6 Ce/Zr, respectively. Such mixtures are used as starting precursors to form mixed metal oxides and solid solutions followed of heat treatment at 200 degrees for 30 minutes for phase formation, called mixed oxides (Ce_xZr_{1-x}O₂) and solid solutions (CeO₂/ZrO₂). The crystallographic characterization (XRD) showed the formation of solid solutions, as long as the cubic ceria and tetragonal zirconia within the mixed oxides, data confirmed by mapping images and EDS analysis. SEM analysis shows particle sizes varying from nearly 5 to 16 nm, which can be considered a good result. The electrochemical characterizations were carried out by depositing the synthesized catalysts on carbon paper (5 cm²) and loading at 1.0 mg cm⁻². The voltammograms obtained showed two peaks for all proportions evaluated at 1.1 V and 1.6 V vs Ag/AgCl.

The electro-oxidation of methane under potentials of 1.1V and 1.6V led to the majority formation of methanol, ethanol, and acetone as the main products of this conversion in sodium carbonate medium as an electrolyte. GC-DEMS data have showed that CeO₂/ZrO₂ (1:1) was able to generate methanol and ethanol with 2.3% and 4.2% efficiency, respectively, while CeO₂/ZrO₂ (1:2) generates only methanol with a higher efficiency of 6.9%.

Thus, under optimized conditions, it was possible to observe that ceria and zirconia oxides can efficiently promote the conversion of methane to other commercially valuable products using suitable oxidation potentials and, therefore, be a promising alternative for this reaction.

EF10.12

Effects of La Content in Ceria-Lanthana Thin Films Prepared by Pulsed Laser Deposition [Raphael A. Martins Pires de Oliveira](#)¹, Andre S. Ferlauto¹, Fabiane d. Trindade¹, Daniel Z. Florio¹ and Fabio Fonseca²; ¹Universidade Federal do ABC, Brazil; ²Instituto de Pesquisas Energeticas e Nucleares, Brazil

Solid oxide electrochemical reactors are a promising alternative for hard to tackle chemical reactions such as oxidative coupling of methane (OCM), in which methane is converted to C_2+ products. They contain oxygen-conducting membranes that deliver oxygen species in a highly controllable way, avoiding undesired complete oxidation, thus enhancing selectivity. Cerium oxide is one the main studied oxide membrane material because, when doped with 3+ rare earth cations such as Gd, Sm or La, it gains high ionic conductivity in the ideal temperature range for conversion reactions (600-900°C). Interestingly, recent works has shown that ceria-lanthana is a promising catalyst for OCM. The presented work investigates the structural properties $La_xCe_{(1-x)}O_{2(1-x/2)}$ thin films covering a wide La content range from $x = 0$ to 0.7. The films were prepared by pulsed laser deposition on Si, quartz and glass substrates, using $La_xCe_{(1-x)}O_{2(1-x/2)}$ targets with same stoichiometry. We have used x-ray diffraction (XRD), scanning electron microscopy (SEM), Raman spectroscopy and spectroscopic ellipsometry (SE) to study the effect of doping on the structural properties of the films. XRD results indicate that the film growth is textured. For low La content ($x \leq 0.5$), the films growth preferably in the [100] direction of the cubic crystalline fluorite, whereas for $x > 0.5$ film crystalline orientation is random. La doping induces an expansion of the fluorite structure reflecting an increase in lattice parameter (from 5.42 Å, for $x=0$, to 5.69 Å, for $x=0.7$) that follows the same trend that is observed for the powders from which the PLD targets were made. The doping effects in Ce-La thin films were studied using Raman spectroscopy by following the changes in the main fluorite F_{2g} band at $\sim 464 \text{ cm}^{-1}$. La doping induces a significant broadening of this peak. Such effect is usually attributed to reduced size in pure ceria nanoparticles, but in this case, it is probably associated to cationic (or anionic) disorder that exists in the so- disordered fluorite structure that is characteristic of ceria-lanthana solid solutions. The disorder results in a reduced phonon correlation length that induces the broadening. These results will pave the way for the application of Ce-La oxides thin films as catalysts for OCM in electrochemical reactors based on ceria.

EF10.13

Fabrication of Bundle-Type Columnar Cuprous Oxide Photocathodes with Vertical Grain-Boundaries by Metallic Seeds and Their Enhanced Photoelectrochemical Water Splitting Performance [Ji Hoon Choi](#), Dong Su Kim, Hak Hyeon Lee and Hyung Koun Cho; Sungkyunkwan University College of Natural Science, Korea (the Republic of)

Controlling and designing grain-boundaries (GBs), which cause recombination losses as planar defects in the absorbing layers are an essential strategy for the development of the highly efficient photoelectrochemical reaction systems. We suggest the method to design progressive bundle-type columnar structure as an alternative of single crystal with the fewest defects, where the GBs were aligned in parallel with charge transport movement and electric field direction. The instant strike bias (10 ms) in the same electrolytes induces the formation of island-shaped metallic Cu nanoparticles in the initial stage as seed crystals for controlling the Cu_2O growth evolution, and results in the dramatically high density Cu_2O nuclei and bundle-type columnar Cu_2O growth with longitudinal GBs, contrary to the typical randomly-crystallized Cu_2O . The metallic Cu seeds with stronger electric field than the exposed ITO region provide the selective crystallization sites for Cu_2O growth along the $\langle 111 \rangle$ ionic bonding. Despite ultimately instant strike interval, the p-type Cu_2O photoelectrodes retain outstanding photocurrent of 5.2 mA/cm^2 and on-set potential of 0.7 V at 0 V_{RHE} , owing to highly improved transport and transfer efficiencies inside the Cu_2O by suppressing effectively charge scattering in the GBs. Consequently, it is decisive that designing the bundle-type columnar structure could be a good strategy in developing the photocathodes with enhanced photoelectrochemical reaction.

EF10.14

Novel High Entropy Oxides for Oxygen Storage and Generation [Alicja Klimkowicz](#)^{1,2}, Shotaro Dokin¹ and Akito Takasaki¹; ¹Shibaura Kogyo Daigaku, Japan; ²Kanagawa Daigaku, Japan

Oxygen is an essential industrial gas utilized in many sectors, such as steel production. On a large scale, oxygen is produced by cryogenic distillation and used in many technologies, such as steel, paper, methanol production. However, the need for local, scattered oxygen generation for healthcare, sterilization, and wastewater treatment is rapidly growing. A small-scale oxygen generator relying on the adsorption (or absorption) method can satisfy the oxygen demand. In the Temperature Swing Absorption (TSA) method, the oxygen is absorbed at a lower temperature and released at a higher temperature, and the oxygen partial pressure remains constant. Analogously, in the Pressure Swing Absorption (PSA) method, the oxygen is absorbed into the material at a higher oxygen partial pressure over the sample and released at a lower pressure. The PSA process takes place at a constant temperature. The TSA and PSA methods rely on appropriate absorbing material, which is a device's heart. Oxygen storage materials (OSM) are used as absorbers for oxygen production using absorption methods. Naturally, the efficiency of the oxygen generation process depends on the performance of those materials. Therefore, the ideal OSM should reversibly absorb/desorb a large amount of oxygen (high δ) that translates to a high oxygen storage capacity ($OSC > 3 \text{ wt. \%}$). The oxygen absorption and desorption kinetics should be fast; the operating temperature should be below 400 °C. Currently, there is no material that meets all the requirements. Therefore, a search for new OSMs is ongoing. A new group of materials, high entropy oxides (HEO), is proposed as potential OSM absorbers. The HEOs are defined as multi-elemental compounds in equimolar or near-equimolar ratios stabilized in a simple solid solution structure due to the high configurational entropy. In 2015, Rost et al. synthesized the first entropy-stabilized oxide (Mg-Ni-Co-Cu-Zn)O. In 2017, Sarkar et al. examined the formation of high entropy oxides and showed that using theoretical calculations, HEO can exhibit high oxygen vacancies (δ). The calculated oxygen vacancies (δ) increase with the number of cations in HEOs, and it can be as high as $\delta = 0.38$ for $(CeLaPrSmY)O_{2-\delta}$ resulting in a 3.54 theoretical OSC. The HEOs look very promising since a high and reversible oxygen content change is a prerequisite for good OSMs. In this research, the sinterability of the $(nLn_{1/n})O_{2-\delta}$ (where $L_n = \text{Lanthanides}$, $n = 4, 5, 6, 7$) high entropy materials will be confirmed. The crystal structure of the multi-elemental compounds will be investigated. The amount of oxygen vacancies will be studied together with oxygen storage and generation properties of novel high entropy oxides.

EF10.15

NMR Investigation of Proton Transport in Mechanically Robust Polybenzimidazole/Polyphosphoric Acid Membranes [Laura Murdock](#)¹, [Tawhid Pranto](#)², [Mounesha Garaga](#)³, [Sophia Suarez](#)⁴, [Brian Benicewicz](#)¹ and [Steve Greenbaum](#)³; ¹University of South Carolina, United States; ²CUNY The Graduate Center, United States; ³Hunter College of CUNY, United States; ⁴Brooklyn College, United States

Previous work by some of us has demonstrated enhanced electrochemical performance of polybenzimidazole (PBI) membranes with high phosphoric acid content prepared by the so-called PPA process.¹ We report here a new synthetic route to dense PBI films, with repeat unit para-PBI and without the use of any organic solvents, which were originally developed for flow battery applications. However these films also can be re-doped in phosphoric acid to be used as membranes in high-temperature PEM fuel cells. The re-doped PBI films display high ionic conductivity at elevated temperatures, similar to the starting PBI gel membranes prepared by the PPA process¹, while also exhibiting enhanced mechanical properties. Thus, in high-temperature PEM fuel cell operation the electrochemical performance is similar, but performance degradation due to mechanical creep is reduced, leading to greater durability of the modified and re-acidified PBI membrane.

In attempting to understand the enhanced proton conductivity of the modified PBI membrane despite its lower acid content, by nearly a factor of two, we performed ^1H , ^{13}C , and ^{31}P nuclear magnetic resonance (NMR) measurements. Proton self-diffusion coefficients for membranes prepared by the modified process and by the original PPA process, were measured by pulsed field gradient NMR.

The results show significantly enhanced proton diffusivity, both in magnitude and in lower activation energy for the dense and re-acidified membrane, which is consistent with its high conductivity despite lower acid content compared to the original PPA-processed membranes. We have also performed solid state magic angle spinning cross-polarization one-dimensional $^{13}\text{C}\{^1\text{H}\}$, $^{31}\text{P}\{^1\text{H}\}$ and two-dimensional $^{31}\text{P}\{^1\text{H}\}$ and $^{13}\text{C}\{^1\text{H}\}$ HETCOR NMR measurements, which yield additional information on structural differences between the membranes and how these differences may affect transport properties. In particular, the results demonstrate a more rigid glassy structure of the polymer and stronger coupling between phosphate moieties and the polymer backbone in the modified membrane, which may enhance proton transport via the Grothuss mechanism.

1. Multinuclear NMR Study of the Effect of Acid Concentration on Ion Transport in Phosphoric Acid Doped Polybenzimidazole Membranes, S.N. Suarez, N.K.A.C. Kodiweera, P. Stallworth, S.G. Greenbaum, S. Yu, and B. Benicewicz, *Journal of Physical Chemistry B*, 116, 12545-51(2012).

EF10.16

Tuning of Shape, Disorder and Oxygen Vacancies in Lanthanum-Doped (0-70%) Ceria Shaped Nanoparticles for Oxidative Coupling of Methane Fabiane d. Trindade¹, Sergio Damasceno¹, Larissa Otubo², Daniel Z. Florio¹, Fabio Fonseca² and Andre S. Ferlauto¹; ¹Universidade Federal do ABC, Brazil; ²Instituto de Pesquisas Energeticas e Nucleares, Brazil

The abundance of natural gas due to the advancements in exploration and extraction has increased the interest in the direct conversion of methane to C_2 molecules via oxidative coupling of methane (OCM) reactions. However, the achievement of viable catalytic routes for such reactions has been a challenge due to thermodynamic limitations. In this work, we investigate lanthanum doped cerium oxide nanoparticles as catalysts for OCM. La was chosen due to its 3+ valence, which results in the formation of oxygen defect sites in Ce:La solid solutions, and to its high thermal stability and basicity. The fine-tuning of the size, shape and defects of cerium-lanthanum oxide nanoparticles was achieved by varying La concentration and synthesis temperature. $\text{La}_x\text{Ce}_{x-1}\text{O}_{2-x/2}$ nanoparticles having La^{3+} concentration, x , varying between 0 and 70 mol% were synthesized via a template-free hydrothermal process. Two series of samples were investigated using a hydrothermal temperature of 110 °C (nanorods) to 180 °C (nanocubes) and keeping all other synthesis parameters equal. The morphology of the $\text{La}_x\text{Ce}_{x-1}\text{O}_{2-x/2}$ NPs was determined by scanning electron microscopy (SEM) and high-resolution electron microscopy (HRTEM). The SEM and TEM images reveal that La^{3+} addition significantly impacts the morphology of the obtained $\text{La}_x\text{Ce}_{x-1}\text{O}_{2-x/2}$ -110 °C and $\text{La}_x\text{Ce}_{x-1}\text{O}_{2-x/2}$ -180 °C nanostructures. As the La^{3+} doping increases, the rods and cubes organize themselves in an oriented attachment mechanism. X-ray diffraction analysis indicates that, upon doping ceria with La^{3+} , no separate peaks corresponding to La_2O_3 are observed for $\text{La}_x\text{Ce}_{x-1}\text{O}_{2-x/2}$ -110 °C for $x < 0.7$. The incorporation of La^{3+} into the CeO_2 crystal structure results in an expansion of the fluorite lattice. On the other hand, for the $\text{La}_x\text{Ce}_{x-1}\text{O}_{2-x/2}$ -110 °C, for La^{3+} content $x > 0.40$, extra broader reflections are observed, indicating that two fluorite phases are present which have different lattice parameters and crystallite sizes. They can be associated with two distinct morphology, cubes and rods. In addition, La^{3+} addition results in a significant increase in microstrain reflecting the large disorder of the structure associated with the difference in cations size, excess of vacancies and random distribution of cations and anions in their sublattices. Raman spectroscopy was also used to investigate the disorder and defect formation. A red-shift of the main fluorite F_{2g} peak is observed that reflects the expansion of the structure. More interestingly, as La^{3+} concentration increases, the F_{2g} broadens significantly and the formation of different amounts of extrinsic and intrinsic oxygen vacancies is revealed by the emergence of a "defect" band at 500-600 cm^{-2} . Such effect is stronger in the $\text{La}_x\text{Ce}_{x-1}\text{O}_{2-x/2}$ -110 °C series, indicating that the rod-like nanostructures prepared at lower T can accommodate a much higher level of defects and disorders.

The catalytic performance of the $\text{La}_x\text{Ce}_{x-1}\text{O}_{2-x/2}$ NPs for the OCM reaction was evaluated in a fixed-bed reactor at 750 °C. The reagents CH_4 and O_2 and the products H_2 , CO , CO_2 , C_2H_4 , and C_2H_6 , were measured by an in-line mass spectrometer. $\text{La}_x\text{Ce}_{1-x}\text{O}_{2-1/2}$ -110 °C ($x = 0.5$) showed the best catalyst performance has 25% of methane conversion and 48% of selectivity for the formation of C_2 products. By increasing La^{3+} , the selectivity to C_2 hydrocarbons was increased. The correlation of Raman spectroscopy and catalysts results suggests that the high concentration of defects and/or high disorder in the $\text{La}_x\text{Ce}_{1-x}\text{O}_{2-1/2}$ -110 °C ($x = 0.5$) nanorods were crucial to improving conversion rates and selectivity.

EF10.17

Doping Effect on the Hydrogen Production via Microwave Assisted Water Splitting in Doped-Ceria Materials Aitor Domínguez¹, Laura Navarrete¹, Maria Balaguer¹, Joaquin Santos¹, Pedro José Plaza², José Manuel Catalá² and José Manuel Serra¹; ¹Instituto de Tecnología Química, Spain; ²Institute of Information and Communication, Spain

Nowadays, hydrogen is being used as an energetic vector for saving excess of renewable energy. The most used techniques to generate hydrogen are thermochemical looping's, electrolyzers and hydrocarbons reforming. However, all these techniques have several drawbacks, namely the high temperatures needed, the use of sophisticated machinery and the long operation times required for the hydrogen production. Recently, the possibility to generate green hydrogen using electric energy, as microwave radiation, has been reported. This process uses metallic oxides as catalysts, e.g. CeO_2 , and it occurs in a reactor at temperatures lower than 250 °C in less than five minutes.

The hydrogen production mechanism happens in two steps. First, the material is irradiated with a microwave electromagnetic field, producing the reduction of the material with the concomitant release of oxygen. This radiation is able to stabilize a higher amount of oxygen vacancies in the fluorite structure at lower temperatures than the conventional radiative processes, as it is the case of thermosolar (>1000 °C). When the microwaves are turned off in the presence of water, the material splits the H_2O molecule, therefore liberating a stream of molecular hydrogen and filling its oxygen vacancies. One example of this process is noted in the material $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_2$.

The release of oxygen is accompanied by an increase in the material electrical conductivity. Besides, it has been observed that a different conductivity behaviour can be inferred depending on the irradiated microwave power. If the microwave radiation power is lower than the activation energy (P_{TH}), the material conductivity behaves similar to conventional heating process. On the other hand, for a microwave radiation power higher than the P_{TH} , the material undergoes a sudden spike in the conductivity. This rise is mainly ascribed to an increase of the electronic conductivity. Ionic conductivity can be tuned by doping the ceria lattice with iso and aliovalent cations. For example, incorporating Zr^{4+} into the structure, the ionic conductivity decreases, while Gd^{3+} generates oxygen vacancies in the anionic sublattice, thus, increasing the ionic conductivity. In this work, we have synthesized and characterized a set of ceria doped materials, e.g. $\text{Ce}_{1-x}\text{M}_x\text{O}_2$ ($\text{M} = \text{La}, \text{Y}, \text{Yb}, \text{Tb}, \text{Zr}$, and Gd) ($x = 0.1$ and 0.2). Their interaction with microwave radiation has been monitored in order to study their modulability regarding conductivity behaviour and hydrogen production capacity.

EF10.18

Experiment Driven Computational Analysis of Solar Thermochemical Hydrogen Production Materials Andrew I. Smith; Sandia National Laboratories, United States

The production and use of clean hydrogen is an important step in the decarbonization of the world's energy economy. Currently hydrogen is used in various important chemical applications and is playing an ever-increasing important role in the difficult to electrify energy markets of construction and long-haul transportation. The US currently produces ~10 million metric tons of hydrogen per year, with most of the hydrogen being produced by steam methane reforming of fossil fuels.¹ The desire for clean hydrogen has resulted in governments and institutions investing in clean hydrogen technologies

that produce hydrogen from water without adding any CO₂ to the atmosphere. These technologies range from electrolyzers, to carbon capture and to thermochemical production. Solar thermochemical hydrogen production (STCH) uses concentrated solar power (CSP) to transform water directly into hydrogen.

SESSION EF11: Proton Conducting Fuel Cells I
 Session Chairs: Vasileios Kyriakou and Neal Sullivan
 Wednesday Morning, July 20, 2022
 Lobby Level, Avenue 34, Studio 1

9:10 AM **EF11.01

Combinatorial Screening of Triple Ionic-Electronic Conducting Oxide Electrodes for Fuel Cell and Electrolysis Applications Meagan Papac^{1,2,3}, Jake Huang^{2,3}, Yewon Shin², Youdong Kim², Andriy Zakutayev³ and Ryan O'Hayre^{2,3}; ¹National Institute of Standards and Technology, United States; ²Colorado School of Mines, United States; ³National Renewable Energy Laboratory, United States

Triple ionic-electronic conducting oxides (TIECs) show great promise in high-temperature electrochemical applications, including ceramic fuel cells and electrolyzers. The transport properties and electrochemical activity of TIECs depend strongly on chemical composition and environmental conditions, such as operating temperature and gas environment. Here, we present the combinatorial investigation of a large family of TIEC oxide perovskite materials with the goal to understand how changes in the TIEC composition correlate with the changes in electronic properties and electrochemical performance. In total, more than 2,500 impedance spectra were analyzed, representing 432 distinct Ba(Co,Fe,Zr,Y)O_{3-d} (BCFZY) compositions synthesized by pulsed laser deposition and measured at three temperatures under two different gas atmospheres, enabling a new scientific insight into the trends governing electrochemical performance. Our combinatorial experiments demonstrate that Co-rich compositions achieve the lowest overall polarization resistance under both dry air and humid N₂, while high Fe content may impede the performance at decreased temperatures. Combinatorial results are confirmed by isotope-labeled SIMS tracer diffusion studies as well as symmetric and full cell protonic-ceramic fuel cell and electrolysis testing of selected compositions of particular interest. Hierarchical Bayesian analysis indicates that the performance-limiting process depends on the chemical composition, measurement temperature, and atmospheric humidity. This work provides a composition map of condition-dependent electronic properties of materials in the BCFZY perovskite family for their application as air electrodes for protonic ceramic fuel cell and electrolysis applications.

9:40 AM *EF11.02

Improving Performance and Durability of Intermediate Temperature Proton Conducting Solid Oxide Electrolysis Cells Via Materials Design and Catalyst Surface Engineering Hanchen Tian, Wenyan Li and Xingbo Liu; West Virginia University, United States

Solid oxide steam electrolysis cell, a promising electrical-chemical conversion device for the next generation efficient hydrogen production and energy storage, has been actively studied because of their high energy conversion efficiencies and prospective applications as electrochemical reactors. After decades of research on protonic ceramic materials, remarkable advances have been made in the protonic ceramic electrochemical cells (PCECs) air electrode and electrolyte. However, the existing air electrodes are far from satisfying the requirements of practical applications, a series of issues, including the lack of active and durable electrodes, greatly limit the commercialization. To date, the systematic development of triple conducting catalysts remains abstruse because of the challenges of characterizing protonic behavior. A quantitative properties assessment and prediction on protonic properties of perovskite are still not available.

Starting with a computational fluid dynamic modeling on the protonic ceramic electrochemical cells (PCECs) air electrode, the dissertation's accomplishments are focused on the materials design of air electrode materials by employing model guidance, operating durability optimization by electrode structure engineering, as well as the air electrode surface tailoring to overcome the most rate-limiting step. Thus, the electrochemical performance and durability of PCEC are comprehensively improved. The fabrication methods, characterization techniques with electrochemical performance are presented. Further work plans and implications are proposed regarding optimizing the structure of materials, preparation technology, and better understanding the role of these triple conductors. This research is expected to provide an in-depth understanding and offer avenues in the rational design of PCEC with long operational life and high energy/power density in the near future.

10:00 AM *EF11.03

Surface and Bulk Oxygen Kinetics of BCFZY Triple Conducting Electrode Materials Kyle Brinkman; Clemson University, United States

Triple ionic-electronic conductors such BaCo_{0.4}Fe_{0.4}Zr_{0.1}Y_{0.1}O_{3-δ} (BCFZY) have received much attention as high performance electrode materials for protonic ceramic fuel cells. The oxygen surface exchange and bulk diffusivity of BaCo_{0.4}Fe_{0.4}Zr_{0.1}Y_{0.1}O_{3-δ} were determined by electrical conductivity relaxation (ECR) in order to quantitatively assess cathode performance. The measurements were performed at 600C, following pO₂ step changes between 80 ppm to pure oxygen. The apparent value of surface exchange coefficient (*k*) and diffusion coefficient *D*, indicates BaCo_{0.4}Fe_{0.4}Zr_{0.1}Y_{0.1}O_{3-δ} is a good oxygen conductor. *k* was found to vary with pO₂ and surface area while the chemical diffusion coefficient *D* remained invariant with pO₂ and surface coating. The fitted kinetic parameters obtained from ECR with reduction process (high to low pO₂) were compared with that of the oxidation process (low to high pO₂). In the presence of H₂O, oxygen exchange kinetics was suppressed because of the competitive adsorption relationship between oxygen and H₂O. As a follow-up to this initial work, the bulk characteristics of oxygen diffusion and surface exchange were determined for the triple-conducting BaCo_{0.4}Fe_{0.4}Zr_{0.2}-XYXO_{3-δ} suite of samples with varying Y composition. Y substitution increased the overall size of the lattice due to dopant ionic radius and the concomitant formation of oxygen vacancies. Oxygen permeation measurements exhibited a three-fold decrease in oxygen permeation flux with increasing Y substitution. The DC total conductivity exhibited a similar decrease with increasing Y substitution. These relatively small changes are coupled with an order of magnitude increase in surface exchange rates from Zr-doped to Y-doped samples as observed by conductivity relaxation experiments. The results indicate that Y-doping inhibits bulk O₂⁻ conduction while improving the oxygen reduction surface reaction, suggesting better electrode performance for proton-conducting systems with greater Y substitution.

10:20 AM *EF11.04

Linking Atomistic and Electrochemical Modelling of Proton Ceramic Electrochemical Cells Jonathan Polfus¹, Jónína Gudmundsdóttir¹, Kalpana Singh¹, Ragnar Strandbakke¹ and Einar Vøllestad²; ¹Universitetet i Oslo Det Matematisk-naturvitenskapelige Fakultet, Norway; ²SINTEF, Norway

Proton ceramic electrochemical cells show great promise for use in fuel cells, steam electrolyzers and electrochemical membrane reactors. To further develop high-performance electrodes and cell architectures, a mechanistic understanding of the electrode processes is required for identification of the rate determining steps.

A broader understanding of the overall cell performance may be achieved through the development of electrochemical models that describe the reaction mechanisms and rates of predominating electrode processes. In particular, different reaction mechanism can dominate for different classes of materials and operating conditions. These mechanisms can in turn be divided into a series of elementary reaction steps, of which one or more can be rate determining.

Atomistic modelling based on density functional theory (DFT) is used to provide material- and reaction specific parameters that enter the electrochemical models. These are based on rate expressions involving concentration/coverage terms, including competitive adsorption, and kinetic terms such as pre-exponential and activation energies for e.g., adsorption, dissociation and diffusion.

The models are supported and compared with experimental studies. Surface exchange rates of oxygen and the influence of steam on the steam electrode is studied by gas phase isotope exchange methods. Electrochemical impedance spectroscopy (EIS) and DC voltammetry is used to extract pre-exponentials, activation energies, pO_2 -dependency, and pH_2O -dependency of the different electrode responses. Furthermore, DC voltammetry can be coupled with EIS under applied load to extract Tafel-slopes and investigate the fundamentals of the current-voltage relationships.

10:40 AM BREAK

SESSION EF12: Unlocking the Potential of Industrial-Scale Electrolysis

Session Chairs: Georgios Dimitrakopoulos and Ryan O'Hayre

Wednesday Morning, July 20, 2022

Lobby Level, Avenue 34, Studio 1

11:00 AM *EF12.01

Solid Oxide Electrolysis Materials Challenges and Compromises [S. Elangovan](#), Joseph Hartvigsen, Tyler Hafen, Jenna Pike, Taylor Rane and Dennis Larsen; OxEon Energy, LLC, United States

The promise of solid oxide electrolysis (SOXE) is based on its high efficiency operation and the flexibility to electrolyze steam, carbon dioxide, or a mixture of the two to produce hydrogen, carbon monoxide, or synthesis gas respectively. The high operating temperature of solid oxide electrolysis makes selection of materials for the construction of cells and stack a challenge as a result of the conflicting requirements of the various functions within the stack. Achieving high electronic and ionic conductivity within the current path, while maintaining the porous microstructure of the electrodes during operation, avoiding interdiffusion, segregation or reaction of various cations during fabrication and operation, matching physical and chemical properties of layers for multiple thermal cycles that may be required in an application environment add to the challenge. Mechanical requirements of the stacks also vary depending upon the nature of system deployment and is the most challenging for space and planetary applications.

The SOXE baseline materials set and processing conditions were developed for solid oxide fuel cell application although the electrolysis operation imposes additional challenges. OxEon Energy's team started SOXE development with the set of materials that provided the necessary functionality in fuel cell operation. However, the challenges for SOXE operation and more specifically certain target applications necessitated a series of changes to the materials set. The overall strategy of developing materials that would have broader applicability to various end use required an approach where the functionality of various layers together took predominance over choosing the best composition for an individual layer. The approach also took into consideration the various operational requirements of the SOXE depending upon the application. Examples of this approach include modification to the fuel electrode to provide reduction-oxidation (redox) tolerance and to the air electrode to eliminate delamination during operation.

Traditionally, SOXE stacks use nickel-zirconia or nickel-ceria composite cathode to reduce the oxidized species. Nickel based electrodes are susceptible to oxidation by the feed gas (CO_2 or steam) at the inlet conditions and are often irreversibly damaged unless reduced species (carbon monoxide or hydrogen) are also present. This necessitates a complex, recycle loop that introduces a fraction of the product gases to the inlet, as was used for the Mars rover mission. Under a NASA SBIR program OxEon investigated a combination of materials and engineering solutions to improve redox tolerance of the nickel based cathode so that 100% dry CO_2 could be fed directly into a stack without damaging the electrode. OxEon has now successfully demonstrated this redox tolerance through the use of a modified nickel based cathode composition. Button cells and a stack have been shown to tolerate complete oxidation of Ni to NiO, with performance recovery occurring in a matter of minutes using only the CO generated by the electrolysis reaction to re-reduce the cathode. The redox tolerant stack was also demonstrated to show improved coking tolerance over the traditional cathode material. This feature allows higher conversion of CO_2 enabling increased O_2 production. Tests are ongoing to evaluate redox tolerance for steam electrolysis.

A composition modification to the air electrode was required to eliminate delamination and to reduce compositional instability arising from cation migration. While the composition by itself is less conductive compared to traditional electrodes, the performance stability was found to improve. An overview of the materials development will be presented.

11:20 AM *EF12.02

Solid Oxide High Temperature Electrolysis [Venkat Venkataraman](#); Bloom Energy, United States

Reducing carbon emissions is the number one priority in the fight against climate change, and green hydrogen will be critical to world's decarbonization objectives. Green hydrogen is produced by electrolyzing water or steam using renewable power. Among the many electrolyzer technologies, Solid Oxide Electrolyzer is the most efficient. It is flexible that can use water and steam feed. The presentation covers the basics of solid oxide electrolyzer configuration, manufacturing techniques and applications.

11:40 AM *EF12.03

Power-to-X and Green Hydrogen at Haldor Topsoe—Status and Plans [Poul G. Moses](#), Peter Blennow, John B. Hansen, Michael Hultqvist, Jeppe Rass-Hansen and Thomas Heiredal-Clausen; Haldor Topsoe AS, Denmark

Haldor Topsoe's strategic vision is to be recognized as the global leader in carbon emission reduction technologies by 2024. As part of that strategy we are changing our direction to accelerate the sustainable transition. We envision a solution rooted in launching the Power-to-X era, enabling electrification of hard-to-abate sectors to support low-carbon chemical and fuel production around the world, as well as enabling green steel production and energy supply. High-temperature electrolysis, empowers producers in hard-to-abate sectors to generate carbon-free hydrogen and/or carbon monoxide using renewable electricity.

Topsoe's solid oxide electrolysis cell (SOEC) technology is designed to integrate seamlessly with downstream processes, so green hydrogen can be

processed into green ammonia, for use in chemical applications or energy storage. It can be processed into eMethanol, for use in chemical or transportation-fuel production, or one of many other green chemicals and fuels. With decades of experience as a world-leading solution provider for all of these applications, Topsoe is one of the very few companies possessing both the expertise and the technologies needed to transform renewable electricity, biomass, and waste into green hydrogen, green ammonia, eMethanol, and eFuels for zero-emission fuels and chemicals that will power a sustainable future.

In March 2020, Topsoe announced to build a large-scale SOEC electrolyzer manufacturing facility to meet customer needs for green hydrogen production. When operational in 2023, the facility will produce electrolysis stacks and modules with a capacity of 500 MW per year.

Here, we will present status updates on our various stepping stone projects, CO₂ electrolysis for CO production and H₂O electrolysis for biogas upgrading, as well as the demonstration project for the electrification of ammonia production. We will also share the status of the manufacturing facility and other relevant demonstration activities.

12:00 PM *EF12.04

Scaling Up Proton Ceramic Electrolysis Technology—An Overview of Materials, Cells, Stacks and System Development [Marie-Laure Fontaine](#); SINTEF Industri, Norway

Developing high temperature electrolyzers (HTEs) using proton conducting electrolytes has gained traction in the research arena and many studies are dedicated to materials and cells development. Existing cell design is based on planar geometry, but the hot seal and vulnerability to single cell breakdown is questionable for operating the cell at pressure to produce pressurized hydrogen. Furthermore scaling up the cell dimensions and production is perceived as challenging due to the challenging sinter-ability of proton ceramic based materials. In this presentation, we report on the development of a tubular Proton Ceramic Electrolyser (PCE) module technology for producing pure dry pressurized hydrogen demonstrated at 10 bar in our laboratories. The cells are designed as innovative single engineering units (SEU) with each cell of 60-70 cm² active surface area encased in a steel shell for operation at 600°C. The tubular cells integrate BZCY based electrolyte, BZCY-Ni hydrogen electrode and BGLC-BZCY based composite steam electrode. Electrochemical performance of the produced SEUs are presented as function of temperature, potential and pressure at up to 10 bar showing high faradaic efficiency and continuous improvement along with optimization of the SEU design and materials. We also report on the design work related to the integration of the SEUs in a 10 kW rated system for delivering pure hydrogen at minimum 30 bars outlet pressure, with the support of advanced modelling and simulation work. The system with necessary balance of plant is under construction and opportunities and challenges towards its finalization will be discussed. Recent results on techno-economic analyses and life cycle studies will be presented to discuss opportunities of integration of PCEs in various industrial plants. This project has received funding from the Fuel Cells and Hydrogen 2 Joint Undertaking under grant agreement (number 779486) and grant agreement (number 101007165). This Joint Undertaking receives support from the European Union's Horizon 2020 Research and Innovation programme, Hydrogen Europe and Hydrogen Europe Research.

12:20 PM *EF12.05

Scalable Electrochemical Proton Ceramic Reactors for Hydrogen Technologies [Christian Kjøelseth](#); CoorsTek Membrane Sciences AS, Norway

High-temperature electrochemical reactors combine in-situ thermal activation with hydrogen separation and compression for efficient production of hydrogen from hydrogen containing energy carriers. Proton ceramic electrochemical reactors (PCERs) based on high-temperature proton (H⁺) conducting ceramics such as Y-doped BaZrO₃-BaCeO₃ solid solutions (BZCY) offer attractive performances including mechanical stability and chemical robustness over a wider range of temperatures and conditions. In PCERs, hydrogen is extracted from hydrogen containing molecules and transported as H⁺ across the membrane, enabling electrochemically assisted hydrogen recovery simultaneously allowing for direct hydrogen compression. For practical implementation of scalable reactor there is a need to manage heat, electric current/voltage and gas flows to achieve near complete hydrogen recovery, while also facilitating fast kinetics and mechanical stability at high temperatures and at elevated pressures. This contribution will report on robust high-performance electrochemical proton ceramic reactors for hydrogen production from various hydrogen containing molecules. Results from a multi-segmented unit with parallel and serial electrically connected single cells assembled using novel thermally matched metal/glass ceramic interconnects will be discussed.

SESSION EF13: Oxygen-Ion Conducting Fuel Cells II
Session Chairs: Albert Tarancón and Andre Weber
Thursday Morning, July 21, 2022
Lobby Level, Avenue 34, Studio 1

9:10 AM **EF13.01

WITHDRAWN (EF13) New Strategy for Boosting Cathodic Performance of Protonic Ceramic Fuel Cells Through Incorporating a Superior Hydration Second Phase [Zongping Shao](#)^{1,2}; ¹Curtin University, Australia; ²Nanjing Tech University, China

Since both oxygen reduction reaction (ORR) and water formation happen over protonic ceramic fuel cell (PCFC) cathode, to maximize cathodic performance it is key to develop material with high intrinsic activity for oxygen activation and high bulk proton conductivity for enabling water formation at entire electrode surface. Hydration of oxygen vacancies in cathode material is key for the creation of protonic conductivity under oxidizing atmosphere, and a higher water content will benefit the hydration reaction, thus increasing the proton conductivity. However, the increase of water content will not only dilute the oxygen in the gas, but also suppress the O₂ adsorption on the electrode surface, thus inhibiting ORR. Herein, we propose a new electrode design concept that may overcome this dilemma. By introducing a second phase with high-hydrating capability into a conventional cobalt-free perovskite with superior ORR activity to form a unique nanocomposite electrode, high proton conductivity can be reached at low water content in atmosphere. Operando X-ray absorption spectroscopy indicates the high-water uptake from the hydrophilic phase can effectively reduce the oxygen vacancies in the perovskite phase and create high proton concentration in the electrode bulk. In addition, the hydration creates additional fast proton (H₃O⁺) transport channel along the two-phase interface. As a result, high protonic conductivity is reached, leading to a new breakthrough in performance for PCFC devices among available cobalt-free cathodes.

9:40 AM *EF13.02

Sintering Aids for Electrolyte in Solid Oxide Cells [Ho-Il Ji](#), Junseok Kim and Jong-Ho Lee; Korea Institute of Science and Technology, Korea (the Republic of)

Solid oxide cells (SOCs) based on oxygen-ion-conducting electrolytes and Protonic Ceramic Cells (PCCs) based on proton-conducting electrolytes are promising sustainable and efficient electrochemical energy conversion devices. The realization of thin and dense electrolytes in SOCs and PCCs is essential to enhance the electrochemical performance. However, the structurally and chemically ideal electrolyte cannot be readily fabricated through conventional ceramic processes. For example, in SOCs, the bilayer electrolyte comprising doped-zirconia and doped-ceria is typically required, but the largely different sintering shrinkage behavior of both layers makes difficult to achieve the dense structure without interfacial defects. In PCCs, owing to the refractory nature of the proton-conducting electrolytes, the densification behavior of the electrolyte difficult to control. Here we describe a strategy of naturally diffused sintering aid allowing the fabrication of electrolytes with full density at lower sintering temperature in both SOCs and PCCs. The amount of supplied sintering aid is small but appropriate for full densification of electrolytes, thereby achieving a minimal ohmic loss and remarkable performances of SOCs and PCCs, respectively. In addition, the probable mechanism on supply of sintering aids during heat-treatment will be discussed.

10:00 AM *EF13.03

Solid-State Climate-Friendly Aviation Propulsion [David Tew](#); Advanced Research Projects Agency-Energy, United States

Modern commercial aviation has transformed our world by dramatically lowering the cost and time required to travel across oceans and continents. To date, this transformation has been powered by fossil-derived fuels that are combusted at high altitudes with the resulting products emitted in a manner that can result in the formation of heat-trapping contrails and cirrus clouds; this effect is potentially even more significant than the warming effect associated with the CO₂ emitted. As a consequence, commercial aviation is a significant contributor to our climate challenge. Without action, COVID-19 notwithstanding, the significance of aviation's climate impact is forecast to grow significantly as the industry expands into emerging markets around the world.

In order to preserve this attractive feature of modern life while protecting our climate, we must both decarbonize our fuel supply and control the either the location or manner in which any reaction products are emitted into the atmosphere. All-electric battery-powered propulsion systems are an attractive option for 'short-haul' flights; however, the limited specific energy (<500 Wh/kg) of batteries will limit the range of such flights to several hundred miles. Consequently, consumable fuels will continue to be critical to long-distance (e.g., trans-oceanic) aviation. However, these fuels must be derived from carbon-neutral sources such as biomass or CO₂, H₂O and renewable electricity; candidates fuels H₂, NH₃, CH₃OH, CH₄, or 'synthetic aviation fuel'. As a result of our need to generate rather than extract (and refine) these fuels, they will be more expensive, and some of them will have significantly lower gravimetric or volumetric energy densities.

Thus, in order to maintain the economic attractiveness of commercial aviation, future propulsion systems will need to use our precious carbon-neutral fuel resources even more sparingly than our current state of the art systems use fossil-derived ones. Solid oxide fuel cell (SOFC)/gas turbine hybrid systems offer the potential for substantial (>50%) increases in conversion efficiency. However, at present, commercial SOFC systems do so with a weight that is unattractive for aviation systems. The ARPA-E REEACH program was developed to address this challenge by accelerating the development of ultra-high specific-power/flight weight SOFC systems—and other advanced gas turbine system concepts.

The early results of the ARPA-E program have demonstrated cell-level specific powers that are indeed consistent with the aggressive weight goals of the program. This talk would present the objectives of the program, progress made and future challenges associated with the development of solid-state climate-friendly aviation propulsion systems.

10:20 AM EF13.04

Low-Temperature Exsolution of Nanoparticles from A-Site Deficient Lanthanum Nickel Ruthenium Double Perovskites [Jia Guo](#)¹, Rongsheng Cai² and Stephen J. Skinner¹; ¹Imperial College London, United Kingdom; ²The University of Manchester, United Kingdom

Exsolution of metal nanoparticles (NPs) from metal oxides has drawn intensive attention as a convenient, one-step synthesis method for catalytically-active, stable catalysts [1]. Especially for the exsolution of bimetallic NPs, the exsolved NPs were reported to present higher catalytic activity and stability compared to monometallic catalysts [2]. However, previous studies mainly focus on exsolution with the high-temperature thermal reduction, which limits the potential application of exsolution[3]. Hence, in this study, we investigated the exsolution of NPs at lower temperatures.

In this work, lanthanum nickel ruthenium double perovskites have been reduced at a lower temperature (300-500°C), and at the same time, A-site deficiency has been introduced to the parent double perovskite to facilitate the exsolution process. High-angle annular dark-field scanning transmission electron microscopy images (HAADF-STEM) and energy-dispersive X-ray spectroscopy (EDX) has shown that the NPs exsolved at 450°C display enrichment of both Ni and Ru elements, indicating the bimetallic composition of the metal NPs. *In-situ* electrochemical impedance spectroscopy (EIS) illustrated that the exsolution of NPs happens after only 10mins of reduction, implying a fast, efficient method for catalyst fabrication.

For the process of exsolution, the stoichiometry of the parent double perovskites, temperature and reduction time has been reported to have a synergistic influence on the exsolved NPs[4]. In this study, thermogravimetric analysis (TGA) and X-ray diffraction (XRD) were used to investigate the oxygen stoichiometry of the parent double perovskites and their phase evolution under 5%H₂/Ar atmosphere. Transmission electron microscopy (TEM) and scanning electron microscopy (SEM) were utilized to investigate the particle size and density of exsolved NPs after reduction at different conditions. The chemical composition and valence state evolution were investigated by energy-dispersive X-ray spectroscopy (EDX) and X-ray photoelectron spectroscopy (XPS) respectively.

In general, we investigate the exsolution of NPs from A-site deficient lanthanum nickel ruthenium double perovskite at low temperatures. The influence of the stoichiometry of the parent double perovskites, temperature and reduction time has been discussed with respect to the morphology and chemical composition of the exsolved NPs.

Reference:

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10:35 AM BREAK

11:00 AM EF13.05

Rationally Design Internal Reforming Catalysts for High-Performance and Durable Methane-Fueled Metal-Supported Solid Oxide Fuel Cells [Chuancheng Duan](#)¹, Fan Liu¹, AbdulJabbar Mohammed Hussain², Nilesh Dale², Yoshihisa Furuya², Yohei Miura³ and Yosuke Fukuyama³; ¹Kansas

State University, United States; ²Nissan Technical Centre North America, United States; ³Nissan Research Centre, Nissan Motor Corporation Limited, Japan

Methane-fueled metal-supported solid oxide fuel cells (MS-SOFC) exhibit unique characteristics, which include high mechanical strength, rapid startup, robust stack, and using readily available fuel with high energy density, making it one of the ideal power sources for vehicles. High performances and durability at <650 °C are essential for implementing methane-fueled MS-SOFCs. However, the alloy support of MS-SOFCs has poor catalytic activity while it is prone to coking, leading to insufficient power density and severe coking. Therefore, modifying the anode with active and coking-tolerant internal reforming catalysts is essential for developing methane-fueled MS-SOFCs. Here, we will present the recent progress in internal methane reforming catalysts that have been rationally designed for MS-SOFCs. Enhanced fuel cell performances and >1000 hours of continuous operation have been demonstrated. Finally, we will provide our insights regarding the further development of methane-fueled MS-SOFCs to facilitate commercialization and deployment.

11:15 AM EF13.06

Ni-Based Bimetallic Catalysts for Internal Reforming of Methane with Steam and Carbon Dioxide at Low-Temperature Proton-Conducting Ceramic Fuel Cells Kyunpyo Hong and Jongsup Hong; Yonsei University, Korea (the Republic of)

A proton-conducting ceramic fuel cells (PCFCs) shows great electrochemical performance at low temperature and has a various fuel utilization exhibits activity with various fuels, which makes it attractive as a next generation fuel cell and green technology. The fuel-flexible proton-conducting ceramic fuel cells (PCFCs) may overcome the global warming issues by using greenhouse gases (i.e., CH₄, CO₂) as fuels. One of its key advantages also includes that it directly (internally) reforms various fuels (e.g., CH₄, H₂O, CO₂) at low temperatures to produce hydrogen, which is a big advantage over other fuel cells. However, carbon formation due to using fuels causes catalytic deactivation causing lowering reduced hydrogen production. In addition, the low operating temperature is associated with sluggish reforming kinetics. In this study, bimetallic alloy catalysts based on Ni are used in the PCFC anode to promote carbon resistance and reforming reaction kinetics at low temperatures. The Rh, Cu, Co metals are used for forming alloys with Ni as candidates with high performance. Their material characteristics and catalytic performance are characterized by using various experimental tools (i.e., TPR, XRD, BET, TEM, and GC). With an aid of these characterization techniques, it is confirmed that all candidate materials form bimetallic alloys with sufficient uniformity and nano-sized particles. The activity test and carbon resistance at SRM or DRM show that the order is Ni-Rh > Ni-Co > Ni > Ni-Cu.

11:30 AM EF13.07

Tailored Nano-Columnar La₂NiO_{4+δ} Thin Films for Enhanced SOC Cathode Performance Alexander Stangl¹, Adeel Riaz¹, Laetitia Rapenne¹, José Manuel Caicedo², Juan de Dios Sirvent³, Federico Baiutti³, Carmen Jimenez^{1,4}, Albert Tarancón^{3,5}, Michel Mermoux⁶ and Monica Burriel¹; ¹Laboratoire des Matériaux et du Génie Physique, France; ²Institut Català de Nanociència i Nanotecnologia, Spain; ³Institut de Recerca en Energia de Catalunya, Spain; ⁴Departament de Materials Chemistry, National Institute of Chemistry, Slovenia; ⁵Institutio Catalana de Recerca i Estudis Avancats, Spain; ⁶Laboratoire d'Electrochimie et de Physico-chimie des Matériaux et des Interfaces, France

Physicochemical processes are at the basis for the operation of electrochemical devices such as solid oxide cells, with the oxygen reduction reaction being among the most relevant ones. High oxygen exchange activity is therefore essential and its optimisation is the goal of various research strategies by tuning the intrinsic and apparent activity. Intrinsic activity is defined by physicochemical properties, such as the charge carrier densities and their mobilities, defect formation enthalpies, etc. On the other hand, the apparent activity is linked to the total number of active sites, e.g. via the available surface area.

In this study, we have selected La₂NiO_{4+δ} (L2NO4), a very promising cathode material for intermediate and low temperature solid oxide cell applications, due to its good electronic and ionic conductivity, together with its high oxygen exchange activity with a low activation energy. Oxygen incorporation and transport in La₂NiO_{4+δ} thin films is limited by surface reactions. Hence, tailoring the surface morphology is expected to lead to an overall improvement of the electrode performance.

We show how to tune the apparent and intrinsic activity of La₂NiO₄ thin films by tailoring their nano-structure. The samples were synthesized by Pulsed Injection Metal Organic Vapour Deposition (PI-MOCVD) on different single crystal substrates with thicknesses ranging between 33 and 540 nm. The microstructure was thoroughly characterised by SEM, TEM and XRD. By varying the deposition temperature (650 - 750 °C) we were able to tune the morphology of the films, in agreement with the structure zone model, achieving, at lower deposition temperatures, a nano-columnar microstructure, with open porosity and a significantly enlarged specific surface area. We found that this nano-columnar structure is rooted in a dense bottom layer, expected to serve as good electronic and ionic conduction pathway.

Further, we studied the effect of surface activity by electrical conductivity relaxation measurements in fully dense and nano-columnar La₂NiO₄ thin films of various thicknesses grown on several different single crystal substrates, revealing remarkably enhanced surface activity in thicker, nano-architected films, as compared to thin, dense ones.

Increasing the exposed surface area by increasing the film thickness (and hence the nano-column height), also led to a reduction in the polarisation resistance of the cathode, measured by electrochemical impedance spectroscopy.

While the larger surface area plays an important role in the observed enhancement, it does not account for the total activity increase. Hence, apparent as well as intrinsic activity were improved. We propose that intrinsic activity was enhanced by changes in the grain orientation and the exposed surfaces with distinct, faster exchange coefficients. Additional features, observed on the lateral side of the nano-columns, such as kinks and edges are also thought to improve oxygen exchange, as these defects are expected to strongly modify surface electronic states involved in the reaction mechanism.

Overall, the growth of nano-architected La₂NiO₄ thin film cathodes by PI-MOCVD resulted in a substantial enhancement of the oxygen exchange activity and opens up a new route towards the optimisation of electrode materials for intermediate to low temperature devices.

A. Stangl et al. "Tailored nano-columnar La₂NiO₄ cathodes for improved electrode performance" *J. Mater. Chem. A*, 2021, doi.org/10.1039/D1TA09110G

11:45 AM EF13.08

Study on Ruddlesden-Popper Materials as Candidates for Methane-Fuelled SOFCs Simone Tomadini¹ and Antonella Glisenti^{1,2}; ¹Università degli Studi di Padova, Italy; ²CNR-ICMATE, Italy

Green energy conversion, transportation and storage are nowadays more and more fundamental. Several devices have been developed at a different degree of optimization to this aim: among them, fuel cells are particularly interesting due to their relative low cost, high reliability, and High Energy Density.¹ Different configurations are possible: the one chosen to be investigated and optimized is based on a solid electrolyte characterized by a high

working temperature: the so-called Solid Oxide Fuel Cell. The advantages of this cell are centred on the high working temperature itself, that grants the possibility of using non-noble metals as catalysts for the electrochemical reactions, as well as using different fuels from pure hydrogen. In the cathode and anode site of the cell various materials can be employed: perovskites; oxides with formula ABO_3 (where A is an alkali, alkaline earth, or rare earth metals and B is a transition metal), are characterized by good composition flexibility, mixed ionic and electronic conductivity and high catalytic activity. A possible improvement over the standard perovskite phase is the adoption of a Ruddlesden-Popper phase, an oxide composed of one or more rock salt layers sandwiched between two perovskite layers. The resultant formula is $A_{n+1}B_nO_{3n+1}$.² The advantages over standard perovskites are a better ionic mobility and ionic conductivity. In this work $LaSr_2CrMnO_7$ (RP-LSCM) has been synthesized and compared with its non-RP equivalent: $La_{0.75}Sr_{1.25}Cr_{0.5}Mn_{0.5}O_3$ (LSCM). Both the materials have been synthesized using a citrate route called Marcellis reaction. RP-LSCM has been calcinated in a reducing environment to obtain the desired phase while LSCM has been calcinated in air. The phase of both the materials has been analysed by means of XRD. SEM analysis allowed to investigate the morphology of the material showing flake-like particles on the surface, similar in both RP-LSCM and LSCM. H_2 -TPR revealed the presence of Cr(VI) in the RP-LSCM. This was not observed in LSCM suggesting that the structure plays a role in stabilizing oxide states. Specific surface area is $2.1 \pm 0.1 \text{ m}^2/\text{g}$ in RP-LSCM, $13.0 \pm 0.1 \text{ m}^2/\text{g}$ in LSCM. The average pore width is $27.1 \pm 0.1 \text{ nm}$ for LSCM and $13.1 \pm 0.1 \text{ nm}$ for the RP-LSCM. Surface and grain atomic composition have been determined by XPS and EDX. A modest segregation of La and Cr is observed on RP-LSCM surface, while the bulk is understoichiometric in Mn. This suggests that Mn possibly migrated towards the first atomic layers of the material or in structural defects as agglomerates inside the rock-salt layers, typically the less stable and most stress-accumulated parts of the structure. Regarding LSCM, both the EDX and XPS analysis proved Cr understoichiometry. A slight Sr surface segregation was not observed for the Ruddlesden-Popper phase. Repeated Electrochemical Impedance Spectroscopy measures have been carried out on symmetric cells under different conditions to emphasize and enhance comprehension of the effect of the structure on performance. The ASR of RP-LSCM in 10% H_2 (in Argon) resulted to be $13.92 \Omega\text{cm}^2$ while the ASR for LSCM was $11.5 \Omega\text{cm}^2$ at 800°C ; much better results have been obtained using gold collector. ($1.7 \Omega\text{cm}^2$ at 810°C for LSCM, as an example). The cells have been tested using CH_4 obtaining an ASR 6 times higher than the one in H_2 . Ni impregnation was then performed to boost the performances in methane and values even lower than those obtained with H_2 have been obtained with a flow of 10% CH_4/Ar at 200 sccm in RP-LSCM. Further work is in progress to reach a better understanding of the behaviour of RP-perovskite with methane.

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doi:<http://dx.doi.org/10.1016/j.jaad.2006.12.015>

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12:00 PM EF13.09

Advantages of Ionic Conductors over Electronic Conductors as Infiltrates in SOFC Electrodes Elucidates Using Microstructurally Resolved HPC Simulations of Electrochemistry [Hokon Kim](#)^{1,2}, William K. Epting¹, Harry W. Abemathy¹, Gregory Hackett¹, Anthony D. Rollett^{1,2} and Paul A. Salvador^{1,2}; ¹National Energy Technology Laboratory, United States; ²Carnegie Mellon University, United States

Solid oxide fuel cells (SOFCs) are very attractive electrochemical devices, because they can generate the electricity directly from the chemical energy of a fuel. SOFCs usually work at relatively high temperatures (600–1000 C) compared to other types of fuel cells. Due to the high operating temperature, it has a high fuel flexibility and the potential to improve efficiencies through waste heat recovery in combined heat and power systems. Unfortunately, even with those advantages, SOFC technology needs further improvement to be economically competitive with conventional energy conversion technologies. For instance, for the commercialization of SOFC, still there are several challenges such as low durability and poor reliability.

Infiltration is the process of introducing nanoscale electrocatalyst phases within a pre-fabricated electrode backbone. Many studies have been shown that the enhancement of electrochemical performance can be achieved by infiltration and it can reduce long-term degradation. Based on the reported results, infiltration modifies the local morphology of the electrode, which has a positive impact on the electrochemical reaction sites and/or mass and charge transport. As a result, the overall performance will be improved. However, how infiltration affects (1) the local electrochemistry is difficult to measure and (2) the distribution of electrochemically active sites is difficult to characterize with appropriate resolution over relevant length scales. On the other hand, simulations of local electrochemistry within fully resolved three-dimensional microstructures are now possible, as are methods to synthetically generate nanoscale infiltrates within such microstructures. Combining these will be useful for connecting the infiltrated microstructures with the electrochemical performance improvements. Such simulations can show us the way to make optimized electrodes for SOFC.

Our research group developed an open-source simulation code, ERMINE, based on a finite element framework. In ERMINE, species transport and the oxidation reduction reaction (ORR) within SOFC cathodes are simulated based on given operational conditions. The original version of ERMINE was used to compare (1) how experimental cathodes compared to synthetics generated with similar volume fractions and particle size distributions as the experimental ones, and (2) how nanoscale infiltrates of perfect electronic conductors improved performance. Relative to the second area, it was shown that (1) the uniformly dispersed infiltrates increased TPB density, (2) performance improvements were linearly correlated to the increased TPB densities, (3) no new ionic transport paths of significance were introduced, and (4) good initial backbones were usually better than poor initial backbones at the same level of infiltrate loading.

A natural extension of this work is to ask whether infiltration with ionic conductors can further improve performance over infiltration with electronic conductors. The hypotheses for this can be summarized by the statement that ionic conductors will improve performance more than electronic conductors because they lead also to similar increases in TPB density while providing pathways to redistribute ionic transport throughout the electrode, reducing overall Ohmic resistances and increasing activation overpotentials throughout the electrolyte, rendering TPBs more active at identical TPB densities. The research goal is to simulate the electrochemical reaction in infiltrated SOFC microstructure by using ERMINE and discover the relationship between the performance and infiltration.

12:15 PM EF13.10

Relationship Between Active Sites Distribution and 3D Microstructure of LSM/YSZ Composite Cathode by Oxygen Isotope Labeling Combined with FIB-SEM Technique [Tsuayoshi Nagasawa](#)¹, Takaaki Shimura², Naoki Shikazono² and Katsunori Hanamura¹; ¹Tokyo Kogyo Daigaku, Japan; ²Tokyo Daigaku, Japan

SOFC has gained a great attention owing to its high conversion efficiency from chemical to electrical energy, high fuel flexibility, and emission of high temperature exhaust gas which can be reused by heat recovery technologies. Composite materials are widely used for SOFC electrodes, such as Ni/YSZ for anode and LSM/YSZ or LSCF/GDC for cathode. These electrodes have micro/nano-scaled complex structures consisting of electron conductor, oxide ion conductor, and pore phases, where chemical species and charges are transported accompanied by electrochemical reaction at the triple-phase boundary (TPB) or double-phase boundary (DPB). The distributions of ionic/electronic paths and of active reaction sites in the microstructures have a great influence on the electrode performance, which have been mainly explored by numerical simulations so far. Since results of numerical simulations strongly depend on calculation models, especially on electrochemical reaction models, experimental investigation of reaction sites/distributions in porous electrodes is of great significance to reveal actual electrochemical reaction mechanism in electrodes.

The authors have developed an imaging technique of active sites in porous electrodes through quenching SOFC reaction using a He gas impinging jet and

oxygen isotope labeling [1]. A power generation equipment with a nozzle for a He gas impinging jet, which is covered by a water cooling jacket, has been constructed. After $^{18}\text{O}_2$ labeling, a cell at 1073 K can be quenched to below 423 K at cooling rate of 460 K/s using the system, then ^{18}O distribution in the cross section of the quenched cell is obtained by a secondary ion mass spectroscopy (SIMS) with a spatial resolution of 50 nm. Through this method, active sites in a LSM-based composite cathodes were successfully visualized in a micrometer-scale [1,2].

In this work, the relationship between active sites distribution and electrode microstructure of the LSM/YSZ cathode was investigated through the above imaging technique combined with a three-dimensional microstructural observation by FIB-SEM. Through FIB-SEM observation and SIMS measurement, 3D microstructure of the quenched cathode with 2D ^{18}O concentration mapping in the intermediate plane of the characterized volume was obtained. The comparison between the microstructural analysis and SIMS results shows that weak ^{18}O concentration was observed in the isolated LSM particles. Also, several percolated LSM particles near the electrolyte with weak ^{18}O concentration were observed, which were discussed in terms of the local 3D microstructure of LSM. Furthermore, the oxide ion flux incorporated from the cathode/electrolyte interface was estimated based on a line profile analysis of the ^{18}O concentration in the electrolyte at two locations in the observed area. There was a clear difference between the calculated oxide ion fluxes at the two locations, the trend of which was discussed with the distributions of percolated TPB density and YSZ volume fraction in terms of effective reaction thickness [3]. In addition, the electrochemical simulation coupled with ^{18}O diffusion using the above 3D microstructure has been developed [4] and compared with the SIMS results, which will be also shown in the presentation.

References

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SESSION EF14: PEM Fuel/Electrolysis Cells II
 Session Chairs: Deborah Myers and Ifan Stephens
 Thursday Morning, July 21, 2022
 Lobby Level, Avenue 34, Studio 2

9:10 AM **EF14.01

Enabling Hydrogen at Scale Using Low-Temperature Electrolysis with Sustainable Materials [Sanjeev Mukerjee](#) and Ian Kendrick; Northeastern University, United States

This presentation will focus on advanced water splitting, enabling a clear pathway for achieving $<\$2/\text{Kg}_{\text{H}_2}$ (at scale) with the efficiency of 43 kWh/Kg using an anion exchange membrane interface. Advances via the fundamental understanding of both hydrogen and oxygen evolution reactions (HER/OER) leading to novel materials will be presented in conjunction with critical improvements in membrane and ionomers and gas evolution electrodes. Mechanistic details of the electrocatalysis, particularly hydrogen evolution reaction will be presented with corresponding characterization and testing. This collaborative effort between Northeastern University (electrocatalyst, electrodes and interfacial characterization), University of Delaware (membranes and ionomers) and National Laboratory partners, Lawrence Berkeley National Lab (multiscale modelling and computation), Sandia National Laboratory (MD simulations of the membrane catalyst interface) will show a comprehensive effort to enable such technology. Progress towards the end of the project goal of $1.76 \text{ V}_{\text{cell(non-iR corrected)}}$ at $2 \text{ A}/\text{cm}^2$ will be highlighted wherein at the modelled scale of 50,000 kg/day and operating at $2 \text{ A}/\text{cm}^2$ results in hydrogen cost at \$2.15, \$1.82, or \$1.76/kg, respectively (2, 20, 200 plants).

9:40 AM *EF14.02

Durability of PEM Water Electrolyzer Against the Voltage Fluctuation Generated by Wind Power [Akari Hayashi](#); Kyushu Daigaku, Japan

Toward the carbon-free society, efficient use of renewable energy becomes important. Combining to hydrogen energy is one solution for such efficient use. Water electrolysis is a core technology to connect renewable energy and hydrogen energy. In this study, PEM water electrolyzer is focused on. We are particularly interested in durability against electric power fluctuation generated by renewable energy.

Among the renewable energy, wind power was chosen to study since it fluctuates regardless of the time of day or night. A typical voltage fluctuation of wind power for 24 hours was obtained and applied to a lab-made water electrolysis cell. The voltage fluctuates mostly between 0.5 V and 2.3 V. This lab-made water electrolysis was composed of commercial Pt/C catalyst and carbon porous transport layer (PTL) for the cathode, commercial IrO_2 catalyst and Titanium PTL for the anode, and Nafion[®] membrane. Pt and IrO_2 loading were both $0.5 \text{ mg}/\text{cm}^2$. Water electrolysis was performed at $80 \text{ }^\circ\text{C}$ under $1 \text{ mL}/\text{min}$ water flow.

When a typical 24-hour voltage fluctuation was repeatedly applied, the current density at 2.0 V kept increasing up to 96 hours, which was probably owing to surface cleaning effect derived by repeated reduction/oxidation of IrO_2 catalyst. After 96 hours, the current started decreasing.

This decrease was considered as temporary current decrease owing to stagnation of produced gases followed by suppressing active sites of IrO_2 catalysts. Therefore, 1-hour rest with only water flow was included every 48 hours. As a result, even after 480 hours, no decrease in current was observed.

Since the short time durability was confirmed against voltage fluctuation generated by wind power, we made an accelerated protocol for durability analyses based on the real voltage fluctuation in order to check the long time durability. With this accelerated protocol, if the highest potential was kept to 2.0 V, even after the time equivalent to 114 days, no degradation was observed. However, the stagnation of produced gases was still seen and the rest was required to recover the current. Also, we realized temporary current decrease rather occurred faster while the number of voltage cycle increased. We think that is somehow related to the change in oxidation degree of IrO_2 catalyst surface resulted by cycling to the high voltage, leading to more hydrophilic surface.

Since the good transport of generated gas is now known to be important, the structurally controlled Ir based catalyst, porous Ir, has been developed in this study and will be introduced.

10:00 AM *EF14.03

Demonstration of Electrolyzer Operation at a Nuclear Plant to Allow for Dynamic Participation in an Organized Electricity Market and In-House Hydrogen Supply [Uuganbayar Otgonbaatar](#); Exelon Corporation, United States

Exelon is partnering with Nel Hydrogen and multiple national laboratories to demonstrate an integrated hydrogen production, storage and utilization facility at an Exelon nuclear plant site. Exelon will install a Proton Exchange Membrane (PEM) electrolyzer and an associated hydrogen storage system, supporting infrastructure, and a control system to enable dynamic operation of the electrolyzer. One project goal includes economic supply of carbon-free

hydrogen for internal nuclear site use. In addition, Exelon will work with the labs to simulate and demonstrate dynamic control of the electrolyzer, paving the way for participation of hybrid power/hydrogen systems in organized power markets.

10:20 AM *EF14.04

Polyketone Functionalization—New Ways to Ion Conducting Polymers Vito Di Noto, Paolo Sgarbossa, Ketì Vezzù, Giovanni Crivellaro, Afaaf Rahat Alvi and Gioele Pagot; Università degli Studi di Padova, Italy

Ion-exchange membranes (IEMs) are at the core of many energy and conversion devices, such as fuel cells and redox flow batteries. For practical applications they are required to possess high ionic conductivity, but thermal stability, long lifetime, and electrical insulation. The preparation of polymeric materials with such high-performance properties is still challenging and can lead to high prices, hindering their widespread use in energy conversion technologies. This is even more difficult when considering anion conducting membranes, due to the need of chemical stability and ability to withstand alkaline conditions at high temperatures for long time [1-3].

Polyketones (PK) are known to be high performance thermoplastic polymers with applications ranging from fire-retardants film coatings, packaging, and fibers, resulting from their high thermal and chemical stability. They can be obtained in high yields by copolymerization of inexpensive and readily available feedstocks such as ethylene and carbon monoxide. Our group proved that PK with alternating 1,4-dicarbonyl repeating units constitute an ideal starting point to access a wide class of modified polymers by simple Paal-Knorr cyclization, to gain pyrrole-N-bound functional groups stemming from the aliphatic backbone [4-5].

This is a new account on our research on the ion conducting polymeric materials derived from PK, obtained by reaction with variously functionalized amines, and their easy conversion to anion exchange materials [4]. The effect of reaction conditions on their thermal properties and chemical stability in alkaline media has been studied, and their conductivity in a wide range of frequencies assessed by broadband electric spectroscopy to shed light on the conduction mechanisms [6].

The proposed conducting polymers combine the thermal stability of the aliphatic PK structure with the chemical flexibility given by the groups derived from functionalized amines branching out, proving to be highly tailorable, with possible applications in current energy conversion technologies.

Acknowledgements: The authors wish to thank the Research Projects of Relevant National Interest (PRIN 2017) of the Italian Ministry of Education, University and Research “Novel Multilayered and Micro-Machined Electrode Nano-Architectures for Electrocatalytic Applications (Fuel Cells and Electrolyzers)” (Prot. 2017YH9MRK) and SID2020 Project of Department of Industrial Engineering, University of Padova “A New frontier in Hybrid Inorganic-Organic Membranes for Energy Conversion and Storage Devices” (Prot. BIRD201244) for funding.

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10:40 AM BREAK

SESSION EF15: Solar Fuels II
Session Chairs: Sean Bishop and Anthony McDaniel
Thursday Morning, July 21, 2022
Lobby Level, Avenue 34, Studio 2

11:00 AM **EF15.01

Decoupled Water Splitting for Green Hydrogen Production at Scale Avner Rothschild; Technion Israel Institute of Technology, Israel

Green hydrogen produced by splitting water molecules into hydrogen and oxygen using renewable sources is expected to play a major role in the transition to carbon neutral economy, serving as an energy carrier that can facilitate the penetration of an higher share of intermittent renewable energy, the decarbonization of hard-to-abate industrial sectors (e.g. industrial processes which require high-grade heating or rely on hydrogen as a feedstock) and the cross-sectorial coupling (linking power, gas and other energy vectors or energy intensive commodities and replacing them in their respective usages). The baseline technology for green hydrogen production is called water electrolysis, where renewable power is applied to break the chemical bonds in water molecules and produce hydrogen and oxygen simultaneously at two electrodes, cathode and anode, in alkaline or acidic solution. The coupled generation of hydrogen and oxygen at the same time in the same cell presents a safety risk, since the mixture of the two is highly flammable. Therefore, a membrane and sealing are used to isolate the electrodes from each other, which complicates cell construction and requires maintenance, both increasing the production cost of green hydrogen. In addition, severe (20-30%) energy losses, mostly due to the difficult reaction that evolves oxygen, increase the cost of energy in this energy intensive technology. These drawback present challenges for wide scale adoption of green hydrogen.

In order to overcome these challenges, we develop an alternative technology that decouples the generation of hydrogen and oxygen into two stages, separated by time, or two cells, space separated, avoiding the need for membrane and sealing. In addition, we divide the oxygen evolution reaction, a difficult electrochemical reaction that requires four electrons to generate an oxygen molecule on an atomic reaction site, into two sub-reactions that occur on four sites instead of one, thereby enabling easier reactions and saving most of the losses in water electrolysis. An ultrahigh efficiency of nearly 99% was demonstrated at lab scale, and we expect reaching 95% at system scale. To bring this transformative concept to reality we established H₂Pro, and Israeli company that aims to provide green hydrogen at scale based on our innovation.

11:30 AM *EF15.02

Mixed Metal Oxides for Enhanced Solar Fuel Production via Thermochemical Redox Cycling Asim Riaz¹, Christopher Bodger¹, Jingjing Chen¹, Adrian Lowe¹, Takuya Tsuzuki¹ and Wojech Lipinski²; ¹Australian National University, Australia; ²Polna 1a, Poland

The area of solar thermochemistry aims at direct thermochemical production of chemical fuels and advanced thermochemical processing of materials.

Cheap and efficient solar production of synthesis gas (syngas), the precursor to synthetic drop-in hydrocarbon fuels such as petrol, diesel and kerosene, is an intriguing approach to transform today's fossil-based to tomorrow's renewable-based transportation sector. Solar-driven thermochemical redox cycles have been demonstrated as a promising approach to water and carbon dioxide splitting. While direct on-sun high-temperature reduction has been demonstrated with various metal oxides, cerium dioxide (ceria) remains the reference metal oxide. Main challenges are related to long-term cyclic chemical and mechanical stability of metal oxide structures at high temperatures required for the direct reduction step. The process conditions become less challenging when solar-driven carbothermal reduction is employed. We have investigated ceria-based and ceria-doped mixed metal oxide partial methane oxidation coupled to redox cycling for enhanced syngas production, materials stability and system scalability. Intriguing interplay effects were found to improve structural and catalytic properties in ceria-containing compositions, of which some resulted in unprecedented fuel production rates using reticulate porous ceramic structures.

11:50 AM EF15.03

Dual Phase Composites of LSM-CeO₂ with Fast Oxygen Exchange for Solar Thermochemical Fuel Production—Exploiting the Full Oxygen Carrier Capacity of Perovskites [Alexander Hansen Bork](#)^{1,2}, Alfonso J. Carrillo^{1,3}, Zachary D. Hood¹, Bilge Yildiz¹ and Jennifer Rupp¹; ¹Massachusetts Institute of Technology, United States; ²Eidgenössische Technische Hochschule Zurich, Switzerland; ³Universitat Politècnica de Valencia, Spain

Solar fuels provide opportunities to convert renewable solar thermal energy directly by a two-step thermochemical redox cycle via metal oxides. The solar-thermally reduced metal oxide splits H₂O and CO₂ to syngas, a mixture of H₂ and CO, which is a precursor to synthetic liquid fuels that can be stored easily in tanks and enable on-demand dispatch for transportation.

Ceria (CeO₂) is considered state-of-the-art material for thermochemical solar fuel production due to its fast redox kinetics and phase stability over a wide temperature window. Just recently, ceria was used as the redox-active material for a demonstration of the full solar fuel production chain under real field conditions.[1] The main drawback of ceria, however, is the relatively low fuel productivity per unit mass of metal oxide, which is limited by its oxygen exchange capacity and high reduction temperature.

Perovskites have garnered much interest as an alternative material class for solar fuels production due to a large oxygen exchange capacity and lower reduction temperature. Moreover, the perovskite structure can host a large variety of cations to optimize its redox thermochemistry. Among perovskites, lanthanum manganite is one of the perovskite compositions that has been studied in most detail for solar-to-fuel conversion.[2] One of the main drawbacks of perovskites studied to this date, however, is that they suffer from poor kinetics for the H₂O and CO₂ splitting reaction.

Here, we explore dual phase composites of the La_{0.65}Sr_{0.35}MnO₃ perovskite and ceria. The driving idea of this study is to benefit from the large oxygen exchange capacity of the perovskite and purposefully utilize ceria, both as an active redox material and a catalyst for faster oxygen exchange from the perovskites. Ceria has been investigated widely as an oxygen exchange promoter and oxidation catalyst for metal oxides employed as an oxygen exchange material. We investigate dual-phase composites of La_{0.65}Sr_{0.35}MnO₃-xCeO₂, with x = 0, 5, 10, 20, 50, 100, for oxygen exchange and CO₂ splitting via thermochemical redox reactions. The composites were tested in a temperature range of 1000 °C to 1400 °C, under isothermal and two-step cycling conditions relevant for solar thermochemical fuel production. Interestingly, the dual phase composite La_{0.65}Sr_{0.35}MnO₃-CeO₂ exhibits synergistic oxygen exchange compared to its individual components. The enhanced oxygen exchange in the composite has a beneficial effect on the rate of oxygen release and the total CO produced by CO₂ splitting for the solar thermochemical technology, while it has an adverse effect on the maximum rate of CO evolution. *Ex situ* Raman and XRD analyses are used to shed light on the relative oxygen content during thermochemical cycling. Based on the relative oxygen content in both phases, we discuss possible mechanisms that can explain the observed behavior. In summary, the results show the beneficial effects of a dual phase composite to promote the oxygen release from the perovskite phase providing a higher solar fuel production capacity.[3]

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12:05 PM EF15.04

Surface Restructuring of Oxygen Carrier Enables Low-Temperature CO₂ Splitting [DongHwan Oh](#), Seyeon Park, Jaewan Ahn, Seunghyun Kim, Il-Doo Kim and WooChul Jung; Korea Advanced Institute of Science and Technology, Korea (the Republic of)

The substantial CO₂ emission has hitherto accelerated climate changes, and eventually, human society is severely jeopardized by global warming. Hence, reverse water gas shift (RWGS) is considered a primary route that splits CO₂ into the CO, thus yielding the feedstock for advanced processes such as Fischer-Tropsch synthesis. However, since RWGS is an endothermic reaction, there is a limitation in the product yield at low-temperature due to the thermodynamic equilibrium [1]. In this regard, chemical looping reverse water gas shift (CLRWGS) is considered an intelligent alternative to thrust the low-temperature CO₂ conversion beyond the thermodynamic ceiling in a co-feeding reaction. CLRWGS is a reaction mediated by the lattice oxygen in metal oxide with a spatially separated H₂ and CO₂ injection step. (1) hydrogen drains lattice oxygen of metal oxide, then generates oxygen vacancies. (2) In the next step, CO₂ is fed to fill up the oxygen vacancies, and CO comes out as a result of the splitting reaction. By repeatedly exposing H₂ and CO₂ gas to the metal oxide, RWGS can be conducted without a thermodynamic barrier and further bring high product capturable [2]. Because the metal oxide both serve as an oxygen reservoir as well as a redox catalyst, the development of a high-performance oxygen carrier is a targeted goal. However, most of the developed oxygen carriers are operated in the high-temperature region above 500 °C so far, which causes an increase in driving cost and sintering of itself [3,4].

Inspired by the lack of research in low-temperature targeted oxygen carriers, we developed novel oxygen sources composed of Pd doped In₂O₃ ((In_{1-x}Pd_x)₂O₃, x = 0, 0.01, 0.02, 0.04). In₂O₃ inherently contains many oxygen vacancies and reacts readily with hydrogen at low temperatures, which implies the possibility of low-temperature operation [5-7]. In addition, to decorate the surface of In₂O₃ with Pd, which shows high reactivity with hydrogen, the in-situ ex-solution was adopted as a core strategy. The oxygen carrier was prepared in a hollow nanofiber to provide better gas permeability using the electrospinning method. Then, in order to showcase the Pd doping effect, its physical and chemical properties were analyzed using synchrotron-XRD, SEM, high-resolution TEM, H₂-TPR, and CO-chemisorption. Ex-solved Pd was confirmed on the host surface in a hydrogen atmosphere, and Pd nanoparticles appear to be re-dispersed in the form of atomic clusters as it sequentially exposed to CO₂. As a result, the Pd-doped sample shows produced amount of CO increased up to five times compared to the bare sample even at the critically low-temperature (350 °C). It is thought that repetitive surface restructuring underpins the high CO production ability over ten redox cycles. Further in-situ techniques will be conducted to figure out the nature of the robust activity.

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12:20 PM EF15.05

Impact of Conductivity on the CO₂ Splitting Kinetics of Lanthanide-Doped Cerium Oxide for Chemical Looping Reforming of Methane Marwan Laqdiem, Alfonso J. Carrillo, Jose M. Serra, Julio Garcia-Fayos and Maria Balaguer; Instituto de Tecnologia Quimica, Spain

Cerium oxide is the state-of-the-art material for syngas production from CO₂ and H₂O splitting via (methane assisted-) solar-driven thermochemical cycles(1). In addition, lanthanide-doped CeO₂ based materials (e.g. Gd_{0.1}Ce_{0.9}O₂) are employed based on their physicochemical properties, such as ionic conductivity, mix ionic-electronic conductivity, high-temperature stability and redox behavior, in several electrochemical and thermocatalytic processes, etc, which have triggered the interest of doped cerium oxides in chemical looping syngas production(2). This technology consists of two separate processes: First, a partial reduction of the oxide with methane at temperatures close to 900 °C. This step produces syngas and generates oxygen vacancies in the oxide. In a second step, oxidation on the reduced oxide takes place with H₂O and/or CO₂ to produce H₂ or CO, re-filling the oxygen vacancies(3). Doping the cerium oxide with other cations have been used as a strategy to increase the amount of oxygen vacancies or changes in the crystal lattice, which could eventually increase the fuel yield or have an impact on the redox oxygen exchange kinetics. Traditionally, the CeO₂ has been doped with lanthanides to improve the reduction of the material and more catalytic behavior and enhance the ionic conductivity. In particular, in previous works we showed the correlation between the dopant's ionic radii and the conductivity for lanthanide-doped cerium oxides. However, little attention has been put in such type of studies, in which a correlation between the lattice properties, conductivity and oxygen exchange kinetics are established for methane-assisted CO₂ splitting. Thus, in this work we doped the cerium oxide with +3 and +3/+4 lanthanides (Ln), Ce_{0.9}Ln_{0.1}O_{2-d} and with different ionic radii and study the impact of the dopant on the methane partial oxidation and CO₂ splitting steps. Our results indicate that there is a correlation between the ionic radii, conductivity and CO₂ splitting kinetics. Based on our observations we could identify the most optimum ionic radii for enhanced CO₂ splitting kinetics. These findings could be useful in the design of more advanced redox materials for chemical looping syngas production.

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12:35 PM EF15.06

Screening Ruddlesden-Popper (n=1) Oxide Materials for Thermochemical Water Splitting by Density Functional Theory George E. Wilson, Ieuan D. Seymour, Andrea Cavallaro, Stephen J. Skinner and Ainara Aguadero; Imperial College London, United Kingdom

Thermochemical redox reactors store concentrated solar power by thermally inducing oxygen defects within a metal oxide structure. The metal oxide's preference to reoxidise upon introduction of H₂O or CO₂ facilitates the production of H₂ or CO for syngas formation.[1] The thermal reduction of the benchmark material, CeO₂, typically requires high temperatures (>1400 °C) under inert sweep gas conditions [2], however there is motivation to lower this temperature and investigate new metal oxides capable of larger fuel productions. Perovskite materials have been thoroughly investigated due to their ability to accommodate relatively large oxygen deficiencies whilst remaining crystallographically stable. Emery et al. [3] conducted a wide computational screening of this family of materials based on a few simple thermodynamic parameters originally proposed by Meredig and Wolverton. [4]

Herein, we extend these previous studies and investigate the A₂BO₄ Ruddlesden-Popper (RP) oxide family [5] of layered perovskites, that have previously demonstrated fast redox kinetics and large oxygen storage as air electrodes in solid oxide cell technologies.[6] A combination of screening parameters based on charge neutrality, Goldschmidt tolerance and computed defect formation energy, identified 38 possible RP candidate materials from an initial starting set of over 27,889. One of which - Ca₂MnO_{4-δ} - was taken forward for experimental testing due to its Earth-abundant elements. The powder was synthesised via a modified Pechini method and thermal analysis experiments demonstrated thermally driven oxygen evolution from 800 to 1200 °C equating to a non-stoichiometry of δ=0.12. High-temperature X-ray diffraction under inert sweep gas alluded to the formation of a CaMn₂O₄ secondary phase above 1100 °C, therefore consequent thermochemical water splitting cycles were carried out at a maximum temperature of 1000 °C. Oxidation under steam at 800 °C demonstrated good hydrogen production volumes, although gas production on further cycles was limited by particle sintering observed by scanning electron microscopy. Further investigations aim to understand and improve cyclability and kinetics under different reaction temperatures and humidity.

This study outlines, with experimental validation, how computational screening can be used to find future suitable RP candidates for thermochemical water splitting whose performance can be further improved with doping strategies and morphological adaptation.

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SESSION EF16: Proton Conducting Fuel Cells II
 Session Chairs: Dong Ding and Jose M. Serra
 Thursday Afternoon, July 21, 2022
 Lobby Level, Avenue 34, Studio 2

2:00 PM EF16.01

Composite Effects on PCFC Cathodes Investigated by Utilizing Patterned Thin-Film Model Electrodes Zhuo Diao, Katsuya Nishidate, Takaaki Imaizumi, Yuta Kimura, Takashi Nakamura, Keiji Yashiro, Tatsuya Kawada and Koji Amezawa; Tohoku Daigaku, Japan

Proton-conducting ceramic-electrolyte fuel cells (PCFCs) are expected to operate at lower temperature with higher energy conversion efficiency and better durability than conventional solid oxide fuel cells (SOFCs). For full-scale commercialization of PCFCs, the decrease of polarization resistance at the cathode is one of major issues because the voltage loss at the cathode occupies the largest part of the total loss. So far, two classes of material are investigated as PCFC cathodes. One is materials expecting proton-electron mixed conduction, and the other is oxide-ion conduction materials conventionally used as SOFC cathodes. In general, the former is thought to show better performance because of the expansion of reaction active site from triple phase boundaries (TPBs) to double phase boundary (DPBs). However, in reality, some typical SOFC cathode materials, for instance $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_{3-\delta}$ (LSC), are reported to exhibit relatively good performance in spite of their poor protonic conduction, suggesting very active TPB reaction.

Considering the above-mentioned facts, making a composite of electrode and electrolyte particles to promote ionic diffusion and increase TPB concentration can be one of effective approaches to improve the PCFC cathode performance. In this study, we aimed to understand the composite effects on the PCFC cathodic reaction. In our previous works, to investigate the reactions in SOFC and PCFC electrodes, we proposed so-called "patterned thin film model electrodes", which could reproduce the electrode reactions in the practical porous electrodes while excluding the influence of complicated geometry and microstructures. By using these model electrodes, we could clarify where the dominant reaction pathway is and how large the contributions of TPB/DPB reactions to the total reaction are. In this work, another new type of model electrode, so-called "composite patterned thin film model electrode", was designed to reproduce the reactions in a porous composite electrode.

The new model electrode is a kind of columnar electrode, consisting of columns of cathode and electrolyte materials. To make the fabrication easier, the columns are put down as layered thin films on the electrolyte substrate. The contact area of the composite cathode to the electrolyte is limited by inserting an insulating layer so that the reaction distribution is formed in the electrode film as a function of the distance from the contact area. Additionally, some parts of the cathode film are removed to expose the interface of cathode/electrolyte layer to gas phase, namely to introduce TPBs. $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_{3-\delta}$ (LSC) and $\text{BaZr}_{0.8}\text{Yb}_{0.2}\text{O}_{3-\delta}$ (BZYb) were chosen as electrode and electrolyte materials. A three-terminal cell with a patterned electrode as WE, and porous palladium electrodes as CE and RE was constructed for evaluating composite effects.

Comparing to the patterned electrode with TPB in our previous study, the composite patterned electrode showed higher current density at 773 K, but lower current density at 973 K. Also, the increase of current caused by composite effects decreased with decreasing ambient $p(\text{O}_2)$ and increasing applied overpotential. Normally, making a composite is an effective way to improve the performance, when the electrode reaction dominantly occurs at TPBs. However, an opposite behavior was observed with the LSC-BZYb composite electrode at 973 K. According to our previous work, it was found that TPB reaction in LSC on the BZYb electrolyte includes a new reaction path followed by oxide ion diffusion in LSC. Making a composite means the decrease of the cathode material accompanying the suppression of oxide ion diffusion, while the increase of the electrolyte material accompanying the enhancement of protonic diffusion. It was therefore concluded that, in the case of LSC-BZYb composite electrode, composite effects can be determined by the competition between diffusions of oxide ion and proton.

2:15 PM EF16.02

Fabrication of High Performance Tubular Protonic Ceramic Fuel Cells Youdong Kim, Charlie Meisel, Carolina Herradon, Jake Huang, Neal Sullivan and Ryan O'Hayre; Colorado School of Mines, United States

Protonic-ceramic fuel cells (PCFCs) are attractive energy-conversion devices for intermediate temperature operation (400 – 600 °C). Although tremendous achievements have recently been realized in lab-scale PCFCs development, scale-up to commercially viable sizes has lagged due to a number of challenges. In particularly thermo-chemo-mechanical reliability has been a major issue. Tubular PCFCs have attractive features to mitigate some of these issues, as they offer high tolerance to thermal cycling, simplified sealing requirements, rapid start-up, and high mechanical strength under thermal variation.

Several pathways can be considered for tubular PCFC fabrication. The extrusion process has been commonly used in the fabrication of tubular anode substrates for ceramic cells because of its low cost and mass production capability. This technique also offers the potential to fabricate long and thin tubes with a wide variety of aspect ratios and uniform density distribution. To form the electrolyte layer on the tubular anode substrate, dip coating has been widely used due to its low cost and simple fabrication process. However, the formation of a thin and uniform electrolyte layer in the direction parallel to the axis is challenging using this technique, particularly for long tubes. In contrast, "atomistic" wet powder spraying can potentially enable facile fabrication of thin electrolyte films on porous anode substrates of arbitrary length and geometry. This technique is also suitable for accurately controlling the thickness of electrolyte and depositing a uniform layer through tailoring of spray time, spray speed, and distance between spray nozzle and substrate. These process-control improvements improve performance and yield for long tubes.

In this presentation, we present our work on tubular anode-supported PCFCs which are fabricated by extrusion of the anode substrate in combination with the atomistic wet powder spray technique for the electrolyte. A $\text{BaCe}_{0.7}\text{Zr}_{0.1}\text{Y}_{0.1}\text{Yb}_{0.1}\text{O}_{3-\delta}$ (BCZYb7111) and Ni cermet anode are extruded. A BCZYb7111 electrolyte is deposited by wet powder spraying technique. The anode-electrolyte assembly is co-fired solid state reaction sintering (SSRS), a time- and cost-saving manufacturing process where the single-phase perovskite is formed from the parent materials during cell fabrication. The $\text{BaCo}_{0.4}\text{Fe}_{0.4}\text{Zr}_{0.1}\text{Y}_{0.1}\text{O}_{3-\delta}$ (BCFZY4411) and BCZYb7111 composite materials are synthesized and applied on the electrolyte surface as a cathode with brush painting. While the fabrication methods continue to evolve, high-performance tubular PCFCs are demonstrated using these advanced ceramic-processing techniques.

2:30 PM EF16.03

3D Printing of Electrodes for Proton Ceramic Electrochemical Cells—Recent Developments and Challenges Sebastian Wachowski¹, Małgorzata Nadolska¹, Mateusz Cieslik¹, Joanna Pospiech¹, Marek Chmielewski¹, Tomasz Sobczyk¹, Aleksandra Mielewczyk-Gryn¹, Maria Gazda¹, Jose M. Serra², Einar Vollestad³ and Ragnar Strandbakke⁴; ¹Politechnika Gdanska, Poland; ²Instituto de Tecnologia Química, Spain; ³SINTEF Industry, Norway; ⁴Universitetet i Oslo, Norway

Additive manufacturing, such as 3D printing, allows to fabricate materials with designed geometries and microstructure. The method enables rapid manufacturing, shortens prototyping time and is considered low-cost. Therefore, 3D printing can further advance development and commercialization of Proton Ceramic Electrochemical Cells. However, ceramics in contrast to polymers cannot be easily formed, melted and need high temperatures for sintering. This impedes implementation of ceramics in 3D printing technologies. To avoid the problem ceramic-polymer composites are used to form the printed objects and the organic part is later on removed during post-processing.

In our work we show recent advances in developing 3D printing of proton ceramic electrodes. The printer uses extrusion-based printing techniques combined with IR laser postprocessing. In our approach we print ceramic powders suspended in a polymer matrix. The developed technology uses two printing heads. One is suitable to work with ceramics suspended in a solid polymer in a form of a filament. This method is called Fused Deposition Modelling and in such a case the polymer is melted in the printer head, the droplet is then deposited on the substrate and solidifies. Point-by-point addition

of droplets leads to formation of designed shape. The second method used uses gel polymers as ceramic powder carriers and it is called Direct Ink Writing. In such a case the droplet is dried after deposition, which leads to the formation of solid printed shape. Using two methods gives flexibility in choice of ceramic loading in the composite as well as the type of polymer used. It also allows to use filaments or gels with filled with ceramics with various compositions, which results with electrodes with gradual change of composition.

In each case the post-processing is performed with IR laser scanning the surface of the ceramic-polymer printout. This allows a point-by-point firing of the organics and simultaneous sintering of ceramic component. As a result, depending on the process parameters such as laser power, scanning speed or laser working frequency, various microstructures can be obtained from dense ceramic, through porous backbones with various pore sizes to ceramic foams composed of large pores with the size of hundreds of micrometers with a few micron-thick walls. Moreover, since the parameters of post-processing can vary in different parts of the printout it allows to produce materials with varying microstructures.

Acknowledgements

Project FunKeyCat is supported by the National Science Centre, Poland under the M-ERA.NET 2, which has received funding from the European Union's Horizon 2020 research and innovation program under grant agreement no 685451.

2:45 PM EF16.04

Revitalizing Performance and Expanding Lifetime of Protonic Ceramic Cells by Interfacial Acid Etch Wenjuan Bian¹, Wei Wu¹, Meng Zhou², Congrui Jin³, Hanping Ding¹, Yanhao Dong⁴, Ju Li⁴ and Dong Ding¹; ¹Idaho National Laboratory Research Library, United States; ²New Mexico State University Board of Regents, United States; ³University of Nebraska, Lincoln, United States; ⁴Massachusetts Institute of Technology, United States

Protonic ceramic electrochemical cells (PCEC), including solid oxide fuel / electrolysis cell, present promising routes to energy harvest and value-added chemical production. Despite tremendous efforts, protonic ceramic electrochemical cell still encounters several emerging problems, such as poor thermal/chemical/mechanical compatibility and inferior solid-solid contact at the interfaces between electrolytes and electrodes. One of the major hurdles for PCEC commercialization is that although the high proton conductivity of the bulk electrolyte has been demonstrated, it cannot be fully utilized in electrochemical full cells. In this representation, we will demonstrate a simple acid treatment, which is completely compatible with the state-of-the-art multilayer processing technique of ceramic fuel/electrolysis cells, can rejuvenate the high-temperature annealed electrolyte surface, improve hetero-oxide bonding, and recover the intrinsic conductivity and activity of the components for maximum performance. This enables exceptional protonic ceramic fuel-cell performance down to 350 °C, with peak power densities of 1.6 W cm⁻² at 600 °C, 650 mW cm⁻² at 450 °C, and 300 mW cm⁻² at 350 °C, as well as stable electrolysis operations with current densities above 3.9 A cm⁻² at 1.4 V and 600 °C. Our work offers new understanding and practices towards sustainable energy infrastructure. The scientific understanding, the practical solution, and the applicability to various interfaces provided here highlights the critical role of interfacial engineering in ceramic electrochemical devices. Beyond ceramic fuel cells, interfacial engineering and specially designed processing techniques are also critical to other electrochemical materials and devices, such as oxide cathodes of lithium-ion batteries, all-solid-state batteries, and metal-ceramic interfaces.

3:00 PM BREAK

SESSION EF17: Oxygen-Ion Conducting Electrolysis Cells II

Session Chairs: Georgios Dimitrakopoulos and Anne Hauch

Thursday Afternoon, July 21, 2022

Lobby Level, Avenue 34, Studio 1

2:00 PM **EF17.01

Emergent Nanomaterials for CO₂ Electrochemical Conversion [John T. Irvine](#); University of St Andrews, United Kingdom

Electricity from solar or wind power can be used in Solid Oxide Electrolysis Cells (SOECs) to convert steam and carbon dioxide to synthesis gas and to upgrade carbon dioxide and methane in biogas to carbon monoxide and hydrogen. Here we report the use of different combinations of transition metal oxides to dope strontium titanate electrodes to increase the performance of Solid Oxide Electrolysis Cells in carbon conversions/upgrading biogas. The work focuses on both exsolution from the perovskite surface and modification of the surface to enhance electrochemical conversion.

2:30 PM **EF17.02

Perspectives of Hydrogen and Syngas Production Using High Temperature Electrolyzers [Olga A. Marina](#), Kerry Meinhardt, Dan Edwards and Jie Bao; Pacific Northwest National Laboratory, United States

We are aiming to develop efficient, lower cost 1-5 kW solid oxide electrolyzer stacks with an active cell area of 300 cm² to enable \$2/kg hydrogen and syngas production. The focus is on reducing the stack manufacturing costs that could be achieved via significantly increasing active cell area that would reduce the number of cells required for stack, employing advanced fabrication techniques to reduce the cell area-specific resistances, component thicknesses, and material volumes.

This presentation will provide an overview of the progress on cell development and manufacturing, cell size scale-up, cell and short stack electrochemical testing, and post-test characterization. Multiple solid oxide electrolysis cells (SOEC) were studied in a wide range of operating conditions with a goal to address the long term SOEC durability and elucidate the potential degradation mechanisms. Cells were tested at varied steam-to hydrogen and CO₂-to steam ratios at 700-800°C up to 3000 hours. Multiple repeats were included into the wide test matrix to eliminate the occasional artifacts. The extensive scanning electron microscopy - energy dispersive spectroscopy and focus ion beam-transmission electron microscopy analyses were performed on tested cells as well as on "as prepared" cells, for comparison. The observed changes at the active electrode/electrolyte interfaces, in the electrodes, and electrode interactions with the gas impurities allowed to identify several degradation mechanisms.

2D and 3D models were constructed to predict expected thermal and electrical performance of SOEC stack and validate reliability.

3:00 PM *EF17.04

Solid Oxide Electrolysis Cells for CO₂ Electroreduction [Weishen Yang](#); Chinese Academy of Sciences, China

CO₂ electroreduction in solid oxide electrolysis cells (SOECs) is considered as a prospective technology for energy conversion and oxygen production. However, Ni oxidation and carbon deposition are addressed as two major issues during CO₂ electroreduction in the state-of-the-art SOECs with the

configuration of NiO-YSZ(support)|YSZ(electrolyte)|Anode. Although perovskite oxides are considered as promising candidates for Ni-based cermet cathode, the lack of highly stable and active cathodes still limit the development of SOECs. This report focuses on our group's research advances in recent years from several aspects, such as materials characteristics, cathode activation process, cathode construction strategies. We hope our efforts in this field are beneficial to the advancement of SOECs.

The relationship between properties of perovskite oxide and CO₂ electroreduction performance was investigated. We found the strength of metal-oxygen bond decides their phase stability under cathode polarization, and further influences performance. In addition, the performance of LaFeO₃ is enhanced due to the improvement in oxygen desorption and CO₂ adsorption abilities, increase of oxygen vacancy and the electron density of Fe site, but too much alkaline earth elements will lead to carbonate formation and degrade their activity and stability. Fe-based perovskite cathodes were activated via surface reconstruction with more generated oxygen vacancies and Fe nanoparticles. The electro-exsolved Fe nanoparticles are the major active site and tridentate carbonate species are considered as the transition species for CO₂ electroreduction. Therefore, the expected cathode should own a stable skeleton with strong metal-oxygen bond, active surface with metal nanoparticles and be free of carbonate formation. Metal nanoparticles were formed under cathode polarization.

Based on the design idea, novel 1/3 A-site deficient perovskite cathodes La_{0.66}Ti_{1-x}Fe_xO_{3-δ} (x=0.2, 0.3 and 0.4; LTF2, LTF3, LTF4) without doping alkaline earth elements were synthesized and tested. These cathodes show superior electrochemical performance with a low polarization resistance of 0.16 W cm² at 1.4 V and 800 °C for CO₂ electroreduction. LTF2 exhibits stable electrochemical performance over 300 h with the current density keeping above 0.5 A cm⁻² and Faradaic efficiency close to 100%. Surface reconstruction with the electrochemically exsolved iron nanoparticles under applied voltages was observed, and it shows high activity towards the CO₂ electroreduction.

Further, an alkaline earth elements free garnet oxide (Gd₃Fe₅O₁₂) was developed for CO₂ electroreduction, which can be converted into perovskite oxide and iron nano particles via *in situ* electrochemical phase transition during CO₂ electroreduction, resulting in high activity with Faradaic efficiency close to 100% and great stability over 1000 h galvanostatic test. A variety of experimental characterizations and density functional theory calculations indicate *in situ* exsolved Fe clusters effectively enhance the adsorption energies of intermediates and lowering the CO₂ dissociation barriers. Microkinetic modelling confirms that CO₂RR goes through a dissociative adsorption mechanism and the electronic transfer for CO₂ dissociation is the rate-determining step.

3:20 PM BREAK

4:00 PM EF17.05

Engineering the Surface of Ceria for CO₂ Reduction in High Temperature Solid Oxide Electrolysis Cells (SOECs) [Elena Marzia Sala](#)¹, Nicola Mazzanti¹, Francesco M. Chiabrera¹, Simone Sanna², Mogens Mogensen¹, Peter V. Hendriksen¹ and Christodoulos Chatzichristodoulou¹; ¹Danmarks Tekniske Universitet, Denmark; ²Universita degli Studi di Roma Tor Vergata, Italy

The electrochemical reduction of CO₂ in Solid Oxide Electrolysis Cells (SOECs) has the potential to alter the landscape of the chemical industry by conversion and storage of renewable energy in the form of hydrocarbons, gradually phasing out the production of chemicals from fossil sources. One of the biggest challenges associated with the large-scale commercialization of SOECs lies in improving the lifetime of the fuel electrode. The state-of-the-art Ni-YSZ composite cathode employed in SOECs nowadays suffers from various degradation mechanisms under operating conditions, such as carbon deposition, poisoning of the electrode surface by impurities present in the gas feed stream and Ni agglomeration/depletion from the electrode/electrolyte interface region¹. All these challenges can be alleviated with the introduction of doped ceria (CeO₂) as component of the fuel electrode. Ceria surfaces are less prone to carbon deposition, and more tolerant to impurities. Furthermore, the mixed ionic electronic conducting (MIEC) nature of ceria, under the reducing conditions of the cathode, extends the electrochemical reaction zone from the typical three-phase boundary (3PB), where YSZ, Ni, and gas phase meet, to a two-phase boundary (2PB) between ceria surface and the gas phase.

Recent research efforts highlight the promising perspective of ceria as single-phase technological fuel electrode². Accelerating this effort entails the optimization of the intrinsic electrocatalytic activity of ceria for CO₂ reduction, through the in-depth atomistic understanding of the underlying reaction mechanism and a systematic study of the levers that can modify the properties of ceria surfaces, by means of model systems with well-defined geometry, composition and surface area.

This work will offer an overview of our efforts investigating how the engineering of ceria surfaces influences its electrocatalytic activity towards CO₂ reduction. Two of the major strategies to tailor the properties of ceria surface consist of promoting a specific surface orientation and incorporating different type and amount of dopants in its fluorite structure. The presence of dopants at the surface and the surface termination have been shown to strongly influence the energy of oxygen vacancy formation and the reducibility of ceria, and to affect the reaction pathway through different types of reaction intermediates forming at the ceria/gas interface³. Dense thin film model electrodes of pure and doped ceria with well-defined surface orientation were produced by pulsed laser deposition and characterized under conditions relevant for SOECs by electrochemical impedance spectroscopy. Our work strives to reveal the role that these two levers play in the electrocatalytic activity of ceria and to unravel the energy landscape of the CO₂ reduction mechanism.

References

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- 2 Nanning, A., Holzmann, M., Fleig, J., & Opitz, A. K. (2021). Excellent kinetics of single-phase Gd-doped ceria fuel electrodes in solid oxide cells. *Materials Advances*, 2(16), 5422-5431.
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4:15 PM EF17.06

Perovskite-Like Pr(A)MnO₃ (A = Ca, Sr) as Anode Materials for Solid Oxide Fuel-Assisted Electrolysis Cells [Aleksy Yaremchenko](#)¹, Dziyana Boiba¹, Mikhail Patrakeev², Aleksey Lisenkov¹, Aleksandr Bamburov¹ and Blanca I. Arias-Serrano^{1,3}; ¹University of Aveiro, Portugal; ²Institute of Solid State Chemistry UB RAS, Russian Federation; ³Leibniz Institute for Plasma Science and Technology, Germany

Long-term degradation remains the main issue for the viability of solid oxide electrolysis cell (SOEC) technology as a practical hydrogen production system. One of the main specific degradation mechanisms in SOECs relates to the delamination phenomena at or near the electrolyte/anode interface. The principle of so-called fuel-assisted electrolysis is to supply the carbon-containing species which can react with oxygen at the anode side thus bringing down the oxygen chemical potential at the electrolyte/anode interface and improving its stability. The present work is aimed at the characterization of PrMnO₃-based perovskites for potential application as anodes in solid oxide fuel-assisted electrolysis cells.

Pr_{0.60-x}A_{0.40}MnO_{3±δ} (A = Sr, Ca; x = 0 and 0.05) were synthesized by glycine-nitrate combustion technique. The characterization included XRD, SEM/EDS, XPS, dilatometry and thermogravimetry, measurements of electrical properties and oxygen permeability, and determination of oxygen nonstoichiometry. XRD analysis confirmed the formation of solid solutions with orthorhombic perovskite structure. The oxides exhibit negligible variations of oxygen content under oxidizing conditions while reducing p(O₂) below 10⁻⁴ atm results in oxygen losses from the lattice and reduction of Mn cations. XPS results

suggest that praseodymium remains in a 3+ oxidation state in the bulk of ceramics but may adopt a mixed 3+/4+ oxidation state at the surface. The low- $p(\text{O}_2)$ stability boundary of the perovskite phase at 800°C corresponds to $\sim 10^{-17}$ - 10^{-16} atm; the stability domain is wider for Ca-substituted compositions and narrows with the introduction of A-site vacancies. Dilatometric studies confirmed good thermomechanical compatibility with common solid electrolytes under oxidizing conditions; however, reduction at operation temperatures (800°C) leads to undesirable chemical expansion. The electrical conductivity of $\text{Pr}_{0.60-x}\text{A}_{0.40}\text{MnO}_{3\pm\delta}$ ceramics is p -type electronic and decreases with reducing $p(\text{O}_2)$ but still exceeds 40-50 S/cm under anticipated oxygen electrode operation conditions. The electrochemical activity of $\text{Pr}_{0.6-x}\text{A}_{0.4}\text{MnO}_{3\pm\delta}$ electrodes was evaluated in contact with yttria-stabilized zirconia solid electrolyte as a function of relevant parameters (fabrication conditions, with and without buffer layers, with modifications via infiltration of praseodymia and/or doped ceria). The best performance was obtained for the cells with $\text{Pr}_{0.55}\text{A}_{0.40}\text{MnO}_{3\pm\delta}$ electrodes (gadolinia-doped ceria buffer layers, PrO_y load of ~ 33 wt.%) that showed anodic overpotential of around 50 mV under 500 mA/cm² at 800°C in air.

4:30 PM EF17.08

Rapid Assessment and Optimization of Electrodes for Solid Oxide Fuel Cells and Electrolyzers Using Long-Term Performance Modeling and Machine Learning William K. Epting^{1,2}, Yinkai Lei^{1,2}, Jerry H. Mason^{1,2}, Thomas Kalapos^{1,2}, Gregory Hackett¹ and Harry W. Abernathy¹; ¹National Energy Technology Laboratory, United States; ²NETL Support Contractor, United States

A major impediment to the widespread commercialization of solid oxide cells (SOCs) for fuel cell and electrolysis usage is the long-term degradation in performance, much of which is driven by the complex 3D microstructure of the electrodes. The 3-phase electrode microstructures are highly heterogeneous, with variations occurring on length scales 2-3 orders of magnitude greater than the characteristic feature size, complicating many efforts to both characterize and model them. Previous works have found that electrode areas on the order of (100 μm)² must be collected to adequately measure the important microstructural parameters that dictate long-term performance [1] – volumes that call for esoteric and time-consuming techniques like Xe-plasma FIB-SEM tomography. The system is also of high dimensionality – even the somewhat simplified description employed in our approach [2] requires 11 independent initial parameters to specify an electrode's microstructure.

In this work, we present a comprehensive framework and toolset for rapid assessment and optimization of SOC electrode microstructures, accommodating both fuel cell and electrolysis operation. A machine learning model was trained on a bank of simulations of lifetime performance over 1,000 hours for hundreds of thousands of unique SOC electrode configurations, in fuel cell and electrolysis operation. The trained model can perform rapid prediction of lifetime cell performance. It can also produce tailored recommendations for improvement of these electrodes using SHAP analysis [3]. This approach has produced general recommendations as well – for example, that the LSM/YSZ or Ni/YSZ ratio is the most impactful parameter on long-term performance, with lower values tending to yield better performance.

To increase the utility of this trained model to cell developers, we have also developed a convolutional neural network (CNN) model that is able to predict microstructural properties from microstructural data with resolutions far coarser than the characteristic feature size. The predicted microstructural properties can then be used with the model described above to generate predictions of lifetime performance and tailored improvement recommendations, with coarse data generated with widely accessible and quick techniques such as microscale X-ray computed tomography. This allows cell developers and other stakeholders to evaluate their cells rapidly, either during development or as a form of quality control, using more widely accessible and rapid techniques such as microscale X-ray computed tomography.

References:

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4:45 PM EF17.09

Designing REBa_{0.5}Sr_{0.5}CoCuO_{5±δ} (RE: Selected Lanthanides, Y) Perovskites for the Anode-Supported Solid Oxide Fuel Cells Piotr Winiarz¹, Keyun Li¹, Kun Zheng¹, Muhammet E. Alagöz², Anna Niemezyk³, Ryszard Kluczkowski⁴, Yevgeniy Naumovich³ and Konrad Swierczek¹; ¹Akademia Gorniczko-Hutnicza imienia Stanisława Staszica w Krakowie Wydział Energetyki i Paliw, Poland; ²Middle East Technical University, Turkey; ³Center for Hydrogen Technologies, Poland; ⁴Institute of Power Engineering, Poland

Cobaltite-based double perovskite REBaCo_{2-x}M_xO_{5±δ} (M: selected 3d elements) oxides are known for their high electrocatalytic activity and mixed ionic-electronic conductivity. These materials have been successfully applied to construct air electrodes in Solid Oxide Fuel Cells (SOFCs), replacing commonly used La_{1-x}Sr_xCo_{1-y}Fe_yO_{3±δ} simple perovskites. The dopant M in REBaCo_{2-x}M_xO_{5±δ} is usually Fe, Mn, or Ni, while substitution with Cu has not been yet studied in much detail for different RE cations and a wide concentration range. At the same time, it has been documented that partial replacement of Ba with Sr is possible, and the A-site layered double perovskite structure may be maintained even if Ba:Sr ratio is 1:1.

In this work, a comprehensive evaluation of the selected REBa_{0.5}Sr_{0.5}CoCuO_{5±δ} (RBSCCO) oxides is given, focusing on their phase composition and crystal structure, thermal expansion, oxygen content, chemical stability, and electrical conductivity. X-ray diffraction (XRD) was performed at room and high temperatures, with Rietveld analysis of the data. Apart from the XRD-derived unit cell expansion on temperature, dilatometry experiments were also conducted. The total oxygen content and its temperature change was evaluated on the basis of iodometric titration combined with thermogravimetric measurements. DC-4W electrical conductivity studies were performed in the air between RT and 900°C. Additionally, ab initio calculations were also done to investigate the energy of defects formation, using VASP and Medea software. General trends could be observed in the series, with smaller RE resulting in the decreased unit cell size, but also lowered oxygen content in the materials. Also, the formation of the layered structure was found to be hindered for larger RE cations, however, preparation of the material with Y substitution was also problematic. The electrical conductivity in the series was found to be adequate concerning the application. According to the expectations, doping with Cu enabled to decrease the thermal expansion, in comparison to Co-based reference samples. Overall, the results suggest that materials with RE = Pr, Nd, Sm, and Gd are the most interesting regarding the application in SOFCs. The chemical reactivity studies were conducted on the selected samples using the X-ray diffraction method. The investigated powders of RBSCCO materials were mixed together in a weight ratio of 1:1 with La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.2}O_{3±δ} (LSGM) or Ce_{0.9}Gd_{0.1}O_{2±δ} (GDC10) electrolytes. After annealing at 900°C for 2 h in air, some additional peaks could be noticed in the RBSCCO:LSGM sample, indicating unwanted reactivity. However, good stability was observed in relation to GDC10, which was selected as a buffer layer in the further electrochemical studies.

Initial evaluation of the selected REBa_{0.5}Sr_{0.5}CoCuO_{5±δ} electrodes was performed on symmetrical cells consisting of 0.6 mm LSGM electrolyte pellet and GDC10 buffer layers screen-printed on both sides, sintered respectively at 1450°C for 8 h, and at 1350°C for 2 h. For the cathode slurries, fine powders of RBSCCO precursors were prepared by the sol-gel method and initially annealed in air at 900°C for 2 h, and then at 1000°C for 12 h. The screen-printed REBa_{0.5}Sr_{0.5}CoCuO_{5±δ} electrodes were sintered at 850 °C for 2 h in air. In general, the polarization resistances for the selected RBSCCO electrodes were found to be small, with the best values on the order of 0.02 $\Omega\cdot\text{cm}^2$ at 850°C, and 0.5 $\Omega\cdot\text{cm}^2$ at 600°C. This suggests possible application for SOFCs operating in the 600-800 °C range. Long-term stability tests were also conducted, e.g. for 120 h at 700°C, in which no significant increase of the polarization resistance was noticed. Finally, commercial-type anode-supported fuel cells based on the Ni-YSZ|YSZ support and the added GDC10 buffer were used with the RBSCCO cathodes. Notably, for the GdBa_{0.5}Sr_{0.5}CoCuO_{5±δ} electrode, the obtained power density at 625°C was measured to exceed 300

mW•cm².

5:00 PM EF17.10

Phase-Field Modeling of Crack Growth and Mitigation in Solid Oxide Cells Fei Xue^{1,2}, Yinkai K. Lei^{1,2}, Tian-Le Cheng^{1,2}, William K. Epting^{1,2}, Gregory Hackett¹, Harry W. Abernathy¹ and You-Hai Wen¹; ¹National Energy Technology Laboratory, United States; ²NETL Support Contractor, United States

Fracture and crack growth is one of the main degradation mechanisms in solid oxide fuel cells (SOFCs). However, the modeling of crack growth is challenging due to the complex microstructures of SOFC electrodes. Here we develop a phase-field model which incorporates the microstructures and phase-dependent material properties, including yield strength and fracture toughness. The model is employed to study the crack initiation and growth under thermal and redox cycling on the anode side of SOFCs. The simulation results demonstrate that under thermal cycling, cracking of interphase boundaries between Ni and YSZ dominates due to the thermal expansion mismatch, with cracks initiated at the triple-phase boundaries. On the other hand, under redox cycling, through-cracking of YSZ in the anode and electrolyte layers dominates due to the volume expansion during Ni oxidation. The simulation results agree well with existing experimental observations. Finally, the phase-field model is employed to develop crack-relieving strategies by balancing the contributions from the thermal strain and oxidation strain.

5:15 PM EF17.11

Ionic Conductivity of LaO_xF_{3-2x} Based Compounds in Air and H₂ Yahir Sadia^{1,2}, Inna Shusterman² and Brian Rosen³; ¹Ben Gurion University of the Negev, Israel; ²Nuclear Research Center of the Negev, Israel; ³Tel Aviv University, Israel

Metal oxides with high oxygen conductivity are highly relevant for applications such as oxygen detectors, fuel cells, water splitting, separation membranes and more. LaOF based materials are well known as O²⁻ conductors with high conductivity at relatively low temperatures. However, these compounds are moisture sensitive at high temperatures with long exposures to moisture converting them into La(OH)₃. Being able to quantify and control this process can allow the use of these compounds for different applications. LaO_xF_{3-2x} compounds with x=0.49,0.51,0.99,1.01 were prepared by solid state reaction of La₂O₃ and LaF₃ with the phases identified by XRD. One sample was tested for the oxygen conductivity at the range of 500-900°C in different O₂ partial pressures. All the samples were tested at high temperature XRD using H₂ to detect their stability in reducing atmospheres. In addition, high temperature EIS was measured on cells based on coins covered in LSM and Ni-GDC were tested for performance as an SOFC electrolyte.

5:30 PM EF17.12

A Highly Robust and Reactive Metal-Oxide Nanocomposite Electrocatalyst for Facile Oxygen Reduction Reaction in Solid Oxide Fuel Cell Cathode SungHyun Jeon¹, Jongsu Seo¹, Jeonwoo Shin², Sung Je Lee², Han Gil Seo^{1,3}, Siwon Lee^{1,4}, Jinwook Kim¹, Nikolai Tsvetkov¹, Jihwan An² and WooChul Jung¹; ¹Korea Advanced Institute of Science and Technology, Korea (the Republic of); ²Seoul National University of Science and Technology, Korea (the Republic of); ³Massachusetts Institute of Technology, United States; ⁴University of Pennsylvania, United States

The need for sustainable and green energy is on the rise as global climate change from accelerated environmental destruction becomes more severe. A solid oxide fuel cell (SOFC) is one of the energy applications that generate electricity without pollutants, and is attracting attention for its high energy efficiency and eco-friendliness. One of the most important challenges for SOFC is to lower the operating temperature, and for this, the development of cathodes is critical. La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-d} (LSCF) is a state-of-the-art perovskite oxide for SOFC cathode because of its high electrical conductivity, good catalytic activity, adequate thermal expansion coefficient, and ease of synthesis. However, insufficient oxygen reduction rate at low temperatures and chemical instability called Sr segregation limit the utilization of LSCF at intermediate temperatures (700-500°C). In this work, we combine two simple techniques: infiltration and atomic layer deposition (ALD), to implement a robust and durable LSCF-based cathode. The Ag nanocatalysts decorated through infiltration significantly reduce the electrode resistance of LSCF, and the ZrO₂ layer deposited through ALD prevents degradations both from the thermal agglomeration of the Ag catalysts and segregation of Sr species in LSCF, which are confirmed through electrochemical impedance spectroscopy, transmission electron microscopy, and X-ray photoelectron spectroscopy. Accordingly, the Ag/ZrO₂ nanocomposite-deposited LSCF cathode shows the electrode resistance of 0.085 Ωcm² at 650°C over 200 hours, which is, *to the best of our knowledge*, the lowest value compared to the results reported in the literature. Our result suggests a new research direction by which to fully utilize nanocatalysts and perovskite oxides in high temperature-used applications, including SOFCs.

SESSION EF18: Oxygen-Ion Conducting Fuel Cells III

Session Chairs: Peter Hendriksen and Xingbo Liu

Thursday Afternoon, July 21, 2022

Lobby Level, Avenue 34, Studio 2

4:00 PM EF18.01

Design, Manufacturing and Performance of High-Power Density Monolithic Metal-Supported Solid Oxide Fuel Cells Stéven Pirou, Belma Talic, Karen Brodersen, Theis Skafte, Anne Hauch, Åsa H. Persson, Henrik Lund Frandsen, Jens Høgh, Henrik Henriksen and Anke Hagen; Danmarks Tekniske Universitet, Denmark

In view of the required transition to a renewable society, the transportation sector is currently undergoing a technology shift from internal combustion engines to electric motors powered by batteries. However, their limited range and long charging times limit wide-spread adoption. Electrified transportation powered by Solid Oxide Fuel Cells (SOFCs) offer an attractive alternative especially for heavy freight and long-range transportation, as this technology can provide high-efficiency and flexible fuel choices. Up to now, the technology is mostly used for stationary applications owing to the high operating temperature, limited volumetric and gravimetric power density, and poor robustness towards thermal cycling and mechanical vibrations of conventional ceramic-based cells.

With this contribution, we will present a novel monolithic metal-supported SOFC design to overcome these issues. The monoliths were fabricated using cost competitive and scalable manufacturing methods such as tape-casting, lamination, and co-sintering. The monolithic SOFC design integrates seals and gas distribution channels, and requires only a single heat treatment to be produced, as opposed to several sintering steps for conventional SOFCs. Key parameters of the manufacturing process such as the co-casting of seals and electrodes, the composition of the seals, the method used to create gas distribution channels and to join the layers of the cell have been optimized to increase the lifetime of the monolith. Initial electrochemical tests exhibiting an exceptionally high power density (5.6 kW/L) will be presented. These results reveal the vast potential of SOFC technology for transport applications.

4:15 PM EF18.02

A-Site Exsolution of Ceria for a High-Performance Fuel Electrode of a Solid-Oxide Cell Chengsheng Ni, Bangxin Li, Debo He and Jiupai Ni; Southwest University, China

Ce doping on the A-site of SrFeO₃ increased the structural stability in a reducing atmosphere, but ceria was found to exsolve from the perovskite during the cooling process in the air if the doping level reached 20 at. %. The additional doping of 5 at. % Ru in Sr_{0.8}Ce_{0.2}FeO₃ on the Fe site could prevent the ceria segregation in air and induced the surface decomposition under fuel conditions for the formation of nanoscale SrO, CeO₂ and Ru⁰. The SSOFC with Ce/Ru co-doped SrFeO₃ on a Sr- and Mg-doped LaGaO₃ (LSGM) electrolyte showed a small R_p value (0.12 W cm²) when H₂ and the ambient air were used as fuel and oxidant, respectively. The peak power densities of 846 mW cm⁻² and 310 mW cm⁻² were achieved at 800 °C using H₂ and C₃H₈ as fuel, respectively. The excellent coke resistance of the anode could be related to the simultaneous *in situ* exsolution of CeO₂, SrO and Ru⁰ nanoparticles.

4:30 PM EF18.03

Structural Investigation of Exsolved Nanoparticles from Thin Films by X-Ray Scattering Emna Fezai¹, Jun Kyu Kim², Matthias Schwartzkopf³, WooChul Jung² and Simone Mascotto¹; ¹Universität Hamburg Fakultät für Mathematik Informatik und Naturwissenschaften, Germany; ²Korea Advanced Institute of Science and Technology, Korea (the Republic of); ³Deutsches Elektronen-Synchrotron, Germany

Exsolution is one of the emerging approaches to produce efficient, stable and recyclable metal catalysts. Despite the outstanding progress achieved in the synthesis and design of exsolved materials, the analyses of these materials are limited to surface characterization and are in most cases not representative of the overall sample. The focus of our work aims to elucidate the growth of transition metal nanoparticles (NP) from the bulk to the surface of the perovskite thin film combining different synchrotron x-ray scattering and spectroscopy methods. Here we report the analyses of transition metal (Ni, Co and Fe) doped and exsolved SrTiO₃ thin film. Using grazing incidence small-angle X-ray scattering (GI-SAXS), we were able to thoroughly analyse how the size and shape of metal-reduced nanoparticles evolved not only by changing the reducing conditions but also by going from the surface to the buried interface. In fact, at the same reducing atmosphere the metal nanoparticles can adopt different shapes while growing out the thin film. This was observed with Ni as well as Co exsolved NP. The degree of crystallinity and the phase orientation were also investigated with Grazing incidence wide angle scattering (GI-WAXS). Phase pure SrTiO₃ was preserved after exsolution at high temperature and no minor impurities or phase degradation were observed. Finally, in attempt to investigate the localisation of the reduced metal NP, the thin films were mapped with X-ray fluorescence (XRF). The fitting of the different spectra obtained confirmed that the majority of the metal NP were indeed localized at the surface, interestingly the population decreased while going deeper in the bulk of the film. In conclusion, these combined X-Ray analyses provide fundamental insights into the exsolution process of both surface and buried metal NP from perovskite oxide thin film matrices.

4:45 PM EF18.04

High Performance Thin-Film Air Electrodes of Ag/Ce_{0.9}Gd_{0.1}O_{2-δ} for Low Temperature Solid Oxide Cells with Vertically Aligned Nanocomposite Design Ozden Celikbilek^{1,2}, Matthew P. Wells³, Judith Macmanus-Driscoll³, Gwilherm Kerherve², Laetitia Rapenne¹, Marlu Cesar Steil¹, Elisabeth Siebert¹, David Muñoz-Rojas¹, Monica Burriel¹ and Stephen J. Skinner²; ¹Université Grenoble Alpes, France; ²Imperial College London, United Kingdom; ³University of Cambridge, United Kingdom

Low temperature (300-500°C) solid oxide cells (SOCs) have become the "next generation" technology following the commercialized high temperature SOC (650–850 °C). Current research is focused on screening new materials and microstructural designs that are ideal for low-temperature operations. This study explores the vertically aligned nanocomposite (VAN) heterostructure design, which has been shown to provide novel properties and new functionalities at the heterointerfaces of two oxide materials. (1) In this original design, we explore the composite Ag and Ce_{0.9}Gd_{0.1}O_{2-δ} (CGO) thin films deposited epitaxially on oriented yttria-stabilized zirconia substrates by pulsed laser deposition. Successful growth of ~34 and ~200 nm thick, dense Ag/CGO VAN films were obtained. The ~200 nm thick films recorded an area specific resistance (ASR) value of 100 Ω cm² at 400 °C in a symmetrical cell design. This result represents a factor of 5 enhancement in the ASR value compared to the state-of-the-art porous LSCF thin films. (2) This study provides insights into the enhanced performance at low temperatures in the metal/oxide VAN design.

(1) Huang, J. et al. MRS Bull. 46, 159–167 (2021).

(2) Wells, M. P. et al. ACS Appl. Mater. Interface, 13, 4117-4125 (2021).

5:00 PM EF18.05

Increasing Functionality While Maintaining Electrochemical Performance - High Entropy-Based Air-Electrodes for Intermediate- and Low-Temperature Solid Oxide Fuel Cells Juliusz Dabrowa¹, Klaudia Zielinska¹, Anna Stepień¹, Marek Zajusz¹, Maria Szymczak¹, Maciej Mozdziej¹, Margarita Nowakowska¹, Katarzyna Berent², Keyun Li¹ and Konrad Swierczek¹; ¹Akademia Gorniczko-Hutnicza imienia Stanisława Staszica w Krakowie, Poland; ²Akademia Gorniczko-Hutnicza imienia Stanisława Staszica w Krakowie Akademickie Centrum Materialow i Nanotechnologii, Poland

The La_{1-x}Sr_x(Co,Cu,Fe,Mn,Ni)O_{3-δ} (x = 0; 0.05; 0.1; 0.15; 0.2; 0.25; 0.3) series of high-entropy perovskites is investigated in the context of the possible application as air-electrode materials for the Solid Oxide Fuel Cell (SOFC) technology. The materials are synthesized using the Pechini method, allowing obtaining nanosized powder precursors. The structure and stability of the obtained materials are evaluated, indicating the presence of R-3c symmetry of the main perovskite phase. In the case of Sr-rich compositions, a tendency towards the formation of Ruddlesden-Popper phases is observed, even though the solubility of strontium in the main perovskite phase remains close to its nominal content. The materials are characterized by moderate values of thermal expansion coefficients, lower than 16 × 10⁻⁶ K⁻¹, with the negligible contribution of the chemical expansion mechanisms even at high temperatures, despite relatively big values of oxygen nonstoichiometry, exceeding δ = 0.1 above 700 °C. The electrical conductivity of all studied materials is within the typical requirements set upon the air-electrode materials, with maximum values in excess of 200 Scm⁻¹ for all compositions. The observed behavior suggests the small polaron hopping mechanisms of conduction, with the values of energy of activation visibly decreasing with the growing Sr content. Based on the results, the Sr-free La(Co,Cu,Fe,Mn,Ni)O_{3-δ} composition is selected for electrochemical evaluation. The material is characterized by high inertness with respect to LSGM and GDC solid electrolytes, also exhibiting remarkable long-term stability in CO₂-rich atmospheres, a feature of particular importance in the context of the envisioned application. The catalytic performance of La(Co,Cu,Fe,Mn,Ni)O_{3-δ} is evaluated in the La(Co,Cu,Fe,Mn,Ni)O_{3-δ}/δ[LSGM]/La(Co,Cu,Fe,Mn,Ni)O_{3-δ} symmetrical cell, with the determined values of polarization resistance R_p being as low as 0.112 Ωcm² at 700 °C and 0.272 Ωcm² at 650 °C, which compares favorably with the state-of-the-art LSCF cathode material, and remains one of the best results ever reported for the alkali metal-free electrodes. The mechanism of the oxygen reduction reaction (ORR) is studied by investigating the oxygen partial pressure dependence of R_p , allowing for identifying the rate-limiting stages of the ORR. Finally, the performance of the selected composition is evaluated in the La(Co,Cu,Fe,Mn,Ni)O_{3-δ}/δ[LSGM]/GDC|YSZ+Ni full cell, further proving the promising characteristics of the considered high-entropy perovskite. Based on the obtained results, it can be stated that the Sr-free La(Co,Cu,Fe,Mn,Ni)O_{3-δ} material shows tremendous potential with respect to application in SOFC technology, including intermediate- and low-temperature devices, combining high all-around functionality with excellent electrochemical performance.

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5:15 PM EF18.06

Exploring the Structures and Properties of Functional High-Entropy Spinel Materials [Miroslaw Stygar](#), Juliusz Dabrowa, Marek Zajusz, Jakub Cieslak, Maciej Mozdziej, Katarzyna Berent and Ewa Durda; AGH University of Science and Technology, Poland

The synthesis, structure, and properties of the high-entropy spinels are discussed on the example of compositions from the Co-Cr-Fe-Mg-Mn-Ni-O system. The single-phase $(\text{Co,Cr,Fe,Mn,Ni})_3\text{O}_4$, $(\text{Cr,Fe,Mg,Mn,Ni})_3\text{O}_4$, and $(\text{Co,Cr,Fe,Mg,Mn})_3\text{O}_4$ materials are obtained, together with the selected quaternary subsystems. The stability of the materials, both in terms of the temperature and oxygen partial pressure dependence is evaluated, showing the profound influence of these parameters on the spinel-forming capabilities of the investigated systems, potentially providing means for further tailoring of their structure, including the transition between $Fd-3m$ spinel symmetry and $Fm-3m$ rocksalt one. Thermomechanical behavior of all single-phase compositions is remarkably similar, with the values of thermal expansion coefficient being in the range of 8.8 to $9.8 \times 10^{-6} \text{ K}^{-1}$, making the materials potentially interesting in terms of compatibility with materials used in the solid oxide fuel cell technology (SOFC), especially interconnects. The temperature dependence of the electrical conductivity indicates the semiconducting character, with a clearly visible change of the energy activation *ca.* 400 °C. To provide a further understanding of these systems, the initial assessment of the cationic occupancy within the tetra- and octahedral lattice sites is carried out for selected compositions, through the use of the Mossbauer spectroscopy measurements combined with the density functional theory *ab initio* calculations (DFT). The results show distinctively different tendencies between quaternary subsystems and $(\text{Co,Cr,Fe,Mn,Ni})_3\text{O}_4$ composition. In the case of the former ones, a preferential occupancy of the lattice sites appears to be energetically favourable, while for the quinary composition, the entropic configuration on both sublattices turns out to be characterized by the lowest energy. The potential for tailoring the occupancy of cationic lattice sites by the introduction of the specific cations is discussed.

Based on the analogy to conventional spinels, as well as the determined electrical and thermomechanical properties of the studied high-entropy spinels, their application as protective-conductive coatings for interconnect elements in SOFCs is proposed. Taking into account some of the established features of the high-entropy systems, such as lattice distortion, potentially affecting the rate of cations' diffusion, it can be postulated that they may carry significant potential with regard to this technology, especially in terms of corrosion protection and suppression of the deleterious Cr-poisoning effect. The initial studies regarding the possibility of applying such coatings on the Crofer 22APU ferritic stainless steel substrate are carried out, together with the preliminary performance assessment of the obtained ceramic/metallic system.

This research was supported by the Polish National Science Center (NCN) under project No. UMO-2021/41/B/ST8/03928

5:30 PM EF18.07

Relating Nanoscale Microstructure and Performance in Nanocatalyst-Infiltrated Solid Oxide Fuel Cell Anodes [Jillian Rix](#), Alexey Nikiforov, Uday Pal, Srikanth Gopalan and Soumendra Basu; Boston University, United States

Solid oxide fuel cells are ideally operated at relatively low temperatures to prevent degradation over long time periods; however, slower reaction speeds at these temperatures necessitate the use of catalysts to improve performance. In SOFC anodes, metal and MIEC (mixed ionic and electronically conducting) nanocatalysts are commonly infiltrated into the anode structure: it is thought that by adding reaction sites to the anode, they improve overall performance by increasing triple phase boundary (TPB) or double phase boundary (DPB) density respectively. Quantifying the relationship between infiltrated microstructure and anode performance is particularly challenging because of the structural complexity of infiltrants and small feature size. In this study, we use a combination of techniques, including FIB-SEM 3-D reconstruction, cross-sectional SEM imaging, electrochemical impedance spectroscopy (EIS) and distribution of relaxation times (DRT) analysis to characterize anode symmetric cells infiltrated with nickel and gadolinium-doped ceria (GDC). We find that the improvement mechanisms in each type of infiltrated cell differ, with the infiltrated GDC mostly providing additional reaction sites, and the infiltrated Ni cell adding reaction sites more active than those at the existing backbone TPBs.

SESSION EF19: Poster Session III: Energy and Fuels Conversion III

Session Chair: Georgios Dimitrakopoulos

Thursday Afternoon, July 21, 2022

6:00 PM - 8:00 PM

Mezzanine Level, Second Floor, Stadler

EF19.01

Stabilization of Delta Bi₂O₃ Phase at Room Temperature by Thermal Nanocrystallization of Bismuth Oxide Glasses [Maciej Nowagiel](#)¹, Tomasz K. Pietrzak¹, Agata Jarocka¹, Tomasz Plocinski¹, Julien Trébossé², Olivier Lafon², Marek Wasuconek¹ and Jerzy E. Garbarczyk¹; ¹Politechnika Warszawska, Poland; ²Universite de Lille, France

Crystalline $\delta\text{-Bi}_2\text{O}_3$ is the best known O^{2-} ion conductor, but it is stable in a relatively narrow temperature range 729–825 °C only. Its very high ionic conductivity (1 S/cm at 750 °C) has motivated many researchers to look for a method to stabilize this fluorite-type structure to lower temperature. So far the successful strategies to achieve the stabilization of the delta phase have included doping (e.g. by rare-earth elements [1]) or synthesis in form of thin layers [2].

Our approach to reach the same goal is significantly different from those two strategies. It consists of two steps: i) preparation of the Bi_2O_3 glass (pure or only slightly doped) and ii) nanocrystallization of the glass prepared in i) stage. The advantages of such an approach are as follows: a) the final material is pure or nearly pure Bi_2O_3 and b) it can be prepared in bulk and is not limited to thin layers only. Our experience with nanocrystallization has shown that by the appropriate heat-treatment one can achieve a gigantic (even by a factor of 10^9) and irreversible electrical conductivity enhancement in glassy analogs of some cathode materials for Li-ion batteries [3,4]. This effect is closely related to changes in the microstructure – namely to formation of nanoscale crystalline olivine grains, with dimensions going down even to a few nanometers, confined in the glassy matrix.

In this research, we first obtained Bi_2O_3 glasses at various synthesis conditions. Al and Si additives, originating from the crucibles, facilitated the glass formation upon quenching. Then we subjected them to an appropriate thermal treatment [5]. As a results, materials with various crystalline Bi_2O_3 phases were obtained: delta, beta and gamma – depending on the synthesis conditions. The phases (including delta) were found to be stable down to room temperature. The microstructure of samples was investigated by electron microscopy techniques (both SEM and HRTEM). The grains of $\delta\text{-Bi}_2\text{O}_3$ phase were observed always as 20–40 nm nanocrystallites, confined in a residual glassy matrix. On the contrary, the grains of beta and gamma phases were of micrometer sizes. The total electrical conductivity of nanocrystallized samples as a function of temperature has been determined in preliminary measurements by impedance spectroscopy.

MAS NMR was applied to determine the neighborhood of Al and Si, and to investigate their role in the stabilization of the Bi₂O₃ phases. From this experiment, one can conclude that Al and Si additives are rather unlikely to stabilize directly the delta-like phase. On the contrary, they are believed to participate in formation of glass and induct the confinement effect of pure delta-Bi₂O₃ nanocrystallites.

Acknowledgments

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EF19.02

Microstructural Changes of Ni/GDC Fuel Electrodes During Operation (SOFC) Florian Wankmueller¹, Tibor Lehnert¹, Felix Kullmann¹, Yanting Liu¹, Andre Weber¹, Heike Stoermer¹, Martin Juckel², Norbert H. Menzler² and Dagmar Gerthsen¹; ¹Karlsruher Institut für Technologie, Germany; ²Forschungszentrum Julich GmbH, Germany

Nickel/gadolinium-doped ceria (GDC) fuel electrodes offer superior properties compared to cermet electrodes based on yttria-stabilized zirconia (YSZ) especially for solid oxide fuel cells (SOFC) operated at temperatures below 700 °C. The mixed ionic and electronic conducting nature of GDC under reducing conditions at the fuel electrode provides more complex reaction pathways for hydrogen electrooxidation compared to a Ni/YSZ cermet [1]. This results in different requirements for the microstructure of the electrode. In addition, GDC does not offer a stable, time-invariant ceramic backbone but changes the microstructure during operation [2,3].

This contribution addresses the changes in Ni-GDC microstructure during operation and sulfur poisoning. Imaging techniques such as focused ion beam/scanning electron microscopy (FIB/SEM) allow detailed microstructure quantification by enabling 3D reconstructions of the μm- and sub-μm-scaled multiphase electrode. Scanning transmission electron microscopy (STEM) combined with energy-dispersive X-ray spectroscopy (EDXS) gives further insight into the distribution of secondary phases and the evolution of the GDC microstructure. The results will be correlated with performance changes measured by electrochemical impedance spectroscopy to show the impact of microstructural changes during operation.

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EF19.03

Ionic Site Occupancy Management in Mn_{1.5}Co_{1.5}O₄ Spinel by Tetrahedral Preferred Zn Substitution Dokyum Kim, Seong-Uk Oh, Woo Seop Shin, Sumi Kim, Jung-A Lee, Young-Woo Heo and Joon-Hyung Lee; Kyungpook National University, Korea (the Republic of)

AB₂O₄ spinel structures are usually cubic close-packed oxides with eight tetrahedral and four octahedral sites per formula unit. B ions occupy half the octahedral holes, while A ions occupy one-eighth of the tetrahedral holes. Spinel may contain various metal ions at A and B sites. The spinels composed of transition metal ions such as Mn, Co, Ni, Cu, etc., exhibit high electrical conductivity. The conduction of Mn-based spinel is explained by the small polaron hopping mechanism between Mn³⁺ and Mn⁴⁺ ions in the octahedral site, and the ions in the tetrahedral site might not play a major role in electrical conduction. For this reason, site occupancy in spinels can be an essential consideration in electrical conductivity.

In this study, tetrahedral-site preferred, and single valence Zn²⁺ was substituted in Zn_xMn_{1.5-0.5x}Co_{1.5-0.5x}O₄ spinel, and the effect of site distribution on electrical conductivity was analyzed. It was found that the pure Mn_{1.5}Co_{1.5}O₄ was composed of a tetragonal-cubic mixed phase. As the Zn content increased in the Zn_xMn_{1.5-0.5x}Co_{1.5-0.5x}O₄, the fraction of the tetragonal phase decreased while the cubic phase increased. As the crystal symmetry increases, the Jahn-teller distortion at the octahedral site will be decreased. When the Zn content exceeds a certain amount, the electrical conductivity will be decreased as Zn occupies the octahedral site, which does not contribute to small polaron hopping. The site occupancy and electrical properties will be discussed in detail.

EF19.04

Material Screening for Protonic Ceramic Fuel Cell Cathode by Using Patterned Thin-Film Model Electrode Teruki Yoshioka, Katsuya Nishidate, Yuta Kimura, Takashi Nakamura, Keiji Yashiro, Tatsuya Kawada and Koji Amezawa; Tohoku Daigaku, Japan

Introduction

Protonic ceramic fuel cell (PCFC) is a fuel cell expecting intermediate temperature operation around 673-873 K. One of challenges for the commercialization of PCFC is to reduce voltage loss due to a large polarization resistance at the cathode. [1, 2]. At the PCFC cathode, oxygen gas, proton, and electron react to generate water vapor. This reaction occurs at triple phase boundary (TPB) of gas/electrode/electrolyte, when electron-conductor is used. On the other hand, when a protonic-electronic mixed conductor is used, the reaction area can extend to the double phase boundary (DPB) of gas/electrode. Therefore, it is believed that the use of protonic-electronic mixed conductor is beneficial to improve PCFC cathode performance. For instance, BaGd_{0.8}La_{0.2}CoO_{3.8}, which is expected as a protonic-electronic mixed conductor, showed relatively good electrode performance [3]. However, comparable performance was reported with many “poorly proton-conducting” materials, such as La_{0.6}Sr_{0.4}CoO_{3.8} [4]. To develop a high-performance PCFC cathode, it is important (i) to quantitatively evaluate activity of the investigated electrode material and (ii) to understand the electrode reaction mechanism, for instance, where is the dominant reaction path and how large the contribution of reactions through TPB/DPB are. In this study, we systematically investigated electrode activity and reaction mechanism of La_{0.6}Sr_{0.4}CoO_{3.8} (LSC64), BaGd_{0.3}La_{0.7}Co₂O_{6.8} (BGLC37), and Ba_{0.5}La_{0.5}CoO_{3.8} (BLC55) by applying our original model electrodes [3-5].

Experiments

We prepared two different types of patterned thin film electrode, which can simulate reactions in a porous electrode while simplifying its microstructure. One type of the electrode is a sort of columnar electrode laying on the substrate as a thin film. This electrode has both DPB and TPB as reaction sites. On the other hand, in the other type of electrode, TPB is eliminated so that electrode reaction occurs only through DPB. Then, by comparing the results obtained with these two types of electrode, the contributions of DPB/TPB reactions to the total reaction can be separately evaluated. In addition, the patterned thin film electrodes can compare electrode activity among various materials directly, because the electrode performance can be quantitatively evaluated without influences by electrode morphology and microstructures.

In this study, electrode reaction of LSC64, BGLC37, and BLC55 on the proton-conducting solid electrolyte, BaZr_{0.8}Yb_{0.2}O_{3.8} (BZYb), were investigated.

Three terminal electrochemical cells were prepared using the patterned thin film electrode as a WE, and porous Pd as RE and CE. DC polarization measurements were performed in two chamber setup. Temperature was 773-873 K. The gas atmospheres were 5% H₂-2% H₂O for WE, and 1-100% O₂-2% H₂O for RE and CE.

Results and discussion

In DC polarization measurements of LSC64 and BLC55, the observed current were 3-6 times higher for the electrode with TPB than the electrode without TPB. This showed that TPB is the dominant reaction pathway in LSC64 and BLC55. On the other hand, in BGLC37, the current was almost independent of the existence of TPB. This demonstrated that DPB is the dominant reaction pathway in BGLC37. Comparing the results for the electrode with TPB, the electrode activity was found to be higher in order by BGLC37, LSC64, and BLC55 at 873 K. This is probably because BGLC37 exhibits protonic-electronic mixed conduction. However, at 773 K, LSC64 showed a comparable electrode activity as BGLC37. This indicated that oxide ion-electron mixed conductors also can be a good PCFC cathode.

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EF19.05

A Self-Assembled Thin-Film Nanocomposite with High Stability as a Functional Layer in Solid Oxide Cell Cathodes Federico Baiutti^{1,2}, Lucile Bernadet¹, Francesco Chiabrera¹, Marina Machado¹, Matias Acosta³, Judith Macmanus-Driscoll³, Alex Morata¹, Marc Torrell¹ and Albert Tarancón^{1,4}; ¹Institut de Recerca en Energia de Catalunya, Spain; ²Kemijski institut, Slovenia; ³University of Cambridge, United Kingdom; ⁴Instituto Catalana de Recerca i Estudis Avancats, Spain

Vertically aligned nanocomposites (VANs) have been recently proposed as an exciting way of inducing new functionalities by interface effects. VANs can be easily fabricated as a result of a one-step deposition process using physical thin-film deposition methods, resulting in the intimate off-plane alternation of the two-phase components at the nanometric scale. In the present contribution, we show results from the fabrication and characterization of (La,Sr)MnO₃ (LSM) – Ce_{0.8}Sm_{0.2}O₂ (SDC) (50% w/w) VANs for cathode application in solid oxide cells. In-depth structural and electrochemical characterization highlights that the LSM-SDC VAN is characterized by a high electrochemical performance towards oxygen reduction reaction ($k_r \approx 10^{-6}$ cm s⁻¹ at 750 °C) and by excellent thermochemical stability against Sr segregation. More importantly, we demonstrate that the heterostructure can be fabricated directly on top of technologically relevant supports (including polycrystalline YSZ electrolyte), i.e. it has straight applicability in real solid oxide cell devices. Tested as a functional cathode layer in state-of-the-art fuel cells, high power values of ≈ 1 W cm⁻² are obtained at 750 °C, which are retained during long-term device operation. The study is complemented by fundamental investigation including atom-probe tomography, transmission electron microscopy and density functional theory calculations which allow rationalizing the observed functionalities in terms of cationic redistribution during fabrication.

EF19.06

Characterization of La-Doped CeO₂ (Ce_{0.6}La_{0.4}O_{1.8}) Materials as a Buffer Layer at YSZ Electrolyte Supported SOFCs Dong X. Nguyen^{1,2}, Sang Won Lee^{3,1}, Seok Hee Lee¹, Hyung Tae Lim² and Tae Ho Shin¹; ¹Korea Institute of Ceramic Engineering and Technology, Korea (the Republic of); ²Changwon National University, Korea (the Republic of); ³Yonsei University, Korea (the Republic of)

Solid oxide fuel cells (SOFCs) have been much attractively emerging in the next generation energy marketplace because of their high energy conversion efficiency, fuel flexibility, and low emission. The main challenges that SOFC developers need to address are high performance, long-term durability, and effective cost. The optimization of SOFC microstructures and manufacturing processes for improved performance of electrolyte-supported type SOFCs (ESCs) has been a continuous goal in the development of these devices. Stabilized zirconia such as yttria-stabilized zirconia (YSZ) and scandia stabilized zirconia (ScSZ) are widely employed as electrolyte self-standing support. However, zirconia-based electrolytes still have a drawback in reacting with Sr-rich cathode materials such as LSC, LSCF, BSCF, etc. Therefore, the ideal buffer interlayered structure between zirconia-based electrolyte and electrodes is required. There is much interest in developing optimal interlayer microstructures that are better able to function at high-performed ESCs. In the present work, we focus on the commercial lanthanum-doped ceria (Ce_{0.6}La_{0.4}O_{1.8} - LDC) as a buffer layer between YSZ electrolyte and LSCF cathode. The reactivity of the YSZ/GDC composite was higher than that of the YSZ/LDC composite. The ratio of Zr/Ce in the inter-diffusion layer of the YSZ/LDC interface was less than that of the YSZ/GDC. However, the pyrochlore-shaped peak of the insulating phase La₂Zr₂O₇ was detected in the YSZ/LDC sintered at 1350 °C. In the term of 1250 °C, the impurity peak disappeared therefore the maximum power density for the electrolyte supported cell SOFC with LDC interlayer was 0.31 W.cm⁻² at 1023 K as opposed to GDC interlayer only 0.28 W.cm⁻². A variety of additives (Co, Mn, and Cu) was added to the LDC buffer layer for examining the sintering properties. The addition of copper obtained the highest microstructural density. A cell comprising one weight percentage Cu added LDC buffer layer, which was fabricated in a single time and using a low-temperature procedure, had suitable performance, lower ohmic and polarization. The result illustrated that the electrochemical properties of the cells assembled by screen printing that suitable for commercial products.

EF19.07

Characterization of SOFC and Symmetrical Cells Using the Fiaxell Open Flange Set-Up Fatima-Ezzahra El Bassiri^{1,2}, Aurélie Rolle^{2,1}, Edouard Capoen^{3,1}, Raphael Ihringer⁴ and Rose-Noëlle Vannier^{2,1}; ¹Unite de Catalyse et Chimie du Solide, France; ²Centrale Lille Institut, France; ³Universite de Lille, France; ⁴FIAXELL, Switzerland

The characterization of SOFC cells, and the study of their performances at specific measurement conditions, requires the use of special well optimized set-up.

One of the most used set-up in Europe is Fiaxell open flange set-up [1]. This set-up has the advantage to carry out cell performance measurements without sealing. The cell is placed between two metal plates protected by alumina foils. One side of the cell is supplied with hydrogen and the other with air. The excess gas is burned all around the cell.

The study focussed on SOFC redox 2R cells developed by Fiaxell, consisting of LSCF as a cathode material deposited on a YSZ electrolyte with a buffer ceria layer and NiO-8YSZ as anode functional layer (AFL). A power of 1W/cm² was obtained at 780°C, by feeding the cathode side with air and the anode side with hydrogen, associated with a polarization resistance of 211 mΩ.cm².

To go further in the characterisation of the oxygen reduction reaction, the open flange set-up which is commonly used to study full SOFC cell was adapted and optimized to characterize symmetrical cells under various oxygen partial pressures. The study was carried out by electrochemical impedance spectroscopy (EIS) on a symmetrical cell with LSCF electrode materials on both sides. Particular attention was paid to the understanding of the involved mechanisms by combination of CNLS-fit and the use of the distribution function of relaxation time (DRT).

Acknowledgements

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EF19.08

Achieving High Performance in Solid Oxide Electrolysis Cell Using LSGM Electrolyte Support for Hydrogen Production Suji Kim¹, Sang Won Lee^{1,2}, Seok Hee Lee¹ and Tae Ho Shin¹; ¹Korea Institute of Ceramic Engineering and Technology, Korea (the Republic of); ²Yonsei University, Korea (the Republic of)

Solid Oxide Electrolysis Cells (SOECs) are considered to be a promising system for generating green hydrogen, which is an alternative source of new energy. In conventional SOEC system, yttria stabilized zirconia (YSZ) is widely being used as an electrolyte that allows to extract oxide ions from water. Despite its pure ionic conductivity, it is limited in temperature over 1073K. YSZ based SOECs still have the continual developing challenges in durability and efficiency because of its high temperature demand. Meanwhile, $\text{La}_{1-x}\text{Sr}_x\text{Ga}_{1-y}\text{Mg}_y\text{O}_{3-\delta}$ (LSGM) has emerged as a rising candidate for the electrolyte for its superior ionic conductivity even in intermediate temperatures ($\leq 1073\text{K}$). Since a cell with LSGM can work in the intermediate temperature, it can have better durability and efficiency in lower temperature operation condition. In this study, LSGM electrolyte support SOEC was tested. Here, we demonstrate the successful electrochemical H_2 production in LSGM based SOEC. During electrochemical electrolysis at 1073K, current densities as high as -1.58 and -1.15 Acm^{-2} were achieved when voltages of 1.4 and 1.3V were applied, respectively. This improved performance is attributed to the high ionic conductivity of LSGM electrolyte, even though the cell employed a 200 μm thick electrolyte support.

EF19.09

Theoretical Analysis of the Crack Formation and Propagation in a Solid Oxide Electrolysis Cell Yudong Wang^{1,1}, Anil Virkar^{1,2} and Xiao-Dong Zhou^{1,1}; ¹University of Louisiana at Lafayette, United States; ²University of Utah, United States

A solid oxide electrolysis cell (SOEC) is a state-of-art device for energy storage and carbon management. The formation and propagation of a crack can be observed in SOECs attributed to oxygen evolution, particularly at a high current density. An anomalous change in the oxygen chemical potential, μ_{O_2} , at the interface between the oxygen electrode and the electrolyte is the driving force for the crack formation and its magnitude can be calculated in an SOEC by assuming that the local thermodynamic equilibrium prevails. The crack growth driven by the overshoot is a mechanical process, determined by the electrochemical properties, elastic properties, and operating conditions of the cell. This work offers a 3-dimensional analysis that considers both electrochemistry and elasticity to study the effect of pertinent parameters on the electrochemically driven crack propagation, crack growth kinetics, and their impact on distributions. Our analysis shows that the cell with an electronic insulating and ionic conductive oxygen electrode/electrolyte interface is stable under high temperature electrolysis with suppressed crack propagation or absence of crack formation. Reducing the operating current or voltage is an operational approach to remedy crack problems and improve the performance durability.

EF19.10

Synthesis of MnO₂ Carbon Nanotubes Catalyst with Enhanced Oxygen Reduction Reaction Abid Ullah^{1,2}; ¹University of Science and Technology South Korea, Korea (the Republic of); ²Korea Advanced Institute of Science and Technology, Korea (the Republic of)

Polymer Electrolyte Membrane Fuel Cell (PEMFC) is an electrochemical cell which undergoes oxygen reduction reaction to produce energy. Platinum (Pt) metal has been used for catalysis since its inception but expensiveness is the major obstacle in commercialization of fuel cell. Herein a non-precious group metal (NPGM) is employed instead of Pt to reduce the cost of PEMFCs. Manganese dioxide based carbon nanotubes (MnO₂ CNTs) is a catalyst having excellent electrochemical properties and offers a better alternative to the Platinum based PEMFC. The catalyst is synthesized by impregnating the transition metal on large surface carbonaceous CNTs by hydrothermal synthesis techniques. To enhance the catalytic activity and increase the volumetric current density, the sample was pyrolyzed at 800 °C temperature under nitrogen atmosphere. During pyrolysis, the nitrogen was doped in the framework of CNTs. The material is then treated with acid for removing the unreacted metals and adding oxygen functional group to the CNT framework. This process ameliorates the catalytic activity of the manganese based catalyst. The catalyst has been characterized by scanning electron microscope (SEM), X-ray diffraction (XRD) and the catalyst activity has been examined by Rotating Disc Electrode (RDE) experiment. The catalyst was strong enough to withstand austere alkaline environment in experimental conditions and had high electro catalytic activity for oxygen reduction reaction (ORR). Linear Sweep Voltammetry (LSV) depicts a current density of -4.0 mA/cm^2 and an over potential of -0.3V vs. Standard Calomel Electrode (SCE) in 0.1M KOH electrolyte. Rotating Disk Electrode (RDE) was conducted at 400, 800, 1200, and 1600 rpm. The results of MnO₂CNT uphold the proponent of desirable and low cost catalyst to supplant the Pt metal in fuel cell.

EF19.11

Electrical and Thermal Properties of PMMA Based Nano-Dispersed Polymer Gel Electrolytes Rajiv Kumar; G.G.D.S.D. College Hariana, India

Nano-dispersed polymer gel electrolytes containing polymethylmethacrylate (PMMA) having different molecular weights, lithium trifluoromethanesulfonate (LiCF₃SO₃), propylene carbonate (PC) and titanium oxide (TiO₂) have been prepared and characterized by ionic conductivity. The addition of PMMA with average molecular weights 15,000; 120,000; 996,000 results in an increase in ionic conductivity as compare to liquid electrolytes LiCF₃SO₃ in PC at all PMMA concentrations, which is due to the dissociation of undissociated salt and ion aggregates present in the electrolytes. The increase in conductivity with PMMA addition also depends upon the molecular weight of PMMA and has been found to be more for gels containing PMMA with lowest molecular weight (15,000). The increase in viscosity with PMMA addition also depends upon the molecular weight of the polymer and is closely related to the conductivity behaviour of these electrolytes. Polymer gel electrolytes have been found to be thermally stable upto a temperature of 125oC. These gels show high value of conductivity (~10–2 S/cm at 25 oC) which does not vary with time and shows only a small increase over the 20–100oC temperature range and is desirable for their potential use in applications.

EF19.12

Optimal Atomic Layer Deposition Prepared Al-Doped ZnO Buffer Layers for Charge Transport Enhancement in Cu₂O Photocathodes Hak Hyeon Lee, Ji Hoon Choi and Hyung Koun Cho; Sungkyunkwan University College of Engineering, Korea (the Republic of)

Among the various technologies for sustainable hydrogen production, photoelectrochemical (PEC) water splitting is a promising and low-cost method with almost negligible carbon emissions. Cu₂O is one of the most promising p-type semiconductors for reducing water to hydrogen due to its favorable conduction band level and high visible light absorption. Using n-type overlayers with appropriate band alignment with Cu₂O can be an effective strategy for improving the charge transport efficiency of Cu₂O photocathodes. Atomic layer deposition (ALD) prepared Al-doped ZnO (AZO) films generate an additional built-in potential at the Cu₂O/AZO interface, as well as a uniform coating with a small thickness over Cu₂O. The charge transport behavior of the photoelectrodes is expected to be influenced greatly by the composition of the Al₂O₃ monolayers and the layer stacking sequence of AZO. We developed optimal atomic stacking orders of AZO layers with Al₂O₃ and ZnO stacking layers using the atomically controlled ALD technique. As a result, the sample with an AZO overlayer including Al₂O₃ monolayers in the bottom and top regions had the best PEC performance. Electrochemical impedance spectroscopy and Mott-Schottky plots were used to investigate the effect of the Al₂O₃ monolayer. With this optimized AZO overlayer, the Cu₂O/AZO/TiO₂/Pt photoelectrode has an open circuit potential of 0.63 V and a high cathodic photocurrent value of 3.2 mA cm^{-2} at 0 V_{RHE} for over 100 minutes.

EF19.13

Understanding the Chemical Transformations and Photoelectrocatalytic Water Oxidation Mechanisms in Ferric Pseudobrookite Photoanodes [Devi Prasad Adiyeri Saseendran](#)¹, Carlos Triana¹, Sergey Peredkov², Serena DeBeer³ and Greta Ricarda Patzke¹; ¹Universitat Zurich, Switzerland; ²Helmholtz Zentrum Berlin, Germany; ³Max Planck Institute for Chemical Energy Conversion, Germany

The design of highly efficient, robust, and green water oxidizing catalysts is one of the most critical challenges in sustainable energy research. Due to the global climate change crisis and energy demand, solar assisted photo-electrocatalytic water splitting has emerged as a promising approach towards producing clean chemical fuels and storable energy resources. Ferric pseudobrookite (Fe_2TiO_5) have recently emerged as a photoanode material for solar water oxidation. In parallel to improving efficiency and activity, a proper understanding of the electronic structure features and valance state/coordination environment changes of the metal centers is of utmost importance, to improve the properties of this material in future. Herein, we report a new synthetic method based on slot-die coating for the fabrication Fe_2TiO_5 photoanode which exhibit a photocurrent density of 0.03 mA/cm² at 1.23 vs RHE. And the chemical transformations and therein derived water oxidation intermediates, has been investigated by employing state of the art synchrotron X-ray Absorption and Emission Spectroscopies. Via post long-term photo-electrolysis EXAFS, we identified a unique morphological transformation at the photoanode surface without the electronic structure being altered at Iron site and the coordination environment being changed at Titanium site. The synergistic effects of Fe and Ti metal centers towards water oxidation and the role of Ti centers under operational conditions have been depicted via two colour valence to core X-ray Emission Spectroscopy.

EF19.14

Enzymatic Fuel Cell—Hydrolytic Stability and Conductivity Investigations of the Ionomer Membrane Separator in Typical Working Conditions [Luca Pasquini](#)¹, Philippe Knauth¹, Maria Luisa Di Vona², Emanuela Sgreccia² and Riccardo Narducci²; ¹Aix-Marseille Universite, France; ²Universita degli Studi di Roma Tor Vergata, Italy

Enzymatic fuel cells (EFCs) are emerging and promising devices for a sustainable and cheap power generation of miniaturized sensors, actuators and medical devices. Recently, promising performance improvements were reported. In the case of double chamber EFCs an ionomer based membrane separator has to be utilized, giving the possibility to miniaturize the device and to feed the electrodes with pure O₂ and H₂ increasing the stability of the enzymes at the anode and the cathode side. However, the hydrolytic behaviour as well as the conductivity of the membrane need to be carefully investigated and can be optimized (by changing the casting procedure and/or membrane composition) with regard to the use of pH-buffered solutions (typically phosphate, citrate and acetate buffers) for the stability of the selected enzyme catalysts.

We will first briefly report the results obtained by the characterization of two model ionomer membranes, cation-conducting sulfonated poly(ether ether ketone) (SPEEK) and anion-conducting PSU-trimethylammonium chloride (PSU-TMA), in term of the gravimetric and volumetric water uptake, the dimensional swelling (area and thickness), the density and the ionic conductivity as a function of the pH, type of buffer and buffer concentration at 25 °C. The hydration data are interpreted using the osmotic swelling pressure dependence on the ion-exchange capacity of the ionomers and the concentration of the electrolyte solutions. In conclusion the best compromise between low swelling and a relatively high ionic conductivity is found in phosphate buffers [1].

We will thus report the optimization in phosphate buffer, in terms of hydrolytic stability, conductivity and mechanical behaviour, of membrane based on proton conducting ionomers, namely SPEEK and sulfonated poly(phenyl sulfone) (SPPSU). The hydrolytic stability can be adapted by changing the casting solvents (DMSO, water or ethanol) and procedure, including a crosslinking heat treatment, or a blend of the two ionomers. The possibility to introduce an inert PPSU based electrospun reinforcement during the casting is also investigated. The performed characterizations showed that the use of ethanol reduces the swelling, but at the same time also the Young's modulus; a shorter casting time results in stiffer membranes, but has no effect on the mass uptake and the conductivity; the crosslinking stabilizes the membranes that shows a better hydrolytic stability, even if with a little decrease of conductivity; the addition of SPPSU to SPEEK membranes improves the ionic conductivity. A comparison with Nafion™ shows the different behaviour of this ionomer versus SPEEK membrane: from a mechanical point of view, after immersion in the buffer solution SPEEK moves from a rigid to a plastic behaviour while Nafion™ does exactly the contrary [2]. The introduction of the PPSU electrospun reinforcement shows that the hydrolytic stability can be further improved without affecting the final ionic conductivity.

The results obtained open interesting perspectives to find out the optimal compromise in order to boost the membrane performances in EFCs containing a buffer solution.

[1] L. Pasquini, et al. *The Journal of Physical Chemistry B* 2018; 122 (50), 12009-12016; 10.1021/acs.jpbc.8b08622

[2] L. Pasquini, et al. *Polymers*. 2021; 13(3):475; 10.3390/polym13030475

EF19.15

Synthesis And Electron-Beam Evaporation of Gadolinium-Doped Ceria Thin Films [Fariza Kalyk](#), Tomas Tamulevičius, Sigitas Tamulevičius and Brigita Abakevičiene; Kauno technologijos universitetas, Lithuania

Gadolinium-doped ceria (GDC) nanopowders synthesised by the co-precipitation synthesis method, were used as a target material to form ceria-based thin films using the electron-beam evaporation technique. The morphological properties of the pressed ceramic pellets were examined using scanning electron microscopy (SEM) and the results showed a dense structure with no visible defects, pores, or cracks. The results of AC impedance spectroscopy showed an increase in the total resistance of ceramics with the increase of the concentration of Gd₂O₃ in GDC. The highest total ionic conductivity of $11 \times 10^{-3} \text{ S} \cdot \text{cm}^{-1}$ at 600 °C was obtained for Gd_{0.1}Ce_{0.9}O_{2-δ} (10 GDC) with the lowest activation energies at both the low- and high-temperature ranges (0.85 and 0.67 eV, respectively). The chemical composition of evaporated GDC thin films obtained from XPS and ICP-OES measurements showed that the stoichiometry deviation of the evaporated thin films is, on average, 28% lower than that of the target material. The annealing of the GDC films at all temperatures (at 600 °C, 700 °C, 800 °C, and 900 °C for 1 h) had a minor affects its surface roughness and the morphology with minimal increase of the densification and roughness. Raman spectroscopy results confirmed the improvement of the crystallinity for corresponding thin films and the decrease of grain boundary phase volume. The optimum heat-treating temperature for GDC thin films does not exceed 800 °C.

EF19.16

Exsolution of the Metallic or Intermetallic Nanoparticles as a Trendy Way of Enhancing Catalytic Activity of Strontium Titanate-Based Anodes Beata M. Bochentyn, Agata Ducka, [Patryk Blaszczyk](#) and Jakub Karczewski; Politechnika Gdanska Wydział Fizyki Technicznej i Matematyki Stosowanej, Poland

Exsolution process is an “inside-out” technique of material modification. Upon a partial reduction process, some cations from the host compound can be

extruded in form of nanoparticles on the oxide support. The exsolution method offers an even distribution of the particles as well as improved attachment to the host material [1]. One-third of exsolved particles is submerged inside the surface, providing an excellent connection compared to deposited counterparts [2]. Additionally, the exsolution process may be partially reversible, meaning the exsolved particles could be incorporated back to the host lattice in oxidative conditions [2]. The reversibility of the exsolution is associated with the “intelligent” catalysts concept [1].

Exsolution of base metal nanoparticles from perovskite oxides may unlock superior catalytic activity towards the CO oxidation reaction [3]. The exsolved Ni nanoparticles in oxidised form exhibit site activities approaching those of noble metals [3]. For example, exsolved nickel (Ni) nanoparticles can exhibit nominal turnover frequencies (nTOF, number of CO molecules converted to CO₂ per second, per exposed metal atom site) of the order of hundreds s⁻¹. This is orders of magnitude higher than the values typically reported for base metal/metal oxide nanoparticles in literature and approaching values observed for noble metals. This unusually high catalytic activity, along with high resistance to carbon deposition, has been assigned to the confined nature of exsolved nanoparticles which are socketed within the perovskite oxide support [3].

The catalytic activity of perovskite materials decorated with exsolved nanoparticles can be even further improved when two or more types of metallic particles exsolve from the structure and form metallic alloys or intermetallics on the surface. As compared to the monometallic Ni nanoparticles, the Fe-Ni alloy nanoparticles exhibit a higher amount of active sites, greatly improved durability over long-term testing and increased tolerance towards sulfur-based atmospheres [3]. Simultaneously, these bimetallic alloys demonstrate outstanding microstructural stability and high tolerance towards coking, similar to that presented by monometallic Ni nanoparticles [3].

The aim of this work is to examine the possibility of exsolving various types of metallic or bimetallic nanoparticles from perovskite-structure compounds and further to determine their influence on the catalytic activity of these materials for various electrochemical applications. For this purpose a set of strontium titanate-based compounds of general formula (La_{0.3}Sr_{0.6}Ce_{0.1})_{0.9}Me_{0.1}Ti_{0.9}O_{3-δ}, where Me are e.g. Ni, Fe, Co or Cu were investigated. Moreover, the compounds with two types of metallic dopants (e.g. Ni-Fe, Ni-Co etc.) were examined. The structure and microstructure were analysed by the XRD, SEM, EDX and TEM techniques. XPS helped to determine the amount of metallic ions that have been transferred into Me⁰ state, and XAS allowed us to examine the possibility of an alloy or intermetallic formation. The TPD and CO chemisorption determined the active surface of exsolved nanoparticles. Finally, the catalytic and electrocatalytic activity was determined either in the catalytic reactor or directly in the operating Solid Oxide Fuel Cell/Solid Oxide Electrolysis Cell combined with a direct system for measuring the outlet gas composition (FTIR/GC).

Based on these tests a systematic description of the exsolution process in perovskite-structure compounds and its influence on material properties, particularly the electro-catalytic activity, will be given.

Literature:

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EF19.17

Novel Ni/YSZ Electrode for SOCs Prepared Using the NaCl/CTAB-Assisted Route Patryk Błaszczak¹, Agata Ducka¹, Sea-Fue Wang², Grzegorz Machowski³, Marta Przesniak-Welenc¹, Beata M. Bochentyn¹ and Piotr Jasinski⁴; ¹Politechnika Gdanska, Poland; ²National Taipei University of Technology, Taiwan; ³AGH University of Science and Technology, Poland; ⁴Gdansk University of Technology, Poland

In recent times, not only the application of novel materials into electrodes of Solid Oxide Cells (SOCs) is of primal importance, but the studies on proper synthesis and development of the state-of-the-art materials are reaching a significant scientific value. The wide palette of the anode functions such as fuel gas diffusion, efficient fuel oxidation, electrical conductivity, and transport of the byproduct mass out of reaction sites introduces an even wider number of requirements to be fulfilled. Despite outstanding progress in the field alternative cermet composites and Mixed Ionic-Electronic Conductors for SOCs, a mixture of Ni and YSZ is still recognized as the most useful material for the construction of the electrodes. It is due to high catalytic activity, high ionic and electronic conductivity, stability, matching technological properties with a YSZ electrolyte, and relatively low price.

Ohmic and polarization losses are, generally speaking, lowering the overall performance of the SOCs under working conditions. The starting microstructure and composition of the electrodes (e.g., grain sizes, porosity, addition of sintering inhibitors) will greatly affect the performance of the SOC devices and, if properly designed, can guarantee long-term stability and maximally enhance the efficiency. To reach higher output of the electrodes it is a known practice to induce smaller particle size of the ceramics, what leads to an increase in the length of the triple phase boundaries and in performance of the electrodes. However, recent studies show that nanostructures undergo faster degradation caused by grain coalescence and coarsening or phase changes. The migration of Ni particles through the porous YSZ backbone leads to breakage of electronic paths and decreases the number of active centres for performing half-reactions. This can possibly be mitigated by introduction of the sintering inhibitors or by proper control over the microstructure and Ni/YSZ dispersion in the composite.

In our study, a novel method of the preparation of the YSZ scaffold was introduced to obtain a tailored, highly porous structure with a homogenous distribution of the wormhole-like pores. The decrease in the size of the YSZ grains and the altered shape of the internal pores was meant to ensure a higher active surface area and a lower Ni agglomeration rate by containing the movement of the metal. The novel YSZ scaffold was prepared using the wet chemistry method with the assistance of a CTAB micelle forming agent. The as-prepared gel was left with the leftover side products – NaCl and organics. This resulted in the formation of highly porous structures reaching 50% total porosity after the high-temperature sintering step without the addition of external polymer/graphite poroforms. The powders were extremely easy to process via dry pressing, allowing one to obtain very thin substrates (400 μm). The samples were characterized using the XRD, SEM, TG-DSC, and Hg porosimetry techniques. The results were compared with the conventional YSZ from commercial cells. The novel structure of YSZ was impregnated with Ni for time-resolved high-temperature SEM imaging to determine the agglomeration rate/mechanisms of metal, and it was found that Ni is less prone to coalesce within wormhole-like pores compared to the macroscopic ones. Additional electrical measurements were performed on the Ni/YSZ samples to determine the conductivity and stability over time at 700 C in H₂ atmosphere. The composite material can be a very promising alternative to the standard cermet prepared using this novel technique due to high conductivity, high dispersion of the metal, developed triple phase boundary, and enhanced stability.

EF19.18

Pr₆O₁₁ Modified Ceramic Cathode for CO₂ Electrocatalytic Reduction in Solid Oxide Electrolysis Cell Wanhua Wang, Haixia Li, Ka-Young Park, Taehee Lee and Fanglin (Frank) Chen; University of South Carolina, United States

Electrochemical CO₂ reduction reaction (CO₂RR) using solid oxide electrolysis cell is a potentially effective approach to achieve CO₂ conversion and intermittent renewable electricity storage simultaneously, which has attracted increasing attention in recent years. However, the lack of highly active and stable cathode catalysts impedes the development of CO₂ electrolysis in SOEC for practical applications. Herein, the Pr₆O₁₁ nanoparticles infiltrated Sr_{1.9}Fe_{1.3}Mo_{0.5}O_{6-δ} (SFM) electrode was studied systematically. When the Pr₆O₁₁ infiltration amount reaches the optimal load, the electrochemical performance for pure CO₂ electrolysis has a significant improvement, which achieved 250% increase in current density at 1.5V and 800°C compared with the SFM electrode without infiltration. X-ray photoelectron spectroscopy characterization indicates the introduction of Pr₆O₁₁ will promote the formation of oxygen vacancy and active site in SFM/Pr₆O₁₁ composite electrode, thus greatly enhancing the adsorption and dissociation of CO₂. Temperature-programmed desorption of CO₂ measurement further illustrates this conclusion.

Acknowledgements

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EF19.19

Improved Sulfur Tolerance with A Site Substituted $\text{Sr}_2\text{Fe}_{1.4}\text{Ni}_{0.1}\text{Mo}_{0.5}\text{O}_{6-d}$ Anodes for SOFCs [Haixia Li](#), Wanhua Wang, Ka-Young Park, Taehee Lee and Fanglin (Frank) Chen; University of South Carolina, United States

$\text{La}_{0.1}\text{Sr}_{1.9}\text{Fe}_{1.4}\text{Ni}_{0.1}\text{Mo}_{0.5}\text{O}_{6-d}$ (LSFNM) and $\text{Pr}_{0.1}\text{Sr}_{1.9}\text{Fe}_{1.4}\text{Ni}_{0.1}\text{Mo}_{0.5}\text{O}_{6-d}$ (PSFNM) materials have been synthesized by a sol-gel method in air and investigated as anode for intermediate temperature solid oxide fuel cells. Metallic nanoparticle-decorated ceramic anodes were prepared by in situ reduction of the LSFNM and PSFNM anode in H_2 at 850 °C. The electrochemical performance of $\text{Sr}_2\text{Fe}_{1.4}\text{Ni}_{0.1}\text{Mo}_{0.5}\text{O}_{6-d}$ (SFNM) ceramic anode is greatly enhanced by A site La doping due to ~50% decrease in the polarization resistance. The maximum power densities of the LSGM (300mm) electrolyte supported single cells with LSFNM as the anode reached 1.37 and 1.26 W cm^{-2} in wet H_2 and H_2 -50ppm H_2S at 850 °C, respectively. Meanwhile, PSFNM shows the improved sulfur tolerance, which can be fully recovered after 6 cycles in operation with H_2 and H_2 -50ppm H_2S at 750 °C.

Acknowledgements:

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EF19.20

Solid Oxide Electrolyzer with Novel Electrode containing *In Situ* Exsolved Nanoparticles for Direct CO_2 to CO Conversion [Ka-Young Park](#), Taehee Lee, Wanhua Wang, Haixia Li and Fanglin (Frank) Chen; University of South Carolina, United States

Unpredictable climate changes due to global warming are continuously threatening human life. Carbon dioxide (CO_2) emissions are one of the critical sources, contributing to the greenhouse effect, and have been increased very fast since the industrial revolution. To mitigate this risk, many efforts have been devoted to develop technologies to convert CO_2 into valuable chemicals such as carbon monoxide (CO), methane, methanol, and dimethyl ether by using surplus energy from sustainable, renewable, and alternative energy sources while lowering the dependence on fossil fuels. Currently, CO_2 conversion can be converted through thermocatalytic, electrochemical, and photochemical reactions. However, CO_2 conversion to useful chemicals would be not simple due to its remarkably strong C=O bonding. The electrochemical reaction has a greater possibility than the other reactions. The electrochemical reaction is controllable and can utilize surplus energy of the alternative energy sources for CO_2 conversion, potentially achieving a carbon-neutral energy cycle.

In this work, a novel perovskite has been developed by introducing active nanoparticles via an *in-situ* exsolution process, which showed high performance for the conversion of CO_2 to CO. Its electrical conductivity and chemical stability in operating conditions for CO_2 electrolysis have been systematically evaluated.

Acknowledgements: Financial support from the U.S. Department of Energy (DE-EE0009427) and NASA EPSCoR (Grant # 80NSSC20M0233) is greatly appreciated.

SESSION EF20: Oxygen-Ion Conducting Fuel Cells IV

Session Chair: Ho-Il Ji

Friday Morning, July 22, 2022

Lobby Level, Avenue 34, Studio 1

9:10 AM EF20.01

Tungsten Doped $\text{Sr}_2\text{Fe}_{2-x}\text{W}_x\text{O}_{6-\delta}$ Electrode Materials with *In Situ* Exsolved Nanoparticles for Significantly Boosting the Performance of Symmetrical SOFCs [Kun Zheng](#)^{1,2}, Jakub Lach¹ and Konrad Swierczek^{1,2}; ¹Akademia Gorniczko-Hutnicza imienia Stanislawia Staszica w Krakowie Wydział Energetyki i Paliw, Poland; ²AGH University of Science and Technology, AGH Centre of Energy, Poland

The energy generation by combustion of fossil fuels (such as: coal, oil and the derivatives) brings many severe environmental problems and the depletion of these traditional fuels urgently requires the development of new alternative clean and green energy. Solid Oxide Fuel Cell (SOFC) is among the most promising technologies for both electrical power generation from renewable and traditional energy sources, and clean, efficient fuel production (in reverse mode/electrolysis). The symmetrical SOFC fuel cell design with identical electrode material simultaneously applied in both anode and cathode, is very promising, due to attractive advantages including: the reduced number of cell components, a considerable simplification of the manufacturing process and reducing the problems associated with the chemical stability of materials. This in consequence will either reduce production costs and ensure a stable, long-term operation of symmetrical SOFCs. Another one of the most important advantages associated with the application of symmetrical SOFCs is the possibility to address problems related to the carbon deposition and sulfur poisoning by simply reversing the gas flows to oxidize the deposited products for SOFC cells fueled by cheap and available non-hydrogen fuels. In addition, symmetrical SOFC systems facilitate the reversible operation of cells, which can produce/consume a wide variety of fuels including hydrocarbons supplied in existing infrastructure - not only hydrogen, unlike most other types of reversible fuel cells. However, the electrode material candidates for symmetrical SOFCs are rather limited due to the strict criteria. Redox stable materials with high mixed ionic-electronic conductivity and excellent electro-catalytic activities in both oxidizing and reducing conditions are required for such devices. The approach of *in situ* exsolution of nanoparticles have been successfully applied to boost the the anode performance of SOFCs. In the reducing operation condition of SOFC anode, metallic nanoparticles *in situ* exsolved from the parent materials decorating on the surface of the electrode, which considerably increases the catalytic activity and electronic conductivity of anode.

In this study, Fe and W contained $\text{Sr}_2\text{Fe}_{2-x}\text{W}_x\text{O}_{6-\delta}$ perovskites ($x = 0.1$ to 1.0) were successfully obtained, and the doping level of W in $\text{Sr}_2\text{Fe}_{2-x}\text{W}_x\text{O}_{6-\delta}$ perovskites was investigated which is limited to $x = 1.0$. The substitution of W in $\text{Sr}_2\text{Fe}_{2-x}\text{W}_x\text{O}_{6-\delta}$ oxides significantly affect the crystal structure and synthesis conditions of materials. For instance, B-site rock salt-type ordered double perovskite $\text{Sr}_2\text{FeWO}_{6-\delta}$ with $P2_1/n$ space group can only be synthesized in reducing condition, while simple perovskite $\text{Sr}_2\text{Fe}_{1.9}\text{W}_{0.1}\text{O}_{6-\delta}$ with $Pm-3m$ space group can be easily obtained in air. In this work, the synthesized single-phase $\text{Sr}_2\text{Fe}_{2-x}\text{W}_x\text{O}_{6-\delta}$ oxides have been systematically investigated as redox-stable electrode materials with the ability of *in situ* exsolution of nanoparticles for boosting the performance of symmetrical SOFCs. Phase composition, crystal structure, oxygen content, transport properties, chemical stability in relation to electrolyte and chemical stability of proposed materials under reducing/oxidizing atmospheres were studied. The *in situ* exsolution and dissolution of nanoparticles have been investigated in $\text{Sr}_2\text{Fe}_{2-x}\text{W}_x\text{O}_{6-\delta}$ oxides. $\text{Sr}_2\text{Fe}_{2-x}\text{W}_x\text{O}_{6-\delta}$ compounds are compatible with classical electrolytes (8YSZ , $\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{3-d}$ and $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9}$). Among all the studied materials, $\text{Sr}_2\text{Fe}_{1.8}\text{W}_{0.2}\text{O}_{6-\delta}$ -based symmetrical cell shows the lowest stable electrode polarization with $R_p = 0.06 \Omega \text{ cm}^2$ at 800 °C over 100 h in air, while $\text{Sr}_2\text{Fe}_{1.6}\text{W}_{0.4}\text{O}_{6-\delta}$ -based symmetrical cell has the best result in reducing condition (5 vol.% H_2 in argon) with $R_p = 0.5 \Omega \text{ cm}^2$ at 800 °C over 100 h. Excellent electrochemical performance was recorded for the constructed quasi-symmetrical

SOFCs with the above selected electrode materials.

9:25 AM EF20.02

Systematical Study of Controlled Exsolution via Phase Transition and Its Application on Solid Oxide Fuel Cell [Chaesung Lim](#) and Jeong Woo Han; Pohang University of Science and Technology, Korea (the Republic of)

The stability is an important issue of the conventional loaded NPs because its main applications (SOFC fuel electrode, and catalysts for gas reforming reaction) require high reaction temperature. Especially for hydrocarbon fuel based SOFC, carbon coking and sintering of metal NPs are the representative examples of SOFC performance degradation. In this respect, exsolution can be an alternative strategy for fabricating well dispersed metal NP instead of conventional loading method. Exsolution is the phenomenon of in-situ growth of metal NPs from B-cation of perovskite matrix in reduction condition. Since the exsolved NPs are strongly confined to the surface of the support, they have stronger resistance on sintering and carbon coking than conventional loaded NPs [*Nat. Commun.*, 6, 8120 (2015)]. Also, in the SOFC application, when exsolved NPs were applied to the fuel electrode, the cell performance was improved than conventional perovskite based SOFC without the exsolved NPs [*Nat. Commun.*, 8, 15967 (2017)]. However, compared with the conventional loaded NP, it is difficult to accurately control the exsolved NPs because exsolution uses metal cations inside the perovskite support, not from external metal source. Therefore, for developing the best SOFC, the systematical studies are required to find the optimized condition of exsolution such as particle size, particle density, and the combination of metal and support.

Herein, we used phase transition to control exsolution for SOFC. When exsolution occurred via phase transition of perovskite (ABO_3) to Ruddlesden-Popper perovskite (R-P, A_2BO_4), it is expected that exsolution can be enhanced by the discarded B-metal during phase transition. To find the condition for phase transition to R-P, we proposed that selectively spontaneous reduction in BO_2 layer is an essential condition for the phase transition to R-P. In our DFT study, we found that the reduction in BO_2 layer was promoted by Sr dopant, and selective reduction in BO_2 layer without surface decomposition was only possible for $Pr_{0.5}Sr_{0.5}MnO_3$ (PSMO) and $Pr_{0.5}Sr_{0.5}FeO_3$ (PSFO) among $Pr_{0.5}(Ba/Sr)_{0.5}MO_3$ perovskites (M: transition metal) [*Nat. Commun.*, 12, 6814 (2021)]. In in-situ XRD measurement, we showed that the complete phase transition of PSFO and verified that the exsolution and the phase transition of $Pr_{0.5}Ba_{0.5}FeO_3$ (PBFO) to R-P can be promoted by Sr doping, as predicted in our DFT study.

Using the controlled phase transition, we fabricated the exsolved NPs with various particle size and particle density. For the rational design of fuel electrode, we performed the mechanism study of hydrogen oxidation reaction (HOR) on the exsolved NP models by DFT calculation and found the HOR activity is dependent on the particle size of the exsolved NPs. Finally, we found the optimized condition of the exsolved NPs for the fuel electrode application. The optimized SOFC showed much higher stability and comparable cell performance than the state-of-art SOFCs. These results may guide further development of a highly stable and active fuel electrode for high performance SOFC.

9:40 AM EF20.03

Exsolution of Single Metals and Alloys for Tailored Adsorption/Desorption of Ammonia and Its Conversion in Hydrogen for Working Solid Oxide Fuel Cells [Jonathan Cavazzani](#)¹ and Antonella Glisenti^{1,2}; ¹Università degli Studi di Padova, Italy; ²Istituto di Chimica della Materia Condensata e di Tecnologie per l'Energia Consiglio Nazionale delle Ricerche, Italy

To counter the actual environmental crisis hydrogen represents the most charming route to promote a large-scale de-carbonization process. Simultaneously, high efficiency devices must be developed and Solid Oxide Fuel Cells exhibits important features to play this role. Nowadays, hydrogen storage is the major of the bottlenecks to increase this technology on the market. Ammonia may be a suitable hydrogen vector because of the well-established plants for its production and distribution, it is a carbon-free chemical and has narrower flammability range compared to hydrogen and hydrocarbons [1]. However, the realization of *ad hoc* materials and devices for running SOFCs with this fuel must be planned.

Supported nanoparticles systems have been receiving increased attention because of their versatility and potential for reaching advanced performance in a wide range of applications such as chemical conversion, photochemistry and electrochemistry. Exsolution of single metal/alloy nanoparticles is an emerging method to counter the main issues typical of nanomaterials, such as poisoning by chemicals or coalescence due to high temperature, thanks to a strong interaction with the support. Recently, it has been demonstrated that the specific reduction conditions strongly influence the shape of exsolved nanoparticles paving the way to the possibility to tailor the activity for the appropriate applications [2,3].

Hereby, the aim of the work is to investigate how the synthesis conditions permit to enhance the activity of the materials towards small strategic molecules, such as ammonia decomposition and hydrogen oxidation. The idea is to fully understand the effect of nanoparticle shape and distribution on their catalytic and electrocatalytic activation. Samples were prepared via wet chemistry using citric acid route and then treated under different atmosphere. Prepared nanocomposites were firstly characterized from a structural and morphological point of view: X-Ray Diffraction (XRD) measurements suggest that metal precursors cations were embedded with success in the perovskite crystal lattice. Scanning Electron Microscopy (SEM) images allow to monitor the formation of highly dispersed nanoparticles on the surface. The effect of exsolved metal cluster on the surface basicity was determined by Temperature Programmed Desorption of carbon dioxide (CO_2 -TPD) in order to analyse the abundance of basic sites which would help the N-H cracking. In addition, adsorption/desorption processes were also studied with the goal to correlate them with single metal/alloy nanoparticles obtained in different synthesis conditions.

Far over, we obtained preliminary but interesting results. Starting from $SrTiO_3$ the effect of the amount of doping Ni on the shape, size, preferred exposed faced of the exsolved metal nanoclusters has been evaluated under different reducing conditions. To boost electronic conductivity and catalytic activity also the possibility of double doping in the B-site (and double exsolution) has been considered focusing on the couple NiMn and NiFe. The work is still under development and investigation, we believe important benefits to this research can be brought using *in-situ* Transmission Electron Microscopy (TEM) and X-Ray Photoelectron Spectroscopy (XPS) in order to monitor the evolution of the metal/alloy nanoparticles, their composition and the parameters which promote, first, the NH_3 adsorption/desorption processes and then the conversion for the production of hydrogen.

Our results underline that exsolution allows to optimize nanocomposites metal/oxide not easy obtainable with different strategies; the properties of these nanocomposites can boost performance in catalysis and electrocatalysis

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9:55 AM EF20.05

Low Temperature Surface Composition of LSM and Its Impact on the Oxygen Reduction Mechanism of ESB/LSM Composite Electrodes [Victor Duffort](#)^{1,2}, [Martin Pajot](#)^{1,3}, [Soukaina Mountadir](#)^{1,2}, [Anne-Sophie Mamede](#)^{1,4} and [Rose-Noëlle Vannier](#)^{1,4}; ¹Unité de Catalyse et Chimie du Solide, France; ²Centre National de la Recherche Scientifique, France; ³Université de Lille, France; ⁴Ecole Centrale de Lille, France

High temperature solid oxide fuel cells (HT-SOFC) typically use a $La_{0.8}Sr_{0.2}MnO_3$ (LSM)/ $Zr_{1.84}Y_{0.16}O_{3.92}$ (YSZ) composite cathode on a YSZ electrolyte and a nickel/YSZ cermet anode. Because of the moderate conductivity of the electrolyte material, high temperatures (> 700 °C) are required in order to achieve sufficient ionic conduction. Nevertheless, elevated temperatures come with significant engineering challenges, motivating the long-standing effort

to decrease the operation temperature of SOFC. The use of more conductive materials such as erbium stabilized bismuth oxide (ESB) or gadolinium doped ceria (GDC) is usually hampered by stability or electronic leakage issues. However, combining these two materials into a bi-layered electrolyte to bypass the shortcomings of each composition has been shown to be one of the most promising strategies to significantly reduce the operating temperatures.¹

In the specific case of LSM composite cathodes, substituting YSZ by erbium stabilized bismuth oxide (ESB) in the cathodic compartment and gadolinium doped ceria (GDC) at the anode, allows for a significant improvement leading to a specific power density of $\sim 1 \text{ W cm}^{-2}$ at $650 \text{ }^\circ\text{C}$.² Based on these results, several groups optimized the microstructure or preparation of the cathode without changing the composition of the LSM.³ However, this stoichiometry was optimized for high temperature compatibility with YSZ and needed to be optimized for lower temperature.

In this presentation, we will focus on the influence of the strontium content in $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ on the area specific resistance (ASR) of composite LSM/ESB electrodes. Several compositions ($x = 0.15, 0.3, 0.4, 0.5, 0.6, 0.8$) were tested to investigate the influence of the structure, the electronic transport mechanism or the $\text{Mn}^{3+/4+}$ ratio. Differently from the well-known high temperature behavior, where surface segregation of SrO is the main deactivation process, at lower temperature it is the surface oxidation that inhibits the oxygen reduction efficiency of LSM. As demonstrated by our structural investigations, thermogravimetric analysis and Low Energy Ion Scattering spectroscopy (LEIS), this oxidation driven by the low temperature reactivity of Mn^{3+} with oxygen, results in the formation of cationic vacancies effectively reducing the density of active site. The catalytic activity of the cathodes was evaluated by Electrochemical Impedance Spectroscopy (EIS) on symmetric cells using an ESB electrolyte. The limitation of the surface oxidation through the increase of the strontium content resulted in a 2-fold decrease of the ASR at $500 \text{ }^\circ\text{C}$ when switching from $\text{La}_{0.85}\text{Sr}_{0.15}\text{MnO}_3$, *i.e.* the high temperature optimized stoichiometry, to $\text{La}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$.⁴

Acknowledgements

The Fonds Européen de Développement Régional (FEDER), CNRS, Région Hauts de France, Ministère de l'Enseignement Supérieur et de la Recherche and Agence Nationale de la Recherche and BIBELOT ANR-18-CE05-0001 are acknowledged for funding.

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10:10 AM EF20.07

Application of Cu-Rich Perovskites for Solid Oxide Cells Operating at Lowered Temperatures Keyun Li¹, Anna Niemczyk², Konrad Swierczek¹, Piotr Winiarz¹, Kun Zheng¹, Yevgeniy Naumovich², Jakub Kupecki², Anna Stepień¹ and Bogdan Dabrowski³; ¹Akademia Gornicza-Hutnicza imienia Stanisława Staszica w Krakowie Wydział Energetyki i Paliw, Poland; ²Instytut Energetyki, Poland; ³Polska Akademia Nauk, Poland

Solid Oxide Cells, which can effectively function in the fuel cell and electrolyzer operating modes, seem as especially attractive for application in the distributed power generation. Since the electrochemical reactions taking place at the electrodes are supposed to be reversible, the designing of the effectively working fuel and oxygen electrode materials is not an easy task. Furthermore, the desired reduction of the operating temperatures to the intermediate temperature range of $600\text{--}800 \text{ }^\circ\text{C}$ requires the candidate materials to possess a series of specific features, involving good structural and thermal stability, high electrocatalytic activity, and high mixed ionic-electronic conductivity. Nowadays, oxygen electrode (cathode) materials have been mainly studied and developed based on the Co-based perovskite-type oxides, which indeed have demonstrated excellent performance. Nevertheless, due to the environmental issues, toxicity and high costs, there is a necessity to introduce another *3d* metal element that can take the role of Co. While doping with a high amount of Fe, Mn or Ni has been shown as successful, there are less literature works mentioning about introduction of Cu. However, the recently published data provide evidence that high Cu-content perovskite-type (or related) electrodes can also work effectively.

In this work, comprehensive evaluation of the development of the Cu-rich oxygen electrode compounds is presented, focused on the selected $\text{RE}_{1-x}\text{A}_x\text{CuO}_{3-\delta}$ and $\text{RE}_{1-x}\text{A}_x\text{Cu}_{1-y}\text{TM}_y\text{O}_{3-\delta}$ (RE: selected rare-earth elements, A: selected alkaline-earth metals) perovskite-type oxides. Cation sublattice-ordered (so called double and triple perovskites), as well as disordered materials were studied. Physicochemical properties, including phase composition and crystal structure, thermal expansion, oxygen content, electrical conductivity and catalytic activity, were measured by the X-ray diffraction, dilatometry, iodometric titration, thermogravimetry, and 4-probe electrical conductivity methods, respectively. Screen-printing technique was used for the preparation of the oxygen electrode layers. The polarization resistance was evaluated in symmetrical cells. Button-type full cells were constructed using thin $\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{3-\delta}$ electrolyte, $\text{RE}_{1-x}\text{A}_x\text{TM}_{1-y}\text{Cu}_y\text{O}_{3-\delta}$, and Ni-Ce_{0.8}Gd_{0.2}O₂ cermet anode.

Comparison of the electrochemical results for the A-site cation-ordered $\text{La}_4\text{BaCu}_5\text{O}_{13+\delta}$, which also shows the oxygen vacancy ordering, with the partially cation-disordered $\text{La}_{1.5}\text{Ba}_{1.5}\text{Cu}_3\text{O}_{7+\delta}$ showing the oxygen sublattice disorder at structural sites clearly indicates favorable transport and electrocatalytic properties in the latter case. Low electrode polarization resistance values were obtained for $\text{La}_{1.5}\text{Ba}_{1.5}\text{Cu}_3\text{O}_{7+\delta}$, below $0.1 \text{ } \Omega \text{ cm}^2$ at $650 \text{ }^\circ\text{C}$, which enabled to achieve power density outputs exceeding 250 mW cm^{-2} at the same temperature. However, the observed reactivity with ceria-based solid electrolytes (often used for preparation of the buffer layers) will require to modify the practical cell design to avoid interaction with the contemporary Zr-based electrolytes. In another approach, $\text{GdBa}_{0.5}\text{Sr}_{0.5}\text{Cu}_{2-y}\text{Co}_y\text{O}_{5+\delta}$ series of double perovskites was evaluated, and showed favorable characteristics. It was found that copper allows to decrease the thermal expansion, while the oxides show suitable stability at high temperatures, as well as very high mixed electrical conductivity. Importantly, it seems that reactivity with ceria-based electrolytes could be mitigated in this case. The materials with ca. 1:1 Cu to Co composition exhibited favourable electrochemical characteristics at temperatures on the order of $800 \text{ }^\circ\text{C}$, with the electrode polarization resistance below $0.05 \text{ } \Omega \text{ cm}^2$. The results clearly indicate that if appropriately designed, the copper-based or Cu-rich perovskite-type oxides show suitable set of physicochemical properties and electrocatalytic activity, making them attractive for the preparation of the effectively-working oxygen electrodes.

10:25 AM EF20.08

Comparison of New Designed Materials as Fuel Electrode for Solid Oxide Cells Applications Simone Tomadini¹, Enrico Squizzato¹, Giovanni Carollo¹ and Antonella Glisenti^{1,2}; ¹Università degli Studi di Padova, Italy; ²CNR-ICMATE, Italy

While the energy consumption and the emission of pollutants are continuously increasing, following the fast development of new technologies and of the global economy, the energy supply is still vastly bound to fossil fuels. Green alternatives are starting to be widespread¹, but a significant contribution could be given by fuel cells. These electrochemical devices convert chemical energy into electrical power with greater efficiency and lower emission of greenhouse gases than well-established technologies based on traditional fossil fuel combustion. Moreover, water is the only by-product when hydrogen is supplied as fuel. In this contribution we focus on the Solid Oxides Fuel cells, characterized by the presence of a solid electrolyte, high working temperatures and the possibility to avoid noble metals as catalysts in the anode and cathode sites. As an alternative to the most used perovskites-based material, such as Sr doped LaMnO_3 (LSM), two new Ruddlesden-Popper phase materials will be herein presented: $\text{La}_{1.2}\text{Sr}_{0.8}\text{Fe}_{0.6}\text{Mn}_{0.4}\text{O}_4$ (RP-LSFM) and $\text{LaSr}_2\text{CrMnO}_7$ (RP-LSCM). These materials are characterized by blocks of perovskite alternated by layers of rock salt phase ($\text{A}_{n+1}\text{B}_n\text{O}_{3n+1}$). Over the standard perovskites this new phase possesses a better ionic conductivity and mobility, making it suitable for SOFC applications. The scope of this study is a preliminary evaluation of their possible use as anodes in SOFCs. Both materials have been synthesized following the so called citrate route²: stoichiometric quantities of La_2O_3 , SrCO_3 , $\text{C}_4\text{H}_6\text{MnO}_4 \cdot 4\text{H}_2\text{O}$ and Fe (or $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, to obtain the second material) were dissolved in deionized water

with nitric acid. Citric acid is added as complexing agent under stirring and then the solution is lead to neutral pH by dropwise addition of ammonia hydroxide. At pH 7 the stirring was stopped, and the solution was heated to eliminate water and to induce the formation of a gel phase. The gel was heated to 400°C, to obtain the powders that were subsequently calcinated at 1150°C for 6 hours. The calcination has been carried out in three atmospheres (hydrogen, argon and air) to test the behaviour of the materials under different synthesis conditions. Both materials have been characterized by XRD, showing the achievement of the target phase in all the atmospheres but showcasing higher purity when hydrogen was used. Reproducibility was also tested. XPS and EDX characterization have been carried out to test the composition. Concerning RP-LSCM, La and Sr surface segregation has been found, the latter depending on the calcination atmosphere: going from oxidizing to reducing environment Sr segregation decreases significantly. In the bulk, La quantity is higher than the nominal composition at the expenses of Cr and Mn. This behaviour is not atmosphere-dependant suggesting that structural defect may contribute. Concerning RP-LSFM, surface segregation of La and Mn is observed when the stoichiometry of the bulk agrees with the expected values. Both the samples have a low surface area (less than 10 m²g⁻¹) as mentioned in literature. To test reducibility, a H₂-TPR analysis has been carried out showcasing, moreover, the presence of impurities dependent of the atmosphere of calcination, as well as some impurities always present as a γ -FeMnO₃ sub-phase for the RP-LSFM. Electrochemical Impedance Spectroscopy analysis has been performed, leading to the understanding of the processes involved for both materials. The preliminary results are promising: at 800°C, (10% H₂) in a single chamber setup (RP-LSFM/LSGM/RP-LSFM and RP-LSCM/LSGM/RP-LSCM) the ASR for the RP-LSFM resulted of 4.35 Ω cm² while the one of the RP-LSCM was 13.92 Ω cm².

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10:40 AM BREAK

11:00 AM EF20.09

Accelerated Degradation of SOFC Anode Under High Siloxane Concentrations Jiashen Tian, Derall M. Riley and Ryan J. Milcarek; Arizona State University Ira A Fulton Schools of Engineering, United States

Biogas as a renewable fuel can be utilized for heat and electricity generation in wastewater treatment plants and landfills. However, the impurities such as siloxanes present in biogas following the digestion process damage the biogas utilization devices especially the prime movers in the system. The solid oxide fuel cell (SOFC) is considered an environmentally friendly and high efficiency prime mover, but is extremely vulnerable to siloxane contamination. Even ppm level siloxanes can cause obvious SOFC performance degradation. Due to low concentration of siloxanes in biogas, most studies about the SOFC degradation under siloxane contamination only contained ppm level concentrations. The degradation rates corresponding to these low concentration studies are around 30%-50% performance loss per 1000 hours. In this case, even with hundreds of hours operation time, the investigations of degradation were only stop at the initial step of entire SOFC failure process. In order to investigate the whole process of SOFC degradation due to siloxanes contamination, the anode supported solid oxide fuel cell with nickel-yttria stabilized zirconia (Ni-YSZ) anode was tested with 0.5% decamethyltetrasiloxane (L4) contamination at 800 °C to accelerate the whole degradation process. The SOFC failure was analyzed with multiple techniques such as scanning electron microscopy (SEM) and wavelength-dispersive X-Ray spectroscopy (WDX) which can illustrate the morphology and elements distribution after L4 deposition. The failure process of SOFC was also analyzed by electrochemical impedance spectroscopy (EIS) as electrochemical characterization method. The gas chromatograph (GC) was utilized for exhaust gas detection with L4 deposition process to determine the gas products. After analyzing results comprehensively, the obstruction of diffusion process of anode by the silicon and carbon depositions is considered as the main reason for the failure of the SOFC. The re-oxidation of anode can also be noticed due to surface layer coverage. Methane formation was confirmed in the exhaust after the deposition process which provides validation for a previously reported mechanism of siloxane contamination.

11:15 AM EF20.10

Electrochemical Performance of YSZ Electrolyte Recycled from Solid Oxide Electrolyzers or Fuel Cells Waste Materials Gudaysew T. Yenesew, Eric Quarez, Annie Le Gal La Salle, Clement Nicollet and Olivier Joubert; Universite de Nantes, France

Due to increasing energy demand and climate change concerns, decarbonized hydrogen production is expected to play a key role in the transition to a sustainable, fossil-free economy. However, high demand for carbon free hydrogen requires large size Solid Oxide Electrolyzers (SOEs) and investment is highly ongoing for electrolyzers manufacturing. Which in turn have economic, environmental and legislative problems of end of life products. Mitigation of those challenges and supporting circular economy is highly important. Here, for the first time, we are exploring a strategy of recycling and recovering component materials from waste materials of SOCs. First, protocol is developed to separate and recover materials from waste commercial solid oxide cells. Second, recovered materials are characterized with regards to their purity, structural and electrochemical properties.

The recovered NiO and LSC are characterized and gives excellent properties in regards to the thermal properties, phase purities, particle size, composition purity and in regards to catalytic properties.

The ionic conductivity and detail characterizations of electrolyte materials made from recycled YSZ is done. Combining X-Ray diffraction and SEM, the recovered YSZ composition from industrial SOCs was analysed as 4YSZ, a mixture of tetragonal, cubic and monoclinic phases. Different pellets have been obtained by varying the temperature and the duration of the sintering heat treatment. The average particle size is measured by LASER diffraction technique and the average particle size of recovered YSZ is comparable with commercial 8YSZ (Tosoh). SEM imaging shows the well crystalline, dense structure separated by visible grain boundaries. Electrochemical Impedance Spectroscopy studies allows extracting the ionic conductivity of pellets from 250°C to 750°C in air. Recovered YSZ (4YSZ) has total conductivity of 1.02x10⁻²S cm⁻¹ at 750°C. The low yttrium content is increased to different yttrium composition to improve the total conductivity. A total electrolyte conductivity of recovered YSZ (4YSZ) modified to 10YSZ shows an improved value of 1.30 x 10⁻² S cm⁻¹ at 750 °C. At lower temperature, the contributions of grain and grain boundary conductivity to the total conductivity are clearly differentiated. The bulk conductivity is higher than grain boundary conductivity. The presence of trace siliceous phase is observed by EDX and is assumed to be the major grain boundary-blocking barrier. Reducing the potential barrier of the grain boundary by removal of trace siliceous impurities and precursors scavenging of siliceous phases will be discussed.

Keywords: Ionic conductivity; Solid Oxide Cells; YSZ; bulk and grain boundary conductivity; Phase separation; Recycling wastes.

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11:30 AM EF20.11

Synthesis and Electrochemical Performance of A-Site Non-Stoichiometry Titanate Electrode in SOFCs Cairong Jiang, Yao Jiang and Jianjun Ma; Sichuan University of Science and Engineering, China

The anode materials of $\text{La}_x\text{Sr}_{1-x}\text{TiO}_3$ (LST) solid oxide fuel cell (SOFC) with potential substitution need to be further improved. $(\text{La}_x\text{Sr}_{1-x})_a\text{Ti}_{0.95}\text{Ni}_{0.05}\text{O}_3$ ($x = 0.1, 0.2, 0.3, 0.4, 0.82 \leq a \leq 1.00$) was synthesized by solid state reaction. The results show that A-site non-stoichiometry can reduce the phase forming temperature (1200 °C) of (La, Ni) co-doped SrTiO_3 solid oxide fuel cell (SOFC) anode material, improve the sintering activity of the material, and obtain dense body by sintering at 1400 °C in 5% H_2/Ar . The A-site non-stoichiometric LSTN has excellent conductivity. The highest conductivity is 331.75 S cm^{-1} in 5% H_2/Ar at 800 °C. The A-site non-stoichiometry improves the chemical compatibility of LSTN and ensures the stability of LSTN and YSZ electrolyte during co-sintering. It is proved that the quantity, size and distribution of B-site element nanoparticles can be controlled by changing the non-stoichiometric level of A-site.

11:45 AM EF20.12

Structure, Electrical Properties and Determination of Phase Stability Region of Mn-Cu-Fe Oxide System Justyna K. Ignaczak¹, Ming Chen², Sebastian Molin¹ and Piotr Jasinski¹; ¹Politechnika Gdanska, Poland; ²Danmarks Tekniske Universitet, Denmark

The recent development of Solid Oxide Cells (SOCs) technology allows lowering the operating temperature and use ferritic stainless steel (Cr_2O_3 -forming steel) for interconnects. Usage of alloys, in addition to many advantages, has several issues: cathode Cr-poisoning caused by evaporation of the volatile CrO_x compounds and low electrical conductivity which with time further decrease due to growing oxide scale on the surface of the material. Developing protective coating material with high electrical conductivity, low chromium diffusion, good matching in thermal expansion is right now one of the biggest challenges in developing SOFC and bringing it to the commercial market.

Currently, cobalt and manganese spinel oxide $(\text{MnCo})_3\text{O}_4$ coatings are the most commonly used coating materials. They show high conductivity at the operating temperature of the cells, effectively stopping the evaporation of chromium, but what should be noted is that cobalt is a carcinogenic element, mined in an unsustainable way and its price in recent years has increased significantly. The element that can replace cobalt is copper, an abundant and cheap element. $(\text{MnCu})_3\text{O}_4$ spinel is a suitable material for protective coating on the interconnects. It is reported that Mn-Cu oxide spinels have higher electrical conductivity at working temperatures (600- 900 °C) than MCO and can also prevent Cr-poisoning. The greater interest in MCO is due to a much wider range of phase stability than those containing copper.

In the presented study novel MnCu spinels, with the addition of iron, are described. According to the previously conducted research, adding Fe stabilizes the spinel structure and positively influences the sinterability of the materials. The study presents the results of the structural and electrical conductivity investigation of Mn-Cu-Fe spinels obtained by the modified Pechinni method.

The aim of the work was to investigate a wide range of stoichiometries of oxides containing Mn, Cu, and Fe and experimentally determine phase stability region and relationships between ratios of elements and properties of materials in terms of using them as a protective coating in SOFC.

Energy Storage

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* Invited Paper

SESSION ES01: Solid State Batteries I
Session Chair: Eric Wachsman
Monday Morning, July 18, 2022
Lobby Level, Avenue 34, The Loft

9:10 AM **ES01.01

The Stability and Kinetics of the Li/Solid Electrolyte Interface Jeff Sakamoto; University of Michigan, United States

Owing to the potential to achieve >1000 Wh/L and >400 Wh/kg while exhibiting a dramatic improvement in safety, Li-metal solid-state batteries (SSBs)

are promising technology to accelerate the widespread adoption of EVs. However, their remain gaps in knowledge in understanding the mechanical and electrochemical phenomena that control the stability and kinetics of the Li/solid electrolyte (SE) interface.

It is well known that Li (and Na) can penetrate ceramic and polymer solid electrolytes during charging. The term critical current density (CCD) is frequently used to determine the maximum charging rate before Li filaments penetrate. When normalized to a flat planar interface, CCDs during plating in literature range between 0.1 and 10 mA/cm². Indeed, there is a broad range CCDs upon charging, moreover the role of pore formation during stripping has shed light on the factors that contribute Li metal penetration. In addition, factors can affect CCD such as charge passed (0.01 to 3 mAh/cm²), temperature (25 to 200 °C), pressure (0 to tens of MPa), and Li thickness (0.1 to 750 microns).

In this presentation, the aspects that collectively contribute to determining the stability and kinetics of the Li/SE will be discussed. The discussion with shift the recent focus on Li penetration during charging to Li void formation at the interface during stripping in cells that use commercially relevant Li thickness (< 20 microns), "anode-free" or in-situ formed Li anodes, LLZO SE. The results of this work can help guide efforts develop Li metal SSB for use in EVs.

9:40 AM *ES01.02

Probing Transport and Chemo-Mechanics in All-Solid-State Batteries [Kelsey Hatzell](#); Princeton University, United States

Energy dense batteries are paramount for decarbonization of transportation and grid applications. Replacing traditional graphite anode materials with lithium metal may provide a pathway for increasing the energy density of a Lithium ion battery. However, lithium metal batteries suffer from consumptive side effects which limits its cycle life and rate performance. Recently, there has been renewed interest in using a solid electrolyte with lithium metal anodes. A solid electrolyte can act as a barrier for unwanted physical and chemical decomposition that leads to unstable electrodeposition (e.g. dendrite and filament growth). However, numerous experimental investigations have revealed that the strength of the separator, alone, does not suppress electrically shorting. Instead, the formation and growth of dendrites or filaments is tied to unique chemo-mechanical properties that exists at solid-solid interfaces. This talk intends to explore the role chemo-mechanics have on the two predominant failure modes in inorganic solid electrolytes: (1) filament formation, and (2) isolated plating. To probe these two degradation processes we explore a range of non-equilibrium x-ray characterization techniques which enable dynamic tracking of material transformation during in situ and operando working environments.

10:00 AM ES01.03

Interfacial Charge Accumulation in Li-Ion Conducting Solid Electrolytes. Theory and Experiments [Leon Katzenmeier](#)^{1,2}, [Manuel Gößwein](#)³ and [Aliaksandr S. Bandarenka](#)¹; ¹Technische Universität München, Germany; ²TUMint.Energy Research, Germany; ³Technische Universität München Fakultät für Elektrotechnik und Informationstechnik, Germany

All-Solid-State Batteries (ASSBs), employing a solid electrolyte (SE), are the most promising candidate for future battery applications. While a variety of models exist for the charge transfer characteristics of SEs, all models rely on a complete and accurate parameterization of the physico-chemical variables used. While easily accessible in liquid electrolytes, the simple question of charge carrier concentration remains unanswered for solid electrolytes in most cases. In a SE, three concentrations must be considered: the mobile Li concentration, the immobile Li concentration, and the vacancy concentration. These form the physical boundary for any accumulation and depletion of charged species, for example, found in space charge layers (SCLs).

In previous work[1], we analyzed the properties and formation of SCLs based on electrochemical impedance spectroscopy (EIS) data. Here, we adopt a theoretical approach for the charge transport characteristics in SE, a so-called modified Poisson-Nernst-Planck equation,[2] to predict the SCL capacitance based on a model including the vacancy and mobile Li concentrations. The charge carrier concentrations can be calculated based on the derived equation and experimental data. A kinetic Monte-Carlo model is developed to further calculate the spatial extend of the charge accumulation.

[1] Katzenmeier, L., Helmer, S., Braxmeier, S., Knobbe, E. & Bandarenka, A.S. Properties of the Space Charge Layers Formed in Li-Ion Conducting Glass Ceramics. *ACS Appl. Mater. Interfaces* **13**, 5853–5860 (2021).

[2] Becker Steinberger, K., Schardt, S., Horstmann, B. & Latz, A. Statics and Dynamics of Space-Charge-Layers in Polarized Inorganic Solid Electrolytes. Submitted to *Phys. Chem. Chem. Phys.* 1–19 (2021).

10:15 AM ES01.04

Evaluation of the Chemical Stability of Sulfide Solid Electrolytes with Lithium Metal Using *In Situ*, *Operando* and Post-Mortem Analyses [Marine Soler](#), Céline Barchasz, Vasily Tarnopolskiy and Frédéric Le Cras; Université Grenoble Alpes, France

The high demand for portable energy storage is driving the development of new, more efficient and safer portable energy storage systems. A lithium-sulfur battery is based on a lithium (Li) metal anode and an elemental sulfur cathode. It is a very promising system thanks to the very high theoretical energy density, while sulfur is also an inexpensive, abundant, non-critical and non-toxic raw material. On the other hand, lithium-sulfur batteries with conventional liquid electrolytes suffer from several problems preventing them from being commercialized today. The development of so-called "all-solid-state" lithium-sulfur batteries with the use of a highly conductive solid electrolyte (SE) could resolve some of these difficulties⁽¹⁾. In particular, solid sulfide electrolytes (SSEs) have received increasing interest in recent years due to their promising ionic conductivities around 10⁻²-10⁻³ S/cm⁽²⁾ and their ductility. However, while it solves some of the problems associated with liquid electrolytes, the all-solid-state system also presents a number of specific challenges.

One major challenge of the all-solid-state systems is the study and the control of the interfacial issues, in particular of the SSE/Li metal anode interface. Indeed, stability issues of the sulfide-based electrolytes with Li metal may be encountered, as being thermodynamically unstable against lithium metal, as well as the possible growth of lithium dendrites through the solid electrolyte separator^(3,4). Since both of these phenomena can severely impact the performance and safety of the battery (poor electrochemical stability of the SSE against Li metal leads to decomposition of the SSE thus increasing the impedance; growth of lithium dendrites leads to short-circuit of the battery), they must be understood and suppressed.

In this work, we study two sulfide electrolytes: argyrodite-type crystalline Li₆PS₄Cl and glass-ceramic Li₇P₃S₁₁. In order to assess and compare their stability against Li metal, Electrochemical Impedance Spectroscopy measurements were carried out over time on symmetric Li/SSE/Li cells. While the impedance is increasing constantly in the case of Li₇P₃S₁₁, it remains relatively stable for argyrodite-type SE. In addition, the nature and the morphology of the decomposition products of the two electrolytes in contact with Li metal have been characterized *post mortem* by XPS,ToF-SIMS and SEM analyses, as well as *in-situ* and *operando* using synchrotron radiation to perform X-Ray Diffraction Computed Tomography and Absorption Tomography. We demonstrate that in the case of argyrodite, the decomposition products limit the further reaction of electrolyte with Li metal, whereas they promote the propagation of the decomposition reaction for Li₇P₃S₁₁.

[1] Wang, HangChao, Xin Cao, Wen Liu, et Xiaoming Sun. 2019. « Research Progress of the Solid State Lithium-Sulfur Batteries ». *Frontiers in Energy*

Research 7: 112.

[2] Busche, Martin R. et al. 2016. « *In Situ* Monitoring of Fast Li-Ion Conductor $\text{Li}_7\text{P}_3\text{S}_{11}$ Crystallization Inside a Hot-Press Setup ». *Chemistry of Materials* 28(17): 6152-65.

[3] Wu, Bingbin et al. 2016. « Interfacial Behaviours between Lithium Ion Conductors and Electrode Materials in Various Battery Systems ». *Journal of Materials Chemistry A* 4(40): 15266-80.

[4] Yue, Junpei, Min Yan, Ya-Xia Yin, et Yu-Guo Guo. 2018. « Progress of the Interface Design in All-Solid-State Li-S Batteries ». *Advanced Functional Materials* 28(38): 1707533.

10:30 AM ES01.05

Understanding Interfacial Resistance and Capacity Behavior During All Ceramic-based Cathode Composite Formation—A Case of Li_2ZrO_3 Coated LiCoO_2 - $\text{Li}_{6.95}\text{Mg}_{0.15}\text{La}_{2.75}\text{Sr}_{0.25}\text{Zr}_2\text{O}_{12}$ Kunjoong Kim^{1,2}, Masaki Wadaguchi^{3,1}, Masato Iwasaki³, Hideaki Hikosaka³ and Jennifer Rupp^{1,2}; ¹Massachusetts Institute of Technology, United States; ²Technische Universität München Fakultät für Chemie, Germany; ³NGK Spark Plug Co. Ltd., Japan

Solid-state lithium metal battery has a huge potential to be a more energy-dense architecture, safety and fast charging capability relative to a current lithium-ion battery. In particular, the cell interface made of oxide-based electrolyte and cathode is believed to withstand more tightly than any other 'soft' solid electrolytes (polymer, sulfide electrolytes) once optimized. Sintering at high temperature is generally required to produce dense interfaces in oxide-based electrochemical devices; however, the poor interfacial compatibility of the oxide electrolyte with common active materials remain unresolved, limiting a wide range of material choice, processing and microstructure-performance relationship. Here, we present a low-temperature fabrication of a model oxide cathode composite, LiCoO_2 (LCO) as an active material and $\text{Li}_{6.95}\text{Mg}_{0.15}\text{La}_{2.75}\text{Sr}_{0.25}\text{Zr}_2\text{O}_{12}$ (LLZO) as a catholyte which the latter is formed by liquid precursor infiltration. To understand the performance with microstructure changes, the 35 micron-thick LCO with mass density of 6.5 mg cm^{-2} (0.9 mAh cm^{-2}) is prepared as a scaffold of active materials, then effect of the number of the catholyte infiltration and annealing cycle ($700\text{--}800 \text{ }^\circ\text{C}$) is observed. Additionally, we apply Li_2ZrO_3 (LZO) as a cathode coating between the cathode/electrolyte interfaces. The structural, compositional and electrochemical performance for the LCO-LLZO cathode composite with and without LZO coating are discussed toward unique opportunities for further optimization.

10:45 AM BREAK

11:00 AM **ES01.06

A Perspective on Solid-State Batteries with LLZO Marca Doeff; E O Lawrence Berkeley National Laboratory, United States

The potential safety and energy density advantages of all solid-state batteries utilizing ceramic electrolytes like LLZO ($\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$) have captured the imagination of the research community. The past decade has seen many advances in the use of this material, including reduction of the impedance at the lithium/LLZO interface and improved processing. In spite of this impressive progress, truly solid-state batteries utilizing LLZO are less far along than other solid-state configurations with, for example, polymer or sulfide-based electrolytes. We recently demonstrated a proof-of-principle cell operating at room temperature, using LLZO and a secondary electrolyte based on an organic ionic plastic crystal in a composite positive electrode. This obviates the need for co-sintering, simplifying fabrication, although many challenges remain. In this talk, we will cover our group's early work on LLZO, which originally focused on improving the sintering process and identifying and mitigating the cause of high interfacial impedance using synchrotron techniques such as ambient pressure XPS and XAS. We will then move on to discuss fabrication of cells with realistic form factors, and what still needs to be done to design robust, high energy devices with LLZO.

11:30 AM *ES01.07

Highly Cyclable Lithium Metal Battery Employing Modified Garnet Electrolyte Sewon Kim¹, Ju-Sik Kim¹, Lincoln Miara², Yan Wang², Seong Yong Park¹, Zhen Song³, Michael Badding³, Dongmin Im¹ and Kisuk Kang⁴; ¹Samsung Advanced Institute of Technology, Korea (the Republic of); ²Samsung Advanced Institute of Technology-America, United States; ³Corning Incorporated, United States; ⁴Seoul National University, Korea (the Republic of)

Lithium metal battery has long been pursued as an advanced energy storage device due to its high energy density, but several technical difficulties such as Li dendrite formation have prohibited its commercialization while lithium-ion batteries are successfully settled down in the market in spite of lower energy density. Recently, $\text{Li}_{7-x}\text{La}_{3-x}\text{Zr}_{2-x}\text{O}_{12}$ (LLZO) solid electrolytes with garnet structure have drawn great attention since their stability against Li metal anode is found to be much better than many other oxide-based lithium ion conductors. Notwithstanding the improved chemical stability, there have been many reports mentioning the short circuit of the cells caused by the penetration of Li metal through the LLZO electrolyte. In this work, we demonstrate a lithium metal battery cell employing an LLZO electrolyte can be cycled over 2,000 times. The bulk dopant and the surface treatment method for LLZO are found to be key parameters leading to such an excellent cycling stability. The strategy and the proposed mechanism will be discussed in the presentation.

11:50 AM ES01.08

Thin and Robust LATP Solid Electrolytes with Close-to-Bulk Ionic Conductivity and its Integration in Solid-State Architectures Juan Carlos Gonzalez-Rosillo¹, Valerie Siller¹, Marc Nuñez¹, Raul Arenal², Juan Miguel Lopez del Amo³, Alex Morata¹ and Albert Tarancón^{1,4}; ¹Institut de Recerca en Energia de Catalunya, Spain; ²Universidad de Zaragoza, Spain; ³Centro de Investigación en Energías Alternativas, Spain; ⁴Institució Catalana de Recerca i Estudis Avançats, Spain

Glassy-type solid state electrolytes such as state-of-the-art LiPON avoid grain boundaries and prevent Li-dendrite propagation leading to extremely good cyclability and the commercialization of planar thin-film LiPON-based microbatteries. However, its reduced ionic conductivity ($\sim 1 \mu\text{S/cm}$) limits its performance at high/discharge rates and the severe degradation of its electrochemical and structural properties upon their exposure to ambient conditions and high temperatures ($> 300 \text{ }^\circ\text{C}$) hinders scalability and manufacturability. Among the next generation solid-state electrolytes, NASICON superionic solid electrolyte $\text{Li}_{(1-x)}\text{Al}_x\text{Ti}_{(2-x)}(\text{PO}_4)_3$ (LATP) with $0.3 \leq x \leq 0.5$ remains one of the most promising solid electrolytes thanks to its good ionic conductivity ($\sim 0.5\text{--}1 \text{ mS cm}^{-1}$) and outstanding stability in ambient air. Despite the intensive research for bulk systems, there are only very few studies of LATP in thin film form. In particular, the only successful reports of relatively high ionic conduction ($\sim 10^{-5} \text{ S cm}^{-1}$) have been achieved through amorphous sputtered films.

In this talk, we will explore the properties of high performance LATP thin films fabricated by Large-Area Pulsed Laser Deposition. The as-deposited thin films exhibit an ionic conductivity around $0.5 \mu\text{S cm}^{-1}$ at room temperature (comparable to the state-of-the-art of LiPON) which increases to remarkably high values of 0.1 mS cm^{-1} after an additional annealing at $800 \text{ }^\circ\text{C}$. We will discuss the formation of a glassy, intergranular phase connecting highly conducting LATP grains as a possible cause for the significant enhancement in ionic conductivity by two orders of magnitude. The performance of both as-deposited and annealed LATP films makes them suitable as solid electrolytes, which opens the path to a new family of stable and highly performing thin solid-electrolytes.[1] We will discuss its integration with other battery components, with special attention to interfacial coatings matching the electrochemical window at low potentials. [2]

[1] V. Siller, A. Morata, M. N. Eroles, R. Arenal, J. C. Gonzalez-Rosillo, J. M. López del Amo and A. Taracón, J. Mater. Chem. A, 2021, 9, 17760–17769.

[2] J.C. Gonzalez-Rosillo et al. Submitted 2021

12:05 PM ES01.09

Chemo-Mechanics and Microstructural Design of Solid-State Batteries [Giovanna Bucci](#); Palo Alto Research Center Incorporated, United States

In all-solid cells, the battery life depends in larger measure on the mechanical integrity of the composite system. Expansion stresses can lead to the formation of cracks at the electrode-electrolyte interfaces. Because the charge-transfer reaction proceeds only if contact is established, fracture and delamination ultimately result in power loss and battery capacity fade.

With quantitative analyses that account for inhomogeneities in the microstructures, this work identified main degradation mechanisms that lead to fracturing of solid electrolyte materials in operando. Random-walk analyses were also employed to show a measurable effect of mechanical degradation on the electrode's transport properties and overall cell power.

This research leads to guidelines for the engineering of particle size, volume ratio of active material, interfacial cohesion, and the electrolyte mechanical properties. It also disputes the common assumption that low stiffness is a desirable property for solid-electrolyte materials, showing that ductility should be a material design target.

Establishing design rules for Li-metal solid-state batteries requires a systematic understanding of Li-dendrite formation and growth. A theoretical framework for electro-deposition, large deformations and fracture mechanics is employed to explore this design space. We envision a composite structured anode that greatly expands the surface area of the charge-transfer interface and provides a conductive scaffold that self-regulates the local current density while maintaining mechanical stability and Li-accessibility during cycling.

12:20 PM ES01.10

Advancing Cycling Capabilities of Composite Polymer Electrolytes with LLZO Nanofibers [Sanja D. Tepavcevic](#), Michael Counihan, Pallab Barai, Devon Powers and Yuepeng Zheng; Argonne National Laboratory, United States

Ceramic $\text{Li}_6\text{.55Al}_0\text{.2La}_3\text{Zr}_2\text{O}_{12}$ (LLZO) is one of the most attractive electrolyte materials for solid-state batteries that combined with metallic Li anodes holds the promise for safer and more energetically dense battery, but its performance is always limited by the high electrolyte-electrode interfacial resistances. The combination of Li^+ -conducting ceramics and polymers offers a new pathway to create better electrolytes with both high ionic conductivity and good (electro)mechanical interfacial properties. We investigated PEO based composite polymer electrolyte (CPE) with a high, 50 wt% loading of Al-doped LLZO nanofibers synthesized by high-yield roll-to-roll (R2R) electrospinning technique. Electrochemical impedance spectroscopy (EIS) analysis showed comparable bulk ionic and interfacial resistances with and without nanofibers, indicating that PEO dominates Li^+ transport and interfacial chemistry with some LLZO contribution to bulk conduction at higher temperatures. X-ray photoelectron spectroscopy, Scanning Electron Microscopy and Computational Modeling results demonstrated that elastic surfaces of the composite electrolyte form stable and stiff SEI layer that well conforms and adapts to the volume changes of the electrodes during the repeated cycles and enables a stable Li plating/stripping cycling for over 250 h. The total Li-ion conductivity of the composite is still governed by the polymer matrix due to high interfacial resistance between the garnet particles and the PEO/LiTFSI matrix. Galvanostatic cycling and EIS measurements revealed that high current density cycling at 8 mA/cm^2 plays a key role in stabilizing the interface exchange between the nanofibers and the surrounding polymer matrix by significantly lowering both interfacial and charge transfer resistances. Once the CPE interfaces are conditioned via high current cycling, stable and low polarization cycling at 1 mA/cm^2 and 1 mAh/cm^2 can be achieved, showing $\sim 36\text{ mV}$ overpotential for over 180h of cycling. In summary, comparison of CPE with 50 wt % LLZO nanofibers with nanofiber-free PEO electrolyte highlighted the key performance improvements in ion transport, (electro)chemical stability in contact with metallic Li electrode, stable Li electrodeposition and no dendrite formation.

SESSION ES02: Solid State Batteries II

Session Chair: Yuan Yang

Monday Afternoon, July 18, 2022

Lobby Level, Avenue 34, The Loft

2:00 PM *ES02.01

An In-Depth Look at of the Degradation Mechanisms of High-Nickel Cathodes in Lithium-Ion Batteries [Arumugam Manthiram](#); The University of Texas at Austin, United States

Lithium-ion batteries have aided the revolution in portable electronics. They are now on the verge of transforming the transportation sector with electrification. They are also being intensively pursued for grid storage of electricity produced from renewable sources, such as solar and wind energies. As we move forward with vehicle electrification and renewable energy storage, cost and sustainability will be the single dominant factor. In addition, driving range is a critical factor for vehicle applications. With this perspective, reducing or eliminating the cobalt content by increasing the nickel content in layered oxide cathodes has been at the forefront to relieve the industry from cost concerns and supply-chain issues, while also advantageously increasing the charge-storage capacity. However, as we reduce the cobalt content and increase the nickel content, the high-nickel cathodes suffer from cycle, thermal, and air instabilities. The cycle instability in particular has largely been attributed to phase transformations and consequent crack formation. However, the behavior of high-nickel cathodes in contact with organic liquid electrolytes is complex. Accordingly, this presentation will focus on an in-depth look at the degradation mechanisms of high-nickel cathodes in high-energy-density lithium-ion batteries.

The low-cobalt and cobalt-free layered oxide cathodes with desired secondary particle size of 12 micron are synthesized by a coprecipitation of the hydroxide precursors with appropriate doping, employing a tank reactor, followed by calcining with lithium hydroxide at optimal temperatures under a flowing oxygen atmosphere. Cathodes with capacities as high as 220 – 230 mAh/g are achieved. The synthesized materials are characterized with a suit of advanced characterization methodologies before and after cycling in lithium-metal cells as well as before and after thousands of cycles of pouch full cells with graphite anode. Specifically, x-ray photoelectron spectroscopy, time-of-flight – secondary ion mass spectrometry, aberration-corrected transmission electron microscopy, and in-situ x-ray diffraction along with in-depth electrochemical analysis are used to assess bulk vs. surface degradation in low-cobalt and cobalt-free cathodes, including LiNiO_2 . In addition to the assessment of cycle instability, air instability and thermal instability are also assessed. Based on the understanding gained, strategies developed to overcome cycle, thermal, and air instabilities will be presented.

2:20 PM *ES02.02

Solid-State Batteries for EV Application—Opportunities and Challenges [Mei Cai](#); General Motors Corp, United States

Despite the current battery technology evolution, battery chemistries have not changed much in the last two decades. Highly emerged EV market evokes the demands on advanced batteries with high energy density. Among the future chemistries, lithium metal and solid-state batteries have great advantages over state-of-the-art lithium ion batteries which bring huge opportunity for long-range and low-cost electrical vehicles in the future. However, automotive industry has critical requirements on specific characteristics of battery cells. In this talk, I will discuss the requirements for future electrical vehicle application and the impact of solid-state batteries on automotive industry. An example of how solid-state electrolyte being used as a separator for Li-S battery will be reviewed. The concerns and challenges of solid-state battery will be discussed.

2:40 PM ES02.03

Design and Production of Three-Dimensionally-Structured Oxide Composite Cathodes for All-Solid-State Lithium Batteries [Johannes Kriegler](#)¹, [Enkhtsetseg Dashjav](#)², [Maximilian Scheller](#)¹, [Fabian Konwitschny](#)¹, [Frank Tietz](#)^{2,3} and [Michael Zaeh](#)¹; ¹Technische Universität München, Germany; ²Forschungszentrum Julich GmbH, Germany; ³Forschungszentrum Julich Helmholtz-Institut Münster Institut für Energie- und Klimaforschung Elektrochemische Verfahrenstechnik, Germany

All-solid-state batteries (ASSB) with a lithium metal anode promise high energy densities and improved safety compared to conventional lithium-ion batteries containing a liquid electrolyte. However, the fabrication of high-performance composite cathodes remains challenging. In particular, this applies to composite cathodes based on mechanically rigid oxide electrolytes, which conventionally are densified via sintering to enhance the electrode-electrolyte contact. Thereby, the applicable process temperatures when co-sintering cathode active material and solid electrolytes are limited to avoid the formation of insulating phases, which lead to high interfacial resistances. However, the resulting porosity and interfacial resistances remain high if the sintering temperature is too low due to limited particle contacts. Therefore, the development of improved cathode designs and fabrication strategies for composite cathodes with a low interfacial resistance remains one of the key challenges in the production of ASSB.

In this work, an alternative processing route for producing oxide-based composite cathodes is proposed. The fabrication strategy includes the infiltration of micro-structures with a solvent-based cathode slurry. The slurry contains a fraction of polymer electrolyte, which is intended to serve as an ionically conductive filler to increase the contact area between the cathode active material particles and the oxide electrolyte. On the one hand, the generation of ceramic substrates with a graded porosity is achieved by sequential tape casting using a pore former. On the other hand, directed micro-structures are inserted into dense, sintered layers of oxide solid electrolyte via laser radiation.

Model calculations are used to substantiate the industrial relevance of the three-dimensional electrode design. The theoretically obtainable volumetric and gravimetric energy densities are assessed for different material compositions, structure geometries, and layer thicknesses. Furthermore, the surface enlargement for different structures and geometries is shown.

Experimental results are presented using the NaSICON-type solid electrolyte $\text{Li}_{1.5}\text{Al}_{0.5}\text{Ti}_{1.5}\text{P}_3\text{O}_{12}$. First, the generation of various directed structure geometries like drilled holes and trenches using laser radiation is evaluated and compared to non-directional pore structures. The laser process is designed to allow the generation of feature sizes well below $50\ \mu\text{m}$ and substrate porosities of up to 70 %. A dense layer is retained at the bottom of the structures to serve as a separator layer. Subsequently, these structures were infiltrated with a slurry-based mixture of cathode active material, conductive carbon, binder, and an ionically conductive polymer electrolyte. The influence of the slurry formulation, e.g., the amount of solvent, on the infiltration process is analyzed, showing that high filling degrees above 60 % can be achieved.

The functionality of the composite cathode is tested in ASSB with lithium metal anode. In this case, an ultra-thin, conventional polymer separator layer is infiltrated with an ionically conductive polymer electrolyte to serve as a protective layer between LATP and lithium metal. This protective layer is laminated onto the composite cathode and the compound is subsequently paired with a lithium metal anode. The reversible cyclability of the manufactured ASSB is proven for more than 100 cycles.

The results of this work assist in developing oxide-based ASSB by demonstrating approaches to both the design and fabrication of oxide composite cathodes.

2:55 PM ES02.05

Improving the Electrochemical Performance of $\text{Li}_7\text{P}_2\text{S}_8\text{X}$ Solid Electrolyte with Compositional Tuning and Doping Process [Rajesh Rajagopal](#) and Kwang-Sun Ryu; University of Ulsan, Korea (the Republic of)

All-solid-state lithium batteries (ASSBs) are considered promising future energy storage devices due to their high energy density and their non-flammable nature. Safety is the major concern in conventional lithium-ion batteries, which will be solved by a non-flammable solid electrolyte. Thus, inorganic non-flammable solid electrolytes are the key component for the fabrication of ASSBs. Among all other inorganic solid electrolytes, sulfide-based solids received much attention due to their high ionic conductivity and mechanical softness. These sulfide based solid electrolytes exhibit high ionic conductivity which is comparable with liquid organic electrolytes. Specifically, Li-argyrodite ($\text{Li}_6\text{PS}_5\text{X}$) based solid electrolytes and LGPS ($\text{Li}_{10}\text{GeP}_2\text{S}_{12}$) based solid electrolytes exhibited the high ionic conductivity value of $\sim 10^{-2}\ \text{S cm}^{-1}$, at room temperature. Unfortunately, the above sulfide-based solid electrolytes has limited stability against lithium metal anode. In addition, interfacial stability between the sulfide-based solid electrolyte and the electrode materials is poorer than the oxide-based electrolytes and organic liquid electrolytes. Thus, it is necessary to develop a novel solid electrolyte with high ionic conductivity and high stability against lithium metal anode. To solve this problem, numerous studies have been carried out in the last decade and the researchers suggested that the $\text{Li}_7\text{P}_2\text{S}_8\text{X}$ -type ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) solid electrolytes exhibit reasonable ionic conductivity and high stability against lithium metal anode. But, reasonable modification is needed to improve the electrochemical performances of $\text{Li}_7\text{P}_2\text{S}_8\text{X}$ -type solid electrolytes. In this work, we have improved the ionic conductivity of the $\text{Li}_7\text{P}_2\text{S}_8\text{X}$ -type solid electrolytes by compositional tuning and doping process and used them for the fabrication of ASSBs. Firstly, the ionic conductivity of the $\text{Li}_7\text{P}_2\text{S}_8\text{X}$ -type solid electrolyte was improved by tuning the concentration halogen with a dual halide process. As a result of the optimization process, the prepared dual halide $\text{Li}_7\text{P}_2\text{S}_8\text{X}$ -type solid electrolyte ($\text{Li}_7\text{P}_2\text{S}_8\text{I}_{0.75}\text{Br}_{0.25}$) exhibited the ionic conductivity value $> 6\ \text{mS cm}^{-1}$ at room temperature, which is higher than single halide based $\text{Li}_7\text{P}_2\text{S}_8\text{X}$ -type solid electrolytes. During the optimization, structural changes were observed through powder X-ray diffraction analysis and this is the reason for the enhancement of ionic conductivity. The ionic conductivity of $\text{Li}_7\text{P}_2\text{S}_8\text{I}_{0.75}\text{Br}_{0.25}$ (LPSIBr) was further increased by metal doping at P-site. The metal doping at P-site was confirmed laser Raman and solid nuclear magnetic resonance (NMR) analysis. After the successful metal doping (at p-site), the ionic conductivity of LPSIBr solid electrolytes was further increased to $> 7.5\ \text{mS cm}^{-1}$, at room temperature. Cryo-high-resolution transmission electron microscope analysis confirmed that the addition of metal atoms damaged the crystal structure of LPSIBr solid electrolyte and widen the Li-ions transport path. In addition, we also doped the metal oxides to the LPSIBr solid electrolyte to improve the moisture stability and electrolyte-electrode interfacial stability. Thus the prepared solid electrolytes via compositional tuning and doping process exhibited high ionic conductivity and structural stability. Finally, the electrochemical performance of the prepared solid electrolytes was studied by cyclic voltammetry techniques and DC polarization techniques. The fabricated ASSB using optimized solid electrolyte exhibited high specific capacity and cycle stability. Additionally, the interfacial stability of the fabricated ASSBs was studied by electrochemical impedance spectroscopy technique (EIS), XPS analysis, charge-discharge cycle test, and C-rate performance analysis.

3:10 PM ES02.06

Ionic and Electronic Transport Properties of $\text{Li}_{0.29+\delta}\text{La}_{0.57}\text{TiO}_3$ Investigated by Electrocoloration, GITT and EIS Joseph R. Ring, Andreas Nennung and Juergen Fleig; Technische Universität Wien, Austria

$\text{Li}_{0.29+\delta}\text{La}_{0.57}\text{TiO}_3$ (LLTO) is a solid-state Li-ion conductor with an A-site deficient perovskite structure. Due to its high Li-ion conductivity ($> 5 \cdot 10^{-4} \text{ S cm}^{-1}$) it is an interesting electrolyte material for all-solid-state Li-ion batteries. However, it gets electrochemically reduced at voltages lower than 1.7 eV vs. Li^0 , which introduces mixed-ionic-electronic-conductivity (MIEC) [1].

In this study, we investigated the transition from ion conductor to MIEC in detail by combining experimental methodology and theoretical concepts from solid state ionics (point defect chemistry, electrocoloration and equivalent circuit modeling) with approaches very common in battery research (charge/discharge curves, galvanostatic intermittent titration and chronoamperometry). By these methods applied to dense LLTO samples, we could identify several interesting electrochemical properties of this material.

Upon electrochemical reduction, Li-ions are intercalated into the vacant A-sites (0.14 per formula unit), and electrons are injected into Ti 3d states, which is visible by a strong darkening (electro-coloration) of the material. In an in-plane electrode configuration, a relatively sharp color front progresses from the cathode through the material during reduction. Due to the high mobility of electronic and ionic charge carriers, the coloration front may move by more than 1 cm/minute at room temperature and potentials of a few volts. A detailed analysis of the coloration front motion indicates the presence of charge trap states within the band gap. Electro-coloration of LLTO is either possible by using two Li-blocking Au electrodes as electric contacts, as well as by immersion of LLTO in a liquid electrolyte and electrochemical Li insertion. Due to the external Li source, the latter configuration also allows investigation of LLTO as a potential Li-ion electrode material. After the coloration front has moved through the entire material, further Li insertion is limited by Li ion transport, and the chemical diffusion coefficient can be obtained from galvanostatic intermittent titration technique (GITT) measurements [1]. Under certain conditions, can also be calculated from electrochemical impedance (EIS) data [2]. Here, we used GITT and electronic conductivity measurements to determine the diffusion coefficients and mobilities of Li ions and electrons individually as a function of δ in $\text{Li}_{0.29+\delta}\text{La}_{0.57}\text{TiO}_3$.

Owing to the absence of structural transformations during the Li insertion (up to $\delta=0.14$), LLTO proves to be an excellent model material for such investigations. Moreover, our studies reveal a potentially high rate capability of LLTO during cycling, at the expense of moderate capacity and cell voltage.

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3:25 PM BREAK**4:00 PM *ES02.07**

The Role of Adhesion on Interfacial Stability in All-Solid-State Batteries with Alkali-Metal Anodes Juan D. Seymour¹, Edouard Querel¹, Rowena Brugge^{1,2} and Ainara Aguadero^{1,3}; ¹Imperial College London, United Kingdom; ²University of Cambridge, United Kingdom; ³Instituto de Ciencia de Materiales de Madrid, Spain

All-solid-state batteries (ASSB) containing fast ion conducting, solid-state electrolyte (SSE) materials such as garnet $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZO) and Na^{β} -alumina are at the forefront of rechargeable battery technology, particularly for the next generation of electric vehicle applications. The introduction of a SSE could enable the use of a pure lithium (Li) or sodium (Na) metal anode with high practical volumetric and gravimetric energy density. However, challenges relating to the dynamic stability of the alkali-metal/SSE interface under fast rates of discharge and charge still need to be addressed to facilitate the adoption of ASSBs with alkali-metal anodes. During discharge, Li(Na) atoms are stripped from the Li(Na) metal surface and inserted into the SSE as Li^+ (Na^+) ions, leaving behind a Li(Na) vacancy in the metal. The accumulation of Li (Na) vacancies can lead to the formation of voids at the Li(Na)/SSE interface, which reduces the contact between the Li (Na) metal and SSE and increases the interfacial resistance.⁽¹⁾ The strongly reducing environment at the alkali-metal/SSE interface can also lead to the presence of resistive solid electrolyte interphases (SEI) that increase the interfacial resistance.

The interfacial adhesion or ‘wettability’ of an alkali metal anode with the SSE and SEI components is a crucial factor that impacts the interfacial stability. In this work we discuss the role of interfacial adhesion on void formation at the alkali-metal/SSE interface. Using simple energetic models in combination with large scale density functional theory (DFT) calculations and local surface analysis techniques, we demonstrate how the preference for alkali vacancy segregation at the alkali-metal/SSE interface is linked to key materials parameters including the interfacial work of adhesion (W_{ad}) and alkali metal surface energy (σ_m).⁽²⁾ The results from this study indicate that large interfacial work of adhesion ($W_{ad} \geq 2 \times \sigma_m$) are required to suppress alkali-metal void formation in the absence of pressure, a criterion that is rarely met by state-of-the-art SSE materials. The importance of tuning the surface properties of SSE materials through the addition of interfacial layers, such as Na_3PO_4 in Nasicon $\text{Na}_3.4\text{Zr}_2\text{Si}_2.4\text{P}_{0.6}\text{O}_{12}$ materials, will further be discussed.⁽³⁾ The conclusions from this work provide novel guidelines for the design of new interlayer materials to suppress alkali-metal void formation in ASSBs.

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4:20 PM ES02.08

Stable Solid-State Sodium Batteries Based on Na-Metal and NASICON Electrolyte Qianli Ma¹, Frank Tietz¹, Dina Fattakhova-Rohlfing^{1,2} and Olivier Guillon^{1,3}; ¹Forschungszentrum Jülich GmbH, Forschungszentrum Jülich GmbH, Jülich, Nordrhein-Westfalen, DE, academic/govt, Germany; ²Department of Engineering and Center for Nanointegration Duisburg-Essen (CENIDE), Universität Duisburg-Essen, Germany; ³JARA, Germany

Compared to their lithium counterpart, the solid-state sodium battery (SSNB) is regarded to have similar properties but is a much less mature technology because it is much less addressed. Besides their well-known natural endowment like high element abundance, in the present study, some technological advantages of SSNBs are discussed in comparison with solid-state lithium batteries (SSLBs). Primarily, $\text{Na}_{3+x}\text{SxZr}_2\text{-xSi}_2\text{PO}_{12}$ was found to show conductivity over $4 \times 10^{-3} \text{ S cm}^{-1}$ at 25 °C, prepared by a solution-assistant solid state reaction method.^[1] More recently, $\text{Na}_{3+x}\text{Zr}_2\text{Si}_2\text{-xP}_1\text{-xO}_{12}$ (NZSP) ceramics were reported to have even higher total conductivity of $5 \times 10^{-3} \text{ S cm}^{-1}$ at 25 °C, better than previously reported polycrystalline Na-ion conductors.^[2] Inhibition of dendrite growth in SSLBs and SSNBs has long been a challenge to the field. In the present study, with simply sticking sodium metal to NZSP ceramic pellets and without external pressure applied during operation, the critical current density of Na/NZSP/Na symmetric SSNBs reaches 9 mA cm^{-2} at 25°C. The cells can be stably operated at areal capacity of 5 mAh cm^{-2} (per half cycle, with 1.0 mA cm^{-2}) at 25°C for 300 h in a galvanostatic cycling measurement without any dendrite formation. This critical current density is much higher than those of existing SSLBs operated at similar conditions. The influence of metal self-diffusion on the dendritic plating is the main explanation of the high dendrite tolerance of SSNBs. In this

report, the inter-ceramic contact problems in the cathode are also solved by combining the infiltration of a porous electrolyte scaffold by precursor solution with *in situ* synthesis of electrode active material.^[3,4] The resulting full cells using $\text{Na}_3\text{V}_2\text{P}_3\text{O}_{12}$, NZSP and Na as the positive electrode, electrolyte and negative electrode materials, respectively, can be stably operated with a capacity of 0.55 mAh cm^{-2} at high rate of 0.5 mA cm^{-2} . This is the first successful example showing that contact problems between rigid electrolyte and electrode materials can be solved without using any soft additive (liquid, polymers, ionic liquids etc.) as an accommodation or wetting medium. Since SSNBs have these advantages while SSLBs have not, the future roadmap of the development of solid-state batteries may shift from SSLBs towards SSNBs despite the higher molar weight of the sodium compounds in comparison to the Li analogues.

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4:35 PM ES02.09

How to Achieve High Room Temperature Li-Ion Conductivity and Cyclability in Complex Hydride Solid-State-Electrolyte Valerio Gulino, Peter Ngene and Petra de Jongh; Universiteit Utrecht, Netherlands

Solid-state electrolytes are promising candidates to replace of the organic liquid electrolyte currently employed in Li-ion batteries. Complex hydrides (e.g. LiBH_4 and closo-borates) solid-state electrolytes are lightweight and electrochemically stable. However, complex hydrides generally possess a low Li-ion conductivity at room temperature (RT).¹

In this work, different approaches to achieve the RT Li^+ conductivity required for batteries applications in LiBH_4 are presented, such as halide substitution and the addition of oxide to form composites.

We investigated the effect of halogenation on the structural and electrochemical properties in the $\text{LiBH}_4\text{-LiI}$, $\text{LiBH}_4\text{-LiBr}$ and $\text{LiBH}_4\text{-LiBr-LiCl}$ systems.^{2,3} In all these systems, the presence of the anions (I^- , Br^- and Br^+Cl^-) leads to a stabilization of the high temperature polymorph of the LiBH_4 , greatly enhancing the Li-ion conductivity at RT.

Secondly, the effect of SiO_2 addition to LiBH_4 by ball-milling on the Li-ion conductivity was analysed. The Li-ion conductivity was enhanced for all the composite conductors by the creation of a 2 nm interface layer where the conductivity is drastically enhanced. In addition, a clear effect of the SiO_2 volume fraction was observed, leading to clear guidelines for optimization of the conductivity of complex-hydrides composites.⁴

Finally, the possibility to have a synergetic effect between these two approaches has been studied. The $\text{LiBH}_4\text{-LiI}$ solid solution was mechanochemical treated with SiO_2 , showing an improved Li-ion conductivity with respect to the starting solid solution. In addition to the higher conductivity, the composites demonstrated higher stability against Li-metal, compared to $\text{LiBH}_4\text{-LiI}$ solid solution, accompanied by a lower polarization evolution in a symmetric $\text{Li}|\text{LiBH}_4\text{-LiI-SiO}_2|\text{Li}$ cell.

The novel electrolyte was implemented in a $\text{Li}|\text{LiBH}_4\text{-LiI-SiO}_2|\text{TiS}_2$ cell and showed reversible and stable cycling with a capacity of 170 mAhg^{-1} and 100 mAhg^{-1} , i.e. more than 70% and 40% capacity retention respectively, after 100 and 200 cycles at C/20 and 60°C . This battery cell not only showed much higher cycling capacities than those previously reported based on $\text{LiBH}_4\text{-LiI}$ electrolytes, but it also showed the highest cyclability of all the other cells tested using LiBH_4 -based electrolytes at 60°C .

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4:50 PM ES02.10

Utilizing Model Thin Film Polymer Electrolytes to Understand Polymer Electrolyte Modification in Polymer-Ceramic Composite Electrolytes Sara C. Sand¹, Jennifer Rupp² and Bilge Yildiz^{1,1}; ¹Massachusetts Institute of Technology, United States; ²Technische Universität München, Germany

Polymer-ceramic composite electrolytes have been thoroughly studied due to their high ionic conductivity, as similar to that of the ceramic, and their flexibility due to the polymer electrolyte. Significant evidence has shown that ionic conductivity of polymer electrolytes increases appreciably even when non-conductive filler particles are dispersed in a polymer electrolyte.^{1,2} This increase in conductivity is caused by modification of the polymer structure through several mechanisms: 1) reduction polymer crystallinity, 2) increased in free volume through polymer confinement, and 3) increased separation of lithium salts due to Lewis acid-base effects on the surface of the ceramic that increases lithium salt segregation in the polymer.^{3,4} Our work utilizes thin film model systems to quantify these effects and understand how various ceramic materials may change the effects. Particularly, we studied polyethylene oxide (PEO) with lithium perchlorate (LiClO_4) as the lithium salt which was spincoated on to substrates to create micrometer thick films to study the interface with the substrate material. We utilized differential scanning calorimetry and x-ray diffraction to show reduced crystallinity in the thin film as compared to the bulk polymer. We also showed that thin film shows an order of magnitude increase in conductivity as compared to the bulk samples as measured by electrochemical impedance spectroscopy. This result illustrates the effects of polymer confinement due to the proximity of the polymer to substrate in the thin film. However, a fractional increase in crystallinity cannot account for an order of magnitude variation in conductivity indicating that free volume or Lewis acid-base effects must play an appreciable role in the increase in conductivity in these studies.

In order to probe the Lewis acid-base effects, we utilized x-ray photoelectron spectroscopy with C60 ion gun sputtering profiling. Literature has identified that the Cls and O1s peak can provide information on the association of lithium ions and the anion of the lithium salt.⁵ We profiled these peaks for polymer films on substrates of various materials with varying degrees of surface acidity: alumina, silica, and tungsten oxide.⁶ Lithium lanthanum zirconium oxide (LLZO) is commonly used as a ionically conductive filler in composite electrolytes and therefore, we additionally measured profiled the LLZO as a comparison, to understand how this ion conducting filler modifies ion separation. Through this study, we can begin to quantifying the thickness of this modified layer of ion conduction and to quantify the modification of the lithium salt segregation.

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5:05 PM ES02.11

Novel Solution-Processing via Dynamic Sulfide Radical Anions for Rapid Synthesis of Sulfide Solid Electrolytes Hirota Gamo, Jin Nishida, Atsushi Nagai, Kazuhiro Hikima and Atsunori Matsuda; Toyohashi Gijutsu Kagaku Daigaku, Japan

Solution processing technology for the manufacturing of all-solid-state batteries (ASSBs) offers scalability, simplicity of electrode fabrication, and intimate contacts between the electrode and solid electrolyte. $\text{Li}_7\text{P}_3\text{S}_{11}$ solid electrolytes (SEs) prepared by liquid-phase method deliver high ionic conductivity and are promising candidate for easier processing into ASSBs. Among organic solvents tested in the previous works, acetonitrile (ACN) solvent was the most suitable solvent for the formation of crystalline $\text{Li}_7\text{P}_3\text{S}_{11}$ SEs due to its high polarity characterized by the dielectric constant.[1] Using ACN as the solvent the wet-chemical reaction for the formation of $\text{Li}_7\text{P}_3\text{S}_{11}$ undergoes a precursor suspension containing the $\text{Li}_3\text{PS}_4 \cdot \text{ACN}$ (75 $\text{Li}_2\text{S} \cdot 25\text{P}_2\text{S}_5$ in mol%) precipitate and the $\text{Li}_2\text{S} \cdot \text{P}_2\text{S}_5$ (50 $\text{Li}_2\text{S} \cdot 50\text{P}_2\text{S}_5$ in mol%) solution.[2] The conventional wet-chemical reaction of sulfide-based SEs without additional energy (microwave or ultrasonication treatment) requires a longer reaction time (at least 24 h) than the mechanochemical reaction because the liquid synthesis of sulfide SEs depends on the reaction rate-limiting step during the formation of the insoluble Li_3PS_4 intermediate in a certain organic solvents. Additionally, the slurry process of $\text{Li}_7\text{P}_3\text{S}_{11}$ SEs causes heterogeneity because of the complicated phase formations, which increases the engineering costs for the large-scale manufacturing of ASSBs. Herein, we report an unprecedented solution-processing via dynamic sulfide radical anions that provides rapid and scalable manufacturing of $\text{Li}_7\text{P}_3\text{S}_{11}$ solid electrolytes. As a mediator, we have introduced the $\text{S}_3^{\cdot -}$ radical anion to activate P_2S_5 for the formation of a precursor solution without the need for ball milling or high-energy treatment. By adding trace amounts of ethanol, the initial mixture of Li_2S and P_2S_5 (7:3 molar ratio) with excess elemental sulfur in a mixed solvent of ACN and tetrahydrofuran (1:1 volume ratio) leads to a change of solution state from inhomogeneous to homogenous black solution in minutes. After drying and heat treatment, $\text{Li}_7\text{P}_3\text{S}_{11}$ with a high ionic conductivity of 1.2 mS cm^{-1} at room temperature forms in total preparation time of 2 h. Ethanol solvent enhances the chemical stability of $\text{S}_3^{\cdot -}$ radical anion, which allows the formation of soluble lithium thiophosphates and polysulfides within a short timescale. The solution-processing technology reported here paves the way for the accelerated adoption of practical ASSBs manufacturing.

Acknowledgements

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5:20 PM ES02.13

3D Operando Visualization and Quantification of Cycle Degradation in Solid-State Battery Electrodes Using CT-XAFS Su Huang¹, Yuta Kimura¹, Takashi Nakamura¹, Nozomu Ishiguro¹, Oki Sekizawa², Kiyofumi Nitta², Tomoya Uruga², Tomonari Takeuchi³, Toyoki Okumura³, Mizuki Tada^{4,5}, Yoshiharu Uchimoto⁶ and Koji Amezawa¹; ¹Tohoku Daigaku, Japan; ²Kokido Hikari Kagaku Kenkyu Center, Japan; ³Sangyo Gijutsu Sogo Kenkyujo Kansai Center, Japan; ⁴Nagoya Daigaku, Japan; ⁵RIKEN SPring-8 Center, Japan; ⁶Kyoto Daigaku, Japan

Solid state batteries (SSBs) have captured extensive attention because of their improved thermal stability and high performances. However, the poor cyclability of SSBs still hinders their practical application. When the SSBs are (dis)charged, Li-ions are extracted from or intercalated into the active materials (AMs), leading to the expansion or shrinkage of AM particles. Such volume changes can result in the loss of inter-particle contacts and the disconnection of Li-ion/electron pathways. Due to such structural changes in SSB electrodes, a part of AM particles hardly take part in electrochemical reactions during cycling, and the cyclability of SSBs is severely deteriorated. To prevent the cycle degradation, it is crucial to understand where, when, and to what extent the cycle degradation occurs, and to establish the guidelines for the electrode design based on fundamental scientific knowledge.

In this study, we performed the three-dimensional (3D) *operando* visualization of the charging state distribution in a SSB electrode during cycling using our visualization technique based on computed-tomography with X-ray absorption fine structure spectroscopy (CT-XAFS)¹, and quantitatively investigated the origins of cycle degradation. We demonstrate that our technique is a valuable tool that can provide quantitative insights into the cycle degradation in SSB electrodes with 3D spatial and temporal resolution.

A model SSB cell with a configuration of $\text{Li}_x\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ (NCM111) and $\text{Li}_{3.75}\text{Ge}_{0.75}\text{P}_{0.25}\text{O}_4\text{-Li}_3\text{BO}_3$ composite electrode| $\text{Li}_{2.2}\text{C}_{0.8}\text{B}_{0.2}\text{O}_3$ electrolyte|poly (ethylene oxide)-based polymer electrolyte|Li metal electrode was prepared following the literature². The SSB cell was (dis)charged with a constant current for 4 cycles. The CT-XAFS measurements were performed near the Ni-K edge during cycling and the 3D charging state distribution in the electrode was estimated from the peak top energy of the Ni-K edge at each voxel.

3D charging state distribution in the SSB electrode and its evolution during cycling were successfully visualized by CT-XAFS. After the 1st charge, the AMs in the observed region generally showed a high charging state (Li content $x = 0.5$). However, such AMs gradually decreased and those with low charging state increased after the 2nd, 3rd and 4th charge. Similarly, the incompletely discharged AMs gradually increased as the (dis)charge cycle proceeded. Such variations in (dis)charging states correspond to the capacity degradation during cycling.

To investigate where the cycle degradation occurred in the electrode, we subtracted the 3D charging state map after each charge/discharge from the one after previous discharge/next charge, respectively. The obtained maps thus stand for to what extent the reaction progressed in AM during each (dis)charge. In these maps, less-reacted AM was preferentially found near AM/solid electrolyte (SE) interfaces, namely, the cycle degradation primarily occurred near AM/SE interfaces in the model SSB. Furthermore, to investigate when the cycle degradation occurred, we calculated the ratio variation of less-reacted AM near AM/SE interfaces after each (dis)charge. From this analysis, we found that the cycle degradation more severely occurred during charge. The volume of NCM111 is known to decrease during charge, *i.e.*, Li extraction³. This volume reduction of NCM111 can cause the loss of inter-particle contacts, which could be the reason why the cycle degradation primarily occurred during charge in the model SSB. The above results demonstrate that our technique can provide deeper and quantitative insights into the cycle degradation in SSB electrodes, and hence the guidelines for optimal electrode design.

Acknowledgement: We acknowledge the financial supports of JST-ALCA SPRING, Japan.

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SESSION ES03: Poster Session I: Energy Storage I
 Monday Afternoon, July 18, 2022
 6:00 PM - 8:00 PM
 Mezzanine Level, Second Floor, Stadler

ES03.01

A₃Ti₅NbO₁₄ Family with A=H, Li, Na, K—Insertion and Ionic Exchange Audric Neveu¹, Justine Jean¹, Philippe Boullay¹ and Valerie Pralong^{1,2}; ¹Normandie Université, France; ²CNRS ENSICAEN, France

The family of compound A_xM_{2n}O_{4n+2} (A = Li, Na, K and M a transition metal) are lamellar structure with zigzag arrangement (ie Na₂Ti₆O₁₃, K₂Ti₈O₁₇). They achieved very good property of ionic exchange due to their structure. Previously, the compound KTiNbO₅ have been studied for this property and the protonated phase and the lithiated phase have been form.

Here, we have explored the ionic exchanges of the phase K₃Ti₅NbO₁₄ phase. By topotactic reactions in an acid medium, the protonated phase H₃Ti₅NbO₁₄ could be prepared for the first time. By electrochemistry and by molten salt, we achieved the lithium insertion inside this structure. By dehydration of the H₃Ti₅NbO₁₄, we were able to stabilize the material the compacted phase Ti₁₀Nb₂O₂₅.

The structure of these new materials was resolved by precession of electrons in tomography mode, thus revealing the very strong family relationship between these structures.

This electrochemistry of this entire compound have been investigated. The Li₃Ti₅NbO₁₄ phase were able to reversibly exchange 3 lithium at 1.7V vs Li⁺/Li for a capacity of 120mAh/g

The synthesis, structure and properties of these families of materials will be discussed during our presentation.

ES03.02

Long-Range Ordering of Two-Dimensional Wide Bandgap Tantalum Oxide Nanosheets in Printed Films Melvin Timmerman, Rui Xia, Mark Huijben and Johan E. ten Elshof; Universiteit Twente Faculteit Technische Natuurwetenschappen, Netherlands

Two-dimensional oxide materials are a well-studied, interesting class of materials, enabled by the fact that their bulk layered metal oxides, such as titanates and niobates, can be easily exfoliated within minutes into 2D nanosheets. However, some promising oxide materials, such as tantalum oxide, are much more difficult to delaminate, taking several weeks, due to the higher charge density resulting in stronger Coulombic interactions between the layers. This intrinsic constraint has limited detailed studies for exploiting the promising properties of tantalum oxide 2D nanosheets towards enhanced catalysis and energy storage. Here, we have studied in detail the exfoliation mechanism of high charge density 2D materials, specifically tantalum oxide (TaO₃) nanosheets.¹ Single monolayers of TaO₃ nanosheets have been achieved by Langmuir–Blodgett deposition, while thicker layers (ranging from several tens of nanometers up to microns) exhibiting long-range ordering of the present nanosheets have been realized through inkjet printing. Interestingly, scanning tunneling microscopy analysis indicated a wide bandgap of ~5 eV for the single TaO₃ nanosheets as well as the density of states. This bandgap is significantly higher than the reported values between 3.5 and 4.3 eV for the layered RbTaO₃ parent compound, and opens up new opportunities for 2D oxide materials.

One area of application for TaO₃ nanosheets is its utilization in Li-ion batteries. Research on TaO₃ nanosheets as a barrier layer on commercial electrode foils and separators, and 2D TaO₃ nanosheets vs 3D TaO₃ bulk material as an electrode is currently being conducted. The most recent progress will be presented.

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ES03.03

Elemental Inhomogeneity the Cause of Ga-Doped LLZO Failure? Nomaan Nabi; Imperial College London, United Kingdom

Currently, a vast amount of research into fast lithium-ion conductors is taking place for application into solid electrolytes. The most attractive compositions are from the garnet family with the chemical composition of Li₇La₃Zr₂O₁₂ [1]. LLZO has high lithium-ion mobility at room temperature, a large electrochemical window that allows high voltage cathodes to be employed and good stability with lithium metal anodes. Typically, LLZO is doped at the lithium position with donor cations these include Al³⁺ and Ga³⁺ which provide stability of the cubic crystal phase thus allowing Li⁺ mobility in three dimensions. The mobility for Ga-LLZO has been reported to be above 10⁻³ S.cm⁻¹ [2], [3] this is the composition that will be mainly focused on in the poster.

Preliminary investigations have shown that due to lithium loss during high processing temperatures oxygen vacancies are formed because of the charge compensation mechanism[4]. The quantification of oxygen vacancies as an effect of the processing conditions and its effect on the conductivity of oxygen and lithium ions have been investigated in this work using electrochemical impedance spectroscopy and cell cycling.

The effect of different densification atmospheres (Ar, Vac, and O₂) on oxygen vacancies are measured using ¹⁸O isotopic labelling coupled with the Time of Flight Secondary Ion Mass Spectrometer (ToF-SIMS) to assess which results in a higher degree of oxygen defects and elemental segregation. This work will be correlated with lithium defect chemistry and mobility to understand the lithium critical current density for dendrite growth which are detrimental to battery life.

ES03.04

Studies on Electrochemical Performance of Co and Fe-Doped CuO Nanostructured as Electrode Material Beer Pal Singh¹ and Rahul Singhal²; ¹Chaudhary Charan Singh University, India; ²Central Connecticut State University, United States

In this research work presents, a facile and cost-effective co-precipitation method to prepare doped (Co & Fe) CuO and undoped CuO nanostructures. The X-ray Diffraction (XRD) analysis of as-prepared samples reveals monoclinic crystal structure of synthesized pure CuO and doped-CuO nanostructures. Field-Emission Scanning Electron Microscopy (FESEM) with Energy Dispersive X-ray Analysis (EDAX) was used to study the morphology and elemental composition of doped (Co & Fe) CuO and undoped CuO nanostructures. The effect of different morphologies on the electrochemical performance of supercapacitors has been found in CV (cyclic voltammetry) and GCD (galvanic charge discharge) investigations. The specific capacitances have been obtained 156 (±5) Fg⁻¹, 168(±5) Fg⁻¹ and 186 (±5) Fg⁻¹ for CuO, Co-doped CuO and Fe-doped CuO electrodes, respectively at scan rate of 5 mVs⁻¹, while it is found to be 114 (±5) Fg⁻¹, 136 (±5) Fg⁻¹ and 170 (±5) Fg⁻¹ for CuO, Co-CuO and Fe-CuO, respectively at 0.5 Ag⁻¹ as calculated from the GCD. The supercapacitive performance of the Fe-CuO nanorods is mainly attributed to the synergism that evolves between CuO and Fe metal ion. The Fe-doped CuO with its nanorods like morphology provides higher specific capacitance value and excellent cyclic stability among all studied nanostructured electrodes. Hence, Fe-doped-CuO nanostructures may be consider as a promising electrode material in supercapacitors.

ES03.05

Towards High-Capacity 3D Thin-Film Batteries—Atomic Layer Deposition of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ Jan Speulmanns, Sascha Bönhardt, Malte Czernohorsky and Wenke Weinreich; Fraunhofer IPMS, Germany

Atomic layer deposition (ALD) of lithium (Li)-compound thin-films has aroused significant interest in recent years. Promising applications are Li-ion thin-film batteries (TFB), protective particle coatings, interface model systems, and neuromorphic computing [1,2]. Here, we evaluate the performance of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (LTO) fabricated by ALD for three-dimensional (3D) solid-state TFBs to power upcoming autonomous sensor systems.

The simultaneous increase of power and energy density of full cell 3D TFBs by coating the battery layer stack over microstructured substrates was recently demonstrated [3]. The required conformal, pinhole-free deposition and stoichiometric control of nanometer-thin films on highly structured surfaces are only accessible via ALD. The vapor-phase technique based on sequential, self-limiting surface reactions is well understood. However, the direct deposition of Li-compound anodes remains challenging [1].

In previous studies, we developed a thermal three-step ALD process for Li-containing mixed oxides on 200 mm silicon wafers [4, 5]. Lithium-tert-butoxide (LTB) and lithium hexamethyldisilazide (LiHMDS) were both proven as suitable precursors forming high-quality spinel LTO with low impurities after rapid thermal processing. The electrochemical behavior of ALD LTO was evaluated for the first time and linked to the film texture [5].

Here, we compare the performance of ALD LTO in 2D and 3D geometries. Planar 30 nm films reveal capacities close to the theoretical value of 600 mAh cm^{-2} at 1 C. Outstanding power capabilities are achieved with around 50 % of the maximum capacity at extreme rates of 200 C. Outstanding cycle performance is demonstrated, exhibiting only 2 % capacity loss after 1000 cycles at 100 C. Excellent conformality and adhesion of ALD LTO in 3D hole structures with high aspect ratios of up to 20:1 will be presented. The resulting increase in energy and power footprint density will be discussed. The superior performance of ALD LTO, compared to other deposition techniques, is a key enabler for scalable high-volume production of high-power 3D TFBs.

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ES03.06

Fluoride Ion Conductivity of Cs-Doped KSbF_4 Kazuaki Kawahara¹, Ryo Ishikawa¹, Naoya Shibata^{1,2} and Yuichi Ikuhara^{1,2}; ¹Tokyo Daigaku, Japan; ²Ippan Zaidan Hojin Fine Ceramics Center, Japan

All solid-state fluoride ion batteries (FIBs) are considered to be higher energy density and safer energy storages than the current lithium ion batteries. There is a serious issue for practical use of FIBs i.e., the F^- ion conductivities of solid electrolytes at room temperature are quite low ($< 10^{-6}$ S cm^{-1}), and operating temperature of FIB should be 420 K or higher. Therefore, the faster F^- ion conductors is strongly desired to operate FIB at room temperature. Potassium tetrafluoroantimonate (KSbF_4) is an air stable F^- ion conductor that can be synthesized from aqueous solution. In this study, we doped Cs into KSbF_4 to expand conduction pathways in volume, and we investigated the composition dependence of F^- ion conductivity of $\text{K}_{1-x}\text{Cs}_x\text{SbF}_4$ by using electrochemical impedance spectroscopy. We found that F^- ion conductivity strongly depends on the chemical composition and conductivity is maximized at $x = 0.08$. The F^- ion conductivity at room temperature in the bulk and at the grain boundary at $x = 0.08$ were $\sigma_{\text{bulk}} = 1.06 \times 10^{-4}$ S cm^{-1} and $\sigma_{\text{GB}} = 8.12 \times 10^{-4}$ S cm^{-1} , respectively. This presentation is based on results obtained from a project, JPNP21006, commissioned by the New Energy and Industrial Technology Development Organization (NEDO).

ES03.07

A Systematic Study on Structure, Ionic Conductivity and Air Stability of Li_4SnS_4 – Li_3PS_4 Solid Electrolytes Misae Otoyama, Kentaro Kuratani and Hironori Kobayashi; Sangyo Gijutsu Sogo Kenkyujo Kansai Center, Japan

Sulfide solid electrolytes (SEs) have attracted much attention because they show high ionic conductivity and deformability. However, sulfide SEs have an issue of low air stability. Therefore, the development of sulfide SEs with high air stability is required. Recently, Zhao *et al* reported that Sn-substituted Li_3PS_4 ($\text{Li}_{3-2x}\text{P}_{0.8}\text{Sn}_{0.2}\text{S}_4$) glass-ceramic shows high ionic conductivity of 1.21×10^{-3} S cm^{-1} at 25°C [1]. In addition, the glass-ceramic exhibits higher air stability than Li_3PS_4 glass-ceramic because it contains air stable Sn–S bonds [1]. For the further material research, in the present study, we prepared $x\text{Li}_4\text{SnS}_4 \bullet (1-x)\text{Li}_3\text{PS}_4$ glasses/glass-ceramics and evaluated their structure, ionic conductivity and air stability systematically [2].

The $x\text{Li}_4\text{SnS}_4 \bullet (1-x)\text{Li}_3\text{PS}_4$ solid electrolytes were prepared by ball-milling. X-ray diffraction (XRD) patterns of as-milled samples with $x = 0-0.5$ and $x = 0.6-1$ showed halo patterns and diffraction peaks of hexagonal Li_4SnS_4 , respectively. Glass-ceramics with $x = 0-0.5$ were prepared by heat treatment of corresponding glass samples. Lattice parameters of glass-ceramics increased with increasing x value. Ionic conductivities of glass-ceramics with $x = 0.1-0.3$ increased to $8-9 \times 10^{-4}$ S cm^{-1} compared with corresponding glasses. From the results of Raman spectroscopy and PDF analysis, glass-ceramics have ordered PS_4 and SnS_4 tetrahedra, suggesting that this ordered structure is one of the reasons of high ionic conductivity. To examine air stability of the samples, H_2S gas generation from aqueous solutions of SEs was monitored. Air stability improved on increasing the amount of Li_4SnS_4 . Moreover, the H_2S amount generated from the sample with $x = 0.3-1$ remained unchanged both before and after the test. Therefore, glass-ceramic with $x = 0.3$ showed both high ionic conductivity and air stability. Cycle performance of all-solid-state batteries with the prepared glass-ceramics will be discussed in the presentation.

Acknowledgement

This work was supported by JSPS KAKENHI Grant Number JP20K22558. The PDF analysis was supported by Masatsugu Yoshimoto and Hikari Takahara (Rigaku Corp.).

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ES03.08

Synthesis of $\text{Na}_{3-x}\text{P}_{1-x}\text{W}_x\text{S}_4$ ($0 < x < 0.20$) Superionic Conductors for All-Solid-State Sodium Batteries Akira Nasu, Fumika Tsuji, Kota Motohashi, Atsushi Sakuda, Masahiro Tatsumisago and Akitoshi Hayashi; Osaka-fu, Japan

All-solid-state sodium batteries are a potential secondary battery with high safety and energy density. Sulfide-based solid electrolytes such as Na_3PS_4 glass-ceramic^[1] have advantages of good formability and high sodium-ion conductivity. Recently, we have reported the partial substitution of Sb^{5+} with W^{6+} in Na_3SbS_4 extremely increased the conductivity up to $3.2 \times 10^{-2} \text{ S cm}^{-1}$ due to doping sodium vacancies.^[2] Additionally, the WS_4^{2-} tetrahedra enlarged the sodium Wyckoff site cages, leading to suppressing the diffusion barrier.^[3]

In this study, we introduced sodium vacancies to Na_3PS_4 electrolytes by partial substitution of P^{5+} with W^{6+} .^[4] These electrolytes were prepared using mechanochemical process and subsequent heat treatment. In a previous report, the similar composition of $\text{Na}_{3-x}\text{P}_{1-x}\text{W}_x\text{S}_4$ were synthesized by high temperature sintering and the obtained electrolyte having WS_2 impurities showed the high conductivity of $10^{-2} \text{ S cm}^{-1}$.^[5] In our process, the $\text{Na}_{2.85}\text{P}_{0.85}\text{W}_{0.15}\text{S}_4$ glass-ceramic electrolyte without WS_2 impurities was synthesized by low temperature at 220°C . The all-solid-state cells using the $\text{Na}_{2.85}\text{P}_{0.85}\text{W}_{0.15}\text{S}_4$ glass-ceramic electrolyte as a separator layer reversibly operated and showed a capacity of 140 mAh g^{-1} at a current density of 0.038 mA cm^{-2} . On the other hand, the $\text{Na}_{2.85}\text{P}_{0.85}\text{W}_{0.15}\text{S}_4$ electrolyte with WS_2 impurities, which was synthesized by high temperature annealing at 550°C , showed an irreversible charge-discharge profile in the all-solid-state cells. The homogeneous synthesis of $\text{Na}_{3-x}\text{P}_{1-x}\text{W}_x\text{S}_4$ via mechanochemical process are important for application to all-solid-state sodium batteries.

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ES03.09

Size Effect of All-Solid-State Battery Performance with Pulverization of $\text{Li}_{10.35}\text{Ge}_{1.35}\text{P}_{1.65}\text{S}_{12}$ [Hanseul Kim](#), Kota Suzuki, Ryoji Kanno and Masaaki Hirayama; Tokyo Kogyo Daigaku, Japan

All-Solid-State Batteries (ASSBs) are attracting attention from many researchers as a next-generation battery due to the excellent thermal stability of solid electrolytes (SEs). Some sulfide-based SEs such as $\text{Li}_7\text{P}_3\text{S}_{11}$ (0.32 mS cm^{-1})^[1], $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ (12 mS cm^{-1})^[2], and $\text{Li}_{9.54}\text{Si}_{1.74}\text{P}_{1.44}\text{S}_{11.7}\text{Cl}_{0.3}$ (25 mS cm^{-1})^[3] exhibit the extremely high ion conductivities which are comparable to organic liquid electrolytes used in conventional lithium-ion batteries (LIBs). Now ASSBs with thick electrode configurations are expected to improve their energy densities, but their current densities are often limited due to poor ionic and/or electronic conductivities. Thus, the mechanical and morphological properties of the sulfide-based SEs are crucial to maintain the sufficient physical contact area between the active material and the SEs during charging and discharging. Several previous studies have succeeded in improving battery performance by controlling the particle size of sulfide-based SEs^[4,5]. In this study, we have succeeded in controlling the particle size distribution of $\text{Li}_{10.35}\text{Ge}_{1.35}\text{P}_{1.65}\text{S}_{12}$ with a LGPS type structure by ball milling with a non-polar solvent with very low reactivity. The structures and electrochemical properties of the size-controlled $\text{Li}_{10.35}\text{Ge}_{1.35}\text{P}_{1.65}\text{S}_{12}$ electrolyte and the composite cathode consisted of LiNbO_3 -modified LiCoO_2 and $\text{Li}_{10.35}\text{Ge}_{1.35}\text{P}_{1.65}\text{S}_{12}$ will be discussed. The average particle size of the wet-milled SEs were about $1 \mu\text{m}$ by the scanning electron microscopy (SEM) and particle size analyzer (PSA). According to the cross-sectional observation of the electrode, it was observed that the wet-milled SEs formed a better uniform mixing state with active materials and dense contacting interface than the hand-milled SEs. As a result, charge/discharge capacity and efficiency were improved by applying the wet-milled SEs to the electrode. Furthermore, many ion and electron paths formed by the contribution of the pulverized electrolyte enabled the operation of high-mass loading electrodes (thick electrodes) along with the high ion conductivity of the LGPS material. Therefore, the particle size control of LGPS material suggests the possibility of allowing the battery to reach a higher energy density as next-generation battery.

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ES03.10

Anhydrous Grotthuss Mechanism for Fast Proton Transport in Dense Oxide-Ion Array of $\alpha\text{-MoO}_3$ [Zihan Ma](#)¹, Xiang-Mei Shi¹, Shin-ichi Nishimura¹, Seongjae Ko¹, Masashi Okubo² and Atsuo Yamada¹; ¹Tokyo Daigaku, Japan; ²Waseda Daigaku, Japan

Developing high-power battery chemistry is an urgent task to buffer the fluctuating renewable energies for sustainable and flexible power supply. Owing to the small size of proton and its ultrahigh mobility in water via the Grotthuss mechanism, aqueous proton batteries are an attractive candidate for high-power energy storage devices. $\alpha\text{-MoO}_3$ possesses a unique bi-layered structure that is considered as a promising cathode material for proton batteries. However, H^+ intercalation behavior in $\alpha\text{-MoO}_3$ with various aqueous electrolytes remains controversial. Herein, coupled with a zinc anode, we provide the full comprehension of the H^+ intercalation in $\alpha\text{-MoO}_3$ as the cathode materials for aqueous $\text{Zn}^{2+}/\text{H}^+$ batteries.

$\alpha\text{-MoO}_3$ was synthesized by a hydrothermal method. To study the H^+ intercalation mechanism in $\alpha\text{-MoO}_3$, ZnCl_2 was selected as an electrolyte salt. In addition to the compatibility with a Zn anode, the high solubility of ZnCl_2 enables to form a superconcentrated liquid structure with limited free water molecules while the Brønsted acidity generates a low pH environment with high H^+ concentration. P_2O_5 was added to further decrease the free water amount and provide higher proton concentration, forming a dual-ion ($\text{Zn}^{2+}/\text{H}^+$) electrolytes (32 mol/kg ZnCl_2 and 1 mol/kg $\text{P}_2\text{O}_5/\text{H}_2\text{O}$). *In situ* XRD was performed to clarify the asymmetric structural evolution of the $\alpha\text{-MoO}_3$ electrode, DFT calculations on H^+ dynamics in $\alpha\text{-MoO}_3$ was conducted to understand the proton intercalation mechanism.

$\alpha\text{-MoO}_3$ electrode in the proposed aqueous $\text{Zn}^{2+}/\text{H}^+$ dual-ion electrolyte delivers a large capacity of 465 mAh/g at a rate of 0.5 A/g during the first discharge, corresponding to 2.5 H^+ intercalation per the formula unit of MoO_3 with an average voltage of approximately 0.9 V . It retains 98% of the initial capacity after 1000 cycles at a rate of 2 A/g , 62% of the specific capacity at 1 A/g is available at the fast discharge rate of 16 A/g . These performances indicate the stability of the MoO_3 framework against (de)protonation as well as the fast proton diffusion therein. Indeed, climbing image nudged elastic band (CI-NEB) calculations revealed that H^+ rotates and hops consecutively with a low energy barrier of 0.13 eV at the beginning of protonation, that could be explained by a solid-state anhydrous Grotthuss mechanism. Contrary to the conventional intercalation chemistry that requires a porous host that accommodates ion diffusion and storage, the solid-state anhydrous Grotthuss mechanism enables fast H^+ transfer and accumulated H^+ storage in dense oxide-ion arrays. This study gives hint for further exploration for other host materials capable of H^+ intercalation.

ES03.11

Super Halogen Based Double Anti-Perovskite Composite Electrolyte for Solid State Lithium-Metal Batteries [Md Momnin Islam](#); South Dakota State University, United States

Solid-state batteries are being widely explored to meet next-generation energy storage demand with a great potentiality of achieving high energy and power densities at All-solid-state Lithium-ion batteries (LIBs). In recent years, electronically inverted lithium-rich anti-perovskite (LiRAP) solid electrolytes with the formula Li_3OX , where X is a halogen or mixture of halogens have appeared as a prospective alternative of the commercially available flammable and corrosive organic liquid electrolytes because of their high ionic conductivity, structural variety and wide electrochemical window. Here, For the first time, we have successfully formulated and synthesized a completely new class of super halogen based double anti-perovskite named $\text{Li}_6\text{OS}(\text{BH}_4)_2$ using thin film methodology. As the earliest step, using density functional theory (DFT), the formation energy approach has been employed to determine the thermodynamically stability of $\text{Li}_6\text{OS}(\text{BH}_4)_2$. Experimental characterization supported the theoretical prediction that super halogen substitution of X (X= Cl, Br etc) leads to stabilization of the double anti-perovskite structure with a fairly low activation barrier for Li^+ diffusion. The solid-state $\text{Li}_6\text{OS}(\text{BH}_4)_2$ electrolyte membranes were produced by a drop casting method after successive ball-milling for about 5 hours and deposited on a Li metal anode. The electrolyte charge transfer resistances, electrochemical performance, and chemical stability in a half-cell configuration were evaluated over a broad frequency range from 1 MHz to 100 mHz. The symmetrical $\text{Li}/\text{Li}_6\text{OS}(\text{BH}_4)_2/\text{Li}$ cell performance was stable and ran around 1300 h without short circuit. The stable specific capacity of solid-state $\text{LiFePO}_4/\text{Li}_6\text{OS}(\text{BH}_4)_2/\text{Li}$ battery is as high as 132 mAh g^{-1} at 0.5 C. The advantages and disadvantages of designing and using the reported material in cutting-edge solid-state batteries are also explored. This new class of super-halogen based double anti-perovskite is a promising way to develop the compact solid electrolyte at low temperature for solid-state lithium-ion batteries.

ES03.12

High Performance Sulfur Cathode in Platelet N-Doped Mesoporous Carbon for All-Solid-State Lithium-Sulfur Batteries Jeong-Hoon Yu¹, Tianwei Jin², Byong-June Lee¹, Yuan Yang² and Jong-Sung Yu¹; ¹Daegu Gyeongbuk Institute of Science & Technology, Korea (the Republic of); ²Columbia University, United States

Lithium-sulfur batteries (LSBs) offer the possibility of five times higher theoretical energy density than state-of-the-art lithium-ion batteries. At present, however, LSBs with liquid electrolytes exhibit poor cycle life and low practical energy density owing to the severe polysulfides shuttling during cycling. The concept of solid-state electrolyte instead of liquid one has been conceived to prevent the migration of polysulfides and to improve the cycle life and safety. Thus, the solid-state LSBs have great potential not only for high energy density, but also for overcoming the troublesome polysulfide shuttling unavoidable for common LSB using organic liquid as electrolyte, resulting in high practical energy density, high efficiency and long cycle life. In this study, we report all solid-state LSBs made of homogenous composites of sulfur confined in platelet N-doped mesoporous carbon along with solid-state electrolytes such as $\text{Li}_6\text{PS}_2\text{Cl}$. Sulfur loading can be easily regulated between 15-70 wt% in the thin plate-like N-doped mesoporous carbon with high surface area of 1,540 $\text{m}^2 \text{g}^{-1}$. Homogenization of sulfur, carbon and solid electrolyte was efficiently carried out through vapor deposition of sulfur into the thin platelet porous carbon with short mesopore channels and ball milling of the full composite ensuring homogenization. The all solid-state LSB exhibits a high discharge specific capacity of 1410 mAh/g at 0.1C and room temperature, attributable to unique thin platelet mesoporous carbon with short mesopore channels and N doping good for easy and homogeneous filling of high amount of sulfur and effective function of $\text{Li}_6\text{PS}_2\text{Cl}$ solid-state electrolyte in the system. Atomic scale understanding of role of the solid-state electrolyte is further performed through theoretical quantum mechanical approach.

ES03.13

Proton-Conductive Coordination Polymer Glass for Solid-State Anhydrous Proton Batteries Nattapol Ma and Satoshi Horike; Kyoto Univeristy, Japan

Designing solid-state electrolytes for proton batteries at moderate temperatures is challenging as most solid-state proton conductors suffer from poor moldability and thermal stability. Crystal-glass transformation of coordination polymers (CPs) and metal-organic frameworks (MOFs) *via* melt-quenching offers diverse accessibility to unique properties as well as processing abilities. Here, we synthesized a glassy-state CP, $[\text{Zn}_3(\text{H}_2\text{PO}_4)_6(\text{H}_2\text{O})_3](1,2,3\text{-benzotriazole})$, that exhibited a low melting temperature (114 °C) and a high anhydrous single-ion proton conductivity ($8.0 \times 10^{-3} \text{ S cm}^{-1}$ at 120 °C). Converting crystalline CPs to their glassy-state counterparts *via* melt-quenching not only initiated an isotropic disordered domain that enhanced H^+ dynamics, but also generated an immersive interface that was beneficial for solid electrolyte applications. Finally, we demonstrated the first example of a rechargeable all-solid-state H^+ battery utilizing the new glassy-state CP, which exhibited a wide operating-temperature range of 25 to 110 °C.

SESSION ES04: Solid State Batteries III
Tuesday Morning, July 19, 2022
Lobby Level, Avenue 34, The Loft

9:10 AM **ES04.01

Enabling High-Rate Lithium Metal Anodes by Tailored Structures and Interfaces Eric Wachsmann^{1,2}; ¹University of Maryland, United States; ²Ion Storage Systems, United States

Oxide-based solid-state Li-batteries (SSLiBs) have the potential to be a transformational and intrinsically safe energy storage solution due to their non-flammable ceramic electrolyte that enables the use of high-capacity Li metal anodes and high voltage cathodes for higher energy density over a much wider operating temperature range. However, their progress has been limited due to electrode/electrolyte interfacial issues. In particular for Li-metal anodes concerns over dendrite formation/propagation and the requirement for elevated temperature and high stack pressure are still prevalent. To eliminate these concerns a rational design of tailored structures and interfaces in Li-metal anodes will be presented. In addition, progress toward full cells using these tailored structures and interfaces will be presented.

9:40 AM *ES04.02

In Situ Solidification for Forming Continuous Ion Transport Path Hong Li; Institute of Physics, Chinese Academy of Sciences, China

Developing lithium batteries with high energy density, high power density and safety is an effective strategy for improving the driving range of electric vehicles, decreasing the frequency of battery charge, and improving safety. Conventional lithium batteries with liquid electrolyte could increase specific energy density but bring serious safety concern due to high thermal runaway probability. All-solid-state batteries without any liquid electrolyte would theoretically improve the battery safety, because of the “nonflammable” character for solid-state electrolytes. However, all-solid-state batteries (ASSB) still face huge engineering challenges in materials selection, battery design, cell manufacturing, and cost control. It is difficult to create atomic scale solid-solid contact at electrolyte/active materials or electrolyte/electrode interface in ASSB. In our opinion, an effective solution to the current issues is to firstly develop lithium batteries with coexisting solid and liquid electrolyte, especially to develop hybrid solid-liquid electrolyte batteries based on in-situ

solidification technology. And then, it is possible to develop ASSB with deep understanding and precise control of in-situ solidification reactions (ISSR). The advantage of ISSR is to form continuous ion transport path. When the electrode particles and electrode layer expand and contract, the ion transport path between active particles and electrolyte phase should maintain atomic level contact t during thousands of cycling without external pressure. Obviously, ISSR is the most possible solution to achieve this target. The kinetic properties and stability of the hybrid solid/liquid system with ISSR are influenced by the type of solvents, salts and additives as well as solidification processing. Combining prelithiation, nanosized solid electrolyte coating on cathode, the cell can operate at wide temperature range with reasonable rate performance, cycle life and improved safety. Specific energies of the pouch cells are in the range of 150-360 Wh/kg, mainly depending on the selection of electrode and electrolyte materials as well as cell design and fabrication, formation processing. Some scientific and technological problems and progresses will be also discussed and reported.

10:00 AM ES04.03

Combining an *Operando* and an *Ex Situ* XPS Study to Explain the Aging Dynamics of Na Metal|NaSICON Interfaces in Solid-State Batteries Edouard Quérel¹, Nicholas J. Williams¹, Stephen J. Skinner¹ and Ainara Aguadero^{1,2}; ¹Imperial College London, United Kingdom; ²Instituto de Ciencia de Materiales de Madrid, Spain

To harness all the benefits of solid-state battery (SSB) architectures with regards to energy density, their negative electrode should be an alkali metal. Yet, the high chemical potential of alkali metals make most solid electrolytes (SE) unstable against them.[1] In that case, a decomposition layer called the "interphase" (which consists of various phases) forms at the metal|SE interface. Depending on its electronic properties, the interphase will either grow (if a majority of the phases in it are electronically conducting) or reach an equilibrium (if they are electronically insulating). In the case of an electronically conducting interphase, the decomposition layer will grow uninterrupted until all the SE is completely decomposed and a short-circuit occurs. Determining which type of interphase forms is therefore essential as the long-term stability of a SSB depends on it.

To obtain information about the dynamics and chemical composition of metal|SE interphases, a combination of electrochemical and chemical characterization is often employed: time resolved electrochemical impedance spectroscopy (EIS) can be used to monitor the dynamics at which the interphase grows (typically in symmetrical cell configurations); [2] and X-ray photoelectron spectroscopy (XPS) is often employed to determine the chemical composition of the interphase and predict its electronic properties. Analysing the composition of a buried interface is however a challenge because of the limited depth resolution of XPS. Recently, a variety of in-situ [2] and operando techniques [3] have been developed to address this problem. For all of them, the idea is to make an alkali metal layer thin enough so that photoelectrons emitted from the underlying SE and interphase can go through it.

In this presentation, we explore the electrochemical stability of the interface between Na metal (Na^0) and a solid electrolyte of the NaSICON family $\text{Na}_{3.4}\text{Zr}_2\text{Si}_{2.4}\text{P}_{0.6}\text{O}_{12}$ (NZSP). In particular, we explain how our EIS and *ex-situ* XPS results, whose conclusions about the nature of the interphase initially diverged, were reconciled by introducing a second XPS protocol which enabled to plate Na^0 *in-operando* on NZSP samples within our XPS instrument. We demonstrate that impurities in Na^0 electrodes can poison the Na^0 |NZSP interface and that the electrochemical signature of this poisoning should not be confused with the formation of a decomposition layer. Our study concludes more generally that impurities in alkali metal electrodes could play a pivotal (and often neglected) role in the aging dynamics of cells.

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3. Kevin N. Wood *et al* 2018 *Nat. Commun.* **9** (1), 1–10
4. Edouard Quérel *et al* 2021 *J. Phys. Energy* **3** 044007

10:15 AM ES04.04

Electrochemical Kinetics of Solid-Electrolyte Interphase Growth at the Na^0 /NZSP Interface Nicholas J. Williams¹, Edouard Quere¹, Ieuan D. Seymour¹, Stephen J. Skinner¹ and Ainara Aguadero^{2,1}; ¹Imperial College London, United Kingdom; ²Instituto de Ciencia de Materiales de Madrid, Spain

All-solid-state batteries containing an alkali-metal anode and a non-flammable solid-state electrolyte (SSE) can enhance the practical energy density and improve the safety of current Li-ion battery technology. However, issues still remain with the use of alkali-metal anodes and ceramic SSEs relating to mechanical issues such as cracking, as well as chemical issues such as decomposition alkali-metal/SSE interface resulting in the formation of a solid-electrolyte interphase (SEI).1

For all-solid-state sodium batteries, the Nasicon $\text{Na}_{1+x}\text{Zr}_2\text{Si}_x\text{P}_{3-x}\text{O}_{12}$ (NZSP)[IS1] family of materials are one of the most promising candidates for SSEs as they display both fast ionic conductivity and kinetic stability against Na metal (Na^0).^{2,3} The electrical properties of the SEI formed at the Na^0 /NZSP interface is integral for determining the activation polarisation of Na transport. X-ray Photoelectron Spectroscopy (XPS) is a powerful technique for understanding the nature of SEI phases formed during in-situ Na^0 plating, however, the interpretation of in-situ XPS spectra can be challenging due to the dynamic evolution of the Na^0 /NZSP interface.⁴ In this work we demonstrate how operando X-ray Photoelectron Spectroscopy (XPS) can be modelled to characterise the electrochemical performance of SEIs formed as Na^0 plated onto the NZSP surface. Due to relatively low concentrations and attenuation of photoelectrons passing through the Na^0 electrode, it is difficult to characterise its composition of the SEI during operando plating. We show how changes in photoelectron kinetic energy of the NZSP phase can be used to interpret the formation of new interfaces, and the integrated sodium metal peak area to describe the rate of electrode plating. By using this information, we may validate our plating simulations and rationalise the role of SEI components such as Na_3PO_4 on the rate of electrode plating. A kinetic model using coupled ion-electron transfer theory will further be discussed with describes the nonequilibrium thermodynamics of the driven system, where effects of auto-catalysis and auto-inhibition were directly observed.⁵ The models developed in this work are widely applicable for understanding the in-situ XPS spectra of alkali-metal plating and SEI growth in a diverse range of SSE systems.

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137432.

10:30 AM ES04.05

Fabrication of Thin Sheets of the Sodium Superionic Conductor $\text{Na}_5\text{YSi}_4\text{O}_{12}$ with Aqueous Tape Casting [Aikai Yang](#)^{1,2}, [Ruijie Ye](#)^{1,2}, [Qianli Ma](#)¹, [Frank Tietz](#)¹ and [Olivier Guillon](#)^{1,2}; ¹Forschungszentrum Julich GmbH, Germany; ²Rheinisch-Westfälische Technische Hochschule Aachen, Germany

Solid-state battery (SSB) technologies could be a game-changer with the advantages of improved safety and energy densities considering the replacement of flammable liquid electrolytes with stable solid-state electrolytes. Given the high deposits and low cost, all-solid-state sodium batteries (ASSNBs) will be more superior to lithium counterparts in the mass-energy-storage market. However, owing to the fact that the construction of SSBs is different from established lithium-ion batteries with organic electrolytes, their large-scale fabrication has prevented practical applications.

Herein, we developed an aqueous tape casting technique for the continuous fabrication of ceramic sheets made of silicate-based $\text{Na}_5\text{YSi}_4\text{O}_{12}$ (NYS) Na^+ ion superionic conductors for the first time. After sintering, the ceramics showed a total conductivity of 1.0 mS cm^{-1} at room temperature, low activation energy of 0.30 eV, and a wide electrochemical window of over 8 V. The obtained tape has high crystalline purity, dense microstructure, favorable mechanical properties (hardness H of 2 GPa and elastic modulus E of 45 GPa). The facile synthesis of NYS precursor powder and eco-friendly processing of aqueous tape casting make the fabrication of NYS tape low-cost and sustainable.

This work not only highlights the potential of the scarcely studied silicate-based NYS ionic conductor as a functional separator but also presents a cost-efficient and eco-friendly continuous fabrication using the aqueous tape casting technique, thus being expected to boost the practical application of NYS as the solid-state electrolyte in ASSNBs.

10:45 AM BREAK**11:00 AM *ES04.06**

Interfacial Characterizations and Designs for Polymer Electrolyte-Based Solid-State Batteries [Yuan Yang](#); Columbia University, United States

Solid-state batteries are attractive for next-generation energy storage as they have better safety and are potentially compatible with high-capacity lithium metal anodes. Solid polymer electrolytes have advantages of easy processing and low cost, but face challenges in interfacial stability with electrode materials and low conductivities. In this seminar I will present our recent studies on polymer electrolyte-based solid-state batteries. In the first part, I will discuss operando visualization of ion transport in electrolytes by an advanced stimulating Raman scattering microscopy, which provides fundamental understandings of electrolyte dynamics and electrolyte-electrode interactions. We clearly observed phase separation due to concentration polarization in the electrolyte, which leads to a new strategy to suppress lithium dendrites. In the second part, I will discuss how to stabilize the interface between polymer electrolytes and 4V NMC cathode. By applying a ceramic solid electrolyte coating onto NMC cathodes, the interfacial stability between polymer electrolytes and NMC cathodes are significantly enhanced.

11:20 AM *ES04.07

Perspectives on the Opportunity and Challenge of Solid-State Automotive Batteries [Raimund Koerver](#) and [Aron Varga](#); Bayerische Motoren Werke AG, Germany

With on-going electrification of vehicles, the demand for high-performant, safe and low-cost batteries is rising. While conventional lithium-ion batteries have been incrementally improved over the last decade, they will soon reach their physico-chemical limitation in terms of energy density. Especially for automotive applications, the energy density of lithium-ion technology might not be sufficient, and consumers look for improved range and faster charging times at competitive pricing.

Solid-state batteries, in which the liquid-soaked separator is fully or partly replaced by a solid electrolyte, are envisioned to serve as a future battery generation for electric vehicles. The application and integration of these solid-state batteries brings some advantages but also challenges. Especially from an automotive perspective, a key topic is battery safety. The reduction of flammable organic liquids shall make solid-state batteries even safer than the current generation of LIBs and allow for reduction of obsolete safety features on a battery pack level. Additionally, the cell size can be increased if the battery is intrinsically safe, which will further enhance the driving range of the respective vehicle. At the same time, solid-state batteries should enable the use of a lithium metal anode. Lithium, being light-weight and having the most negative electrode potential would offer a further increase in the energy density of battery cells. In practice, however, there are still hurdles to overcome: A homogenous lithium-deposition at high charging rates is challenging. Many solid-state concepts yet require a higher pressure or elevated operating temperatures when compared to their conventional liquid-based counterparts. The integration of such high-energy concepts, considering the product requirements and at the same time exploiting all the potentials of the technology, is a major challenge.

11:40 AM ES04.09

Innovative Single Ion Conducting Block Copolymer for Lithium Metal Batteries [Gabriele Lingua](#)^{1,2}, [Petr S. Vlasov](#)³, [Alexander S. Shaplov](#)⁴ and [Claudio Gerbaldi](#)^{1,2}; ¹Politecnico di Torino, Italy; ²Consorzio Interuniversitario Nazionale per la Scienza e Tecnologia dei Materiali, Italy; ³Sankt-Peterburgskij gosudarstvennyj universitet Institut himii, Russian Federation; ⁴Luxembourg Institute of Science and Technology, Luxembourg

The pressing demand for long-lasting, high-power portable electronics and the emerging large-scale diffusion of electric vehicles (EVs) and energy storage from renewable sources require batteries improved energy density at reduced cost, along with enhanced cycle life and safety. [1] State of the art Li-ion batteries (LIBs) currently on the market contain liquid electrolytes, which makes it difficult to design flexible cells, being also hazardous in terms of leakage and flammability. Within the context of solid-state battery technology development, a variety of solid-state electrolytes have been investigated to date; in principle, they enable extension of the operating temperature range of a device, also ensuring higher safety together with enhanced energy and power densities. Among solid polymer electrolytes (SPEs), the new class of "single ion conducting polymer electrolytes" (SICPEs) has deserved considerable attention. [2-4] Considering their intrinsic properties, this electrolyte family is considered one of the most promising solution among several solid-state electrolyte possibilities. In this work we focus on the development of a specific family of solid-state polymer electrolytes namely polyanions. The novel SICPEs demonstrated greatly enhanced performance towards the state of the art of solid-state systems in terms of mechanical properties and electrode compatibility.

Several polymerization techniques, including also living ones such as reversible addition-fragmentation chain transfer (RAFT) and ring-opening polymerization (ROP), were explored for the synthesis of different SICPEs. The novel solid-state polymer electrolytes were thoroughly characterized in terms of physico-chemical and electrochemical properties. Specifically, we focus on the development of poly(carbonate) macro-RAFT precursor by mean ROP that was further utilized to prepare a series of SICPEs comprising the methacrylate-based ionic monomer (LiMTFSI) and poly(ethylene glycol) methyl ether methacrylate (PEGM) via controlled RAFT polymerization. The novel true solid-state polycarbonate-based block copolymers show greatly enhanced performance towards the state of art of SICPE systems. The electrochemical behaviour of the new family of SICPEs is deeply investigated, including through the assembly of Li metal lab-scale cells using lithium iron phosphate (LFP) and Lithium-Nickel-Manganese-Cobalt-Oxide (NMC) catholytes. Furthermore, the effect of phase separation coming from partial incompatibility between blocks is investigated as well by mean performance

comparison with other SICPEs demonstrating that by mean optimal block copolymers structure design it is possible to achieve several advantages from mechanical/morphological and electrochemical point of views such as enhanced mechanical properties, elevate lithium ion transport, high electrochemical stability towards anodic potential and effective prevention of dendrite growth.

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11:55 AM ES04.10

Challenges Toward Solid-State Lithium-Sulfur Batteries—Transport and Reaction Current Distribution in Composite Cathodes with High Interfacial Area Density [Saneyuki Ohno](#); Kyushu Daigaku, Japan

The energy density of the ubiquitous lithium-ion batteries is rapidly approaching its theoretical limit. The replacement of conventional intercalation-type materials with conversion-type materials possessing substantially higher capacities is one of the promising strategies. An earth-abundant and cost-effective sulfur has a potential to be game-changing among conversion-type materials. Sulfur cathodes are attractive, especially in solid-state battery configuration, because the long-standing inherent problem of conventional lithium-sulfur batteries, arising from the reaction intermediates dissolved in liquid electrolytes, can be eliminated with inorganic solid ion conductors. The lab-scale solid-state lithium-sulfur cells have achieved close-to-theoretical capacities with highly conductive lithium-thiophosphates.

Nevertheless, there are challenges specific to solid-state lithium-sulfur batteries beyond the typical challenges inherent to solid-state batteries in general. The ionically and electronically insulating active material requires composite formation with solid electrolytes and electron-conductive additives to secure sufficient ion and electron supply at a triple-phase boundary. However, the compositing process makes the carrier transport pathways very tortuous and requires balancing and optimizing charge carrier transport to acquire the attainable energy density. Lastly, the requirement of a high interfacial area density to establish sufficient triple-phase boundaries promotes the degradation of the solid electrolytes. The formation of less-conductive interphases further deteriorates the transport in the composites.

This talk focuses on effective charge carrier transport within cathode composites and resulting inhomogeneous reaction current distribution in the thickness direction. Electrochemical monitoring of effective transport in the composites clarifies correlations between transport and cyclability, highlighting the need for quantitative measurements to address the composite carrier transport. Impedance spectroscopy combined with transmission-line model analysis as a function of applied potentials can visualize the stability window of good effective ion transport, showcasing the stability window from a transport point of view. The macroscopic transport limitation can further be corroborated with an operando neutron imaging technique, providing information on reaction current distribution. Overall, developments of even more conductive electrolytes or a cathode composite design principle facilitating fast ion transport within composites are necessary for further developments solid-state lithium-sulfur batteries.

12:10 PM ES04.11

Electronic Conduction Induced Dendrite Formation in Solid Electrolytes [Fudoong Han](#); Rensselaer Polytechnic Institute, United States

The successful integration of Li metal anode with solid electrolytes seems to be a must for a high-energy-density solid-state battery. However, Li dendrites tend to form in solid electrolytes during plating. The formation of dendrites has been observed in solid electrolytes with various crystal structures from glass, glass-ceramic, poly-crystalline to single-crystalline, but the mechanism of such an unexpected dendrite growth remains elusive. In this presentation, we introduce our understandings of lithium dendrite formation in solid electrolytes based on neutron depth profiling characterizations and electrochemical measurements of electronic transport properties of typical solid electrolytes. We highlight the important role of the electronic conductivity of solid electrolytes in the formation of isolating dendrites inside solid electrolytes. We will also discuss corresponding dendrite prevention strategies.

SESSION ES05: Solid State Batteries IV
Session Chairs: Moran Balaish and Yuan Yang
Tuesday Afternoon, July 19, 2022
Lobby Level, Avenue 34, The Loft

2:00 PM **ES05.01

Developments of Lithium-Ion Conductors with the LGPS Type Structure [Ryoji Kanno](#) and Satoshi Hori; Tokyo Institute of Technology, Japan

The solid electrolyte is a key issue for the development of all-solid-state batteries. Among the electrolytes proposed, the sulphide system is a candidate for practical use because of its high ionic conductivity. The LGPS ($\text{Li}_{10}\text{GeP}_2\text{S}_{12}$) electrolyte and its Si- and Sn- substituted phases exhibit a high bulk conductivity reaching $10^{-2} \text{ S cm}^{-1}$ at room temperature and hence are a promising solid electrolyte for batteries with high power and energy densities. Various derivatives of LGPS have been synthesized so far. The Si- and Sn- multi-substituted systems exhibit higher ionic conductivity than the parent crystal, while the LGPS-type phase in the Li-P-S system reported to serve as a separator facing Li metal anode. These substitutional systems form a group of LGPS materials, which provide a variety of ionic conductivity properties, electrochemical stability, and chemical stability. In this report, we give an overview of the various aspects for LGPS materials.

Conduction mechanism: Based on the phase diagram, single crystals of LGPS have been grown. The structure was determined by neutron single crystal structure analysis. Using this structural information and first-principles calculations, the ion conduction mechanism was investigated. The analysis indicated the collective motion of the ions would suppress the diffusion of single ion.

Synthesis: The LGPS materials with complex compositions are often difficult to synthesize as a single phase. The detailed study of the synthesis process based on the phase formation diagram is necessary. Precise synthetic studies of the system with the highest ionic conductivity, $\text{Li}_{9.54}\text{Si}_{1.74}\text{P}_{1.44}\text{S}_{11.7}\text{C}_{10.3}$, revealed that the presence of oxygen favors in obtaining a single phase and thereby increasing in ionic conductivity.

Moisture resistance: It is necessary to develop materials with high moisture resistance. The factors involved in water resistance were investigated in the $\text{Li}_{9.8}\text{P}_{3.8}\text{S}_{12.4}\text{O}_x$ system, which was taken as a model material for the LGPS system. The crystallinity was found to make a significant contribution. **Interfacial stability in solid-state batteries:** The interfacial reaction between the electrode and the electrolyte determines the battery properties. Clarification of the reactions between the electrode, the surface coating material, and electrolyte is necessary to obtain an excellent charge-discharge cycle. Model solid

state cells with LGPS electrolyte were investigated.

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2:30 PM *ES05.02

Solid-State Lithium-Metal Batteries at QuantumScape [Tim Holme](#); QuantumScape, United States

QuantumScape is developing a solid-state battery with a lithium-metal anode to enable long-range, faster charging, low-cost EVs. This talk will highlight recent developments in solid-state batteries as well as the challenges in commercializing a new battery technology. QuantumScape was founded in 2010 with a mission to revolutionize energy storage to enable a sustainable future.

2:50 PM ES05.03

Efficient Process Development and Component Design for Sulfide-Based All-Solid-State Batteries [Hans-Christoph Toepfer](#)^{1,2}, Tobias Kutsch², Robin Schuster² and Rüdiger Daub¹; ¹Technische Universität München, Germany; ²TUMint. Energy Research GmbH, Germany

The successful application of sulfide-based all-solid-state batteries requires cost-effective production technology and precisely designed components. This contribution addresses the impact of component properties and the resulting challenges for large-scale production technology in a quality-oriented production pathway optimization. Experimental results along the entire process chain are shown and serve as the basis for the process and product design and discussing the discrepancy between expected properties and currently achieved performance.

Sulfidic cell components are made in a slurry-based and scalable manufacturing route consisting of mixing, coating, drying, and pressing. Thereby, key component properties such as material composition and loading as well as process strategies are varied. For the holistic and quantitative evaluation and comparison, product-level specifications such as range and charging time of battery electric vehicles are broken down to quality criteria on the microstructural level. Ranging from porosity to microscopic properties such as particle distribution and interfacial contacts, a broad range of characteristics is covered. To evaluate each criterion, scanning electron microscope, mercury intrusion, and electrochemical impedance spectroscopy as well as novel and efficient characterization techniques involving image-based analysis including deep learning methods are applied.

As a result, the influence of component properties and processing strategy on the quality criteria is quantified providing the basis for the process and product optimization. In terms of manufacturing strategy, a multi-step dry mixing procedure is most decisive for achieving the quality criteria and execution of all following process steps. This is because both particle distribution and contact are set influencing characteristics such as homogeneity and porosity. In terms of component design, the ratio of active material to solid electrolyte and its loading most significantly affect the quality criteria. As for the mixing step, the porosity and homogeneity of the particle distribution strongly depend on them.

The experiments reveal that choosing the manufacturing and component design is complex and accelerated by applying a quality-oriented approach. Interactions between process strategies and parameters as well as material properties and compositions must be quantified and taken into account. Based on the quality-oriented approach, an optimized manufacturing procedure and component design are presented.

3:05 PM ES05.04

Influence of Powder and Nanowire LLZO Fillers on Electrochemical Properties of PEO Membranes [Mir Mehraj Ud Din](#)^{1,2} and Daniel Rettenwander^{1,2}; ¹NTNU Norwegian University of Science and Technology, Norway; ²International Christian Doppler Laboratory for Solid-State Batteries, NTNU Norwegian University of Science and Technology, Norway

A fundamental characteristic of PEO polymer solid-state electrolyte is the crystallinity that defines its physical properties. Presence of polymer crystallites in PEO which appear below the melting point leads to a catastrophic collapse of ionic conductivity¹. Therefore, control over the polymer crystallinity is vital to achieve Li-ion conductivity in PEO below its melting temperature^{2,3}. Here, Influence of the Li₇La₃Zr₂O₁₂ (LLZO) filler content (0, 10, and 20 wt.-%) and filler morphology (particles and nanowires) on the electrical and electrochemical properties of the PEO-based composite electrolytes with a constant conductive salt concentration of 31 wt.-%, was studied. Independent of the filler morphology, a decrease in the crystallinity was observed for 10 wt.-% filler compared to pristine PEO, in contrast to 20 wt.-% filler showing an increase in crystallinity. The change in the crystallinity is found to be well correlated with the Li-ion conductivity as measured by impedance spectroscopy. No indication of the participation of LLZO as an active transport mediator has been found. Membranes containing 10 wt.-% LLZO have been subsequently tested in terms of their rate capability in symmetrical Li cells by galvanostatic cycling. A critical current density of up to 1 mA cm⁻² at 60 °C was observed. Galvanostatic cycling was performed at 60 °C for half cells containing NCA cathode, PEO-10 wt.-% LLZO electrolyte and Li metal as anode. A continuous and erratic polarization was observed during charging of a cell above 4.1 V, which was believed to occur due to lithium dendrite formation. A relatively stable voltage profile was observed when limiting the upper cutoff voltage to 3.8 V. However, limiting the upper cutoff voltage resulted in lower capacity of nearly 100 mAh/g (C rate of 0.1C), indicating a compromise between stable cycling and practical energy density.

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Acknowledgments

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3:20 PM ES05.05

Deconvoluting Processing Effects on Interfaces in Solid-State Batteries [Justine Ruhl](#) and Wolfgang Zeier; Westfälische Wilhelms-Universität Münster, Germany

The commercial realization of promising all-solid-state batteries (ASSBs) demands up-scaling of materials synthesis and processing, resulting in growing interest for solution-based approaches.^{1,2} With this comes the need to more deeply understand potential detrimental effects of solvents used in the processes on electrolyte materials, as well as effects on the cell performance that may not have been evident by structural characterizations of the materials alone.

We have investigated the impact of five organic solvents on the superionic solid electrolyte $\text{Li}_6\text{PS}_5\text{Cl}$ (a member of the argyrodite family), observing structure/property changes and ultimately performance in solid-state battery cells. Ethanol and methanol decompose the material, while treatment with acetonitrile (ACN), tetrahydrofuran (THF), and toluene do not cause structural changes (as observed by X-ray diffraction and Raman spectroscopy). For this latter subset of treated materials, a decrease in the ionic conductivity can be observed; however, even the structurally sound material after treatment with toluene showed drastically reduced conductivity. $\text{In/LiIn} \parallel \text{Li}_6\text{PS}_5\text{Cl} \parallel \text{NCM-622:Li}_6\text{PS}_5\text{Cl}$ cells were assembled to study performance. Besides a decrease in the accessible capacities, the interface resistance of the active material and the electrolyte $R_{\text{SE/CAM}}$ is more pronounced, showing that seemingly compatible solvents can impact the cell performance. This work reveals the need for tailoring solution-based processing by detailed examination of the solvent impact on all cell components, helping pave the way for better understanding of ASSBs.³

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3:35 PM BREAK**4:00 PM *ES05.06**

Multiscale Investigation of Sulfide Based Solid Electrolyte Adrien Fauchier-Magnan¹, Patrice Perrenot², Emmanuelle Suard³, François Fauth⁴ and Claire Villeveille¹; ¹Laboratoire d'Electrochimie et de Physico-chimie des Materiaux et des Interfaces, France; ²Commissariat a l'energie atomique et aux energies alternatives Siege administratif, France; ³Institut Laue-Langevin, France; ⁴Consortio para la Construcción Equipamiento y Explotación del Laboratorio de Luz Sincrotron, Spain

All-solid-state batteries have been presented as the ideal solution to address i) the safety limitations of conventional Li-ion batteries by suppressing the flammable organic electrolytes and ii) the problem of insufficient energy densities. To date, two types of solid Li-ion electrolytes have been mainly studied, namely, sulfur-based and ceramic-based materials. As they are easy to process and they offer a high lithium ion conductivity in the range of 1-20 mS/cm [1,2], sulfide-based electrolytes such as e.g. thio-LISICONs and argyrodites are therefore regarded as suitable candidates to be used in lithium all-solid-state batteries.

Despite the progress in the development of superionic conductor, many aspects regarding their chemical and mechanical issues remain unsolved especially during electrochemical activities where the electrolyte is heavily decomposed [3]. If the electrode engineering i.e. composite electrode (mixture of electroactive material, conductive agent and solid electrolyte) is under intense investigation, the role of the solid electrolyte pellet (i.e. separator) is so far poorly studied. As an example, if the sintering (even cold sintering) is not properly performed, the Li-ion conduction will not be optimal that could create kinetics problem, as well as if voids appear in the solid electrolyte pellet, it will lower the ionic conductivity and the voids could then evolve and propagate into cracks during electrochemical cycling. Increasing the temperature to improve the sintering is quite often proposed as a solution since the porosity is then decreasing in the pellet and the grains more easily being joined reducing the grain boundaries resistance. However, the structural impact if the sintering is not yet fully understood, especially that the system Li-P-S is quite sensitive.

In this work, we are proposing an in depth (*operando* and *postmortem*) multiscale investigation of the parameter controlling the “shaping” of thiosulfate-based solid electrolytes and its consequence on the electrochemical activity. We gathered information from bulk to surface analysis using electrochemical (EIS, CV, etc.) X-rays (XRD, XAS, micro and nano-XRT, FIB-SEM, etc.) and X-ray/neutron-based diffraction techniques revealing the relationship between shaping and electrochemical performance. The results obtained here should serve as a preliminary basis to develop better solid-state batteries using sulfide-based electrolyte.

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4:20 PM ES05.07

On the Mixed Ionic-Electronic Conductivity in Co-Doped $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ System Jakub Burnos, Marcin Malys, Przemyslaw Michalski and Michał M. Struzik; Warsaw University of Technology, Poland

Amongst known solid Li-ion conductors, those exhibiting garnet structure are considered as attractive candidates for electrolyte materials dedicated for all-solid-state batteries, due to their thermal, structural, and electrochemical stability, considerably wide electrochemical window, stability against metallic lithium and high Li ion conductivity, comparable to some liquid electrolytes. Probably the best-known representative of this group of materials, $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$, shows high lithium-ion conduction in its cubic phase, which can be stabilized at room temperature by introduction of lithium vacancies using doping strategy. The role of the dopant species and its concentration on the phase stability and ionic transport has been led towards maximization of ionic transport and was widely investigated in recent years. As a result, highest lithium ionic conductivities have been observed in Al^{3+} and Ga^{3+} doped systems, reaching values of ca. $1 \times 10^{-3} \text{ Scm}^{-1}$. That value is still at least one order of magnitude lower than one observed in state-of-the-art liquid-based electrolytes, however taking into account possibility of the thickness reduction for ceramic electrolytes, $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ based materials may play a major role on the way to fully ceramic lithium-ion batteries.

Most of the research activities were directed towards reaching optimal conditions for fast ionic transport in $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$, therefore selection of explored in the literature dopants was limited to cations exhibiting fixed oxidation state. As a result, the possibility of intentional introduction of the electronic contribution to total conductivity has been barely explored.

In this work we explore the possibility of introducing such modifications to the crystal structure of a typical ion conductor, $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$, to introduce electronic contribution and to obtain mixed ion-electron conductor. In order to achieve that goal, we introduce transition metal cations simultaneously on La and Zr sites to form pathways for electronic conduction along the $\text{LaO}_8\text{-ZrO}_6$ chains in cubic garnet structure. We study on the powder processing, analyse the phase composition and crystal structure using XRD and Raman Spectroscopy; finally, we investigate on the electrical properties of new materials by

means of impedance spectroscopy and determine on the Li^+ and e^- transference numbers. In the end, we discuss the impact of the dopant concentration on the charge transport.

4:35 PM ES05.08

Enhancing the Interface Between Polymer Electrolyte and Li Metal in Solid-State Batteries [Ander Orue](#)¹, Mikel Arrese-Igor^{1,2}, Rosalia Cid¹, Nuria Gómez¹, Juan Miguel Lopez del Amo¹, William Manalastas³ and Pedro Lopez-aranguren¹; ¹Centro de Investigación en Energías Alternativas, Spain; ²Universidad del País Vasco, Spain; ³Nanyang Technological University School of Materials Science and Engineering, Singapore

High-voltage Li metal solid-state batteries are in the spotlight of high energy and power density devices for the next generation of batteries. However, the lack of robust solid-electrolyte interfaces (SEI) and the propagation of Li dendrites still need to be addressed for practical application with extended cyclability. In the present work, high-voltage Li metal cells with $\text{LiNi}_{0.6}\text{Mn}_{0.2}\text{Co}_{0.2}\text{O}_2$ active material were assembled with a polyethylene(oxide) based electrolyte mixed with bis(fluorosulfonyl)imide (LiFSI) salt. The addition of $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ garnet to form a composite electrolyte demonstrated the beneficial effect for cell cycling stability. Inspired by the improved interface of ceramic $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ garnet and Li metal, as well as by previous knowledge on favorable SEI forming species, various additive candidates were selected to optimize its electrolyte composition. Among them, lithium hydroxide (LiOH) is a key favorable specie that shows a relevant improvement on the cyclability of the cells. X-ray photoelectron spectroscopy showed that the SEI layer is composed mainly by chemical species arising from the reduction of the Li salt, being the lithium fluoride (LiF) the main product. In addition, solid-state nuclear magnetic resonance proved that LiOH induces the cleavage of the labile S-F bond, increasing the concentration of LiF. Herein, we highlight that SEI-forming additives need to be considered for the interfacial engineering design of stable SEI to expand the performance boundary of SSBs.

4:50 PM ES05.09

3D Operando High-Resolution Imaging of Inhomogeneous Electrochemical Reaction in Composite Solid-State Battery Electrodes [Yuta Kimura](#)¹, Su Huang¹, Takashi Nakamura¹, Nozomu Ishiguro¹, Oki Sekizawa², Kiyofumi Nitta², Tomoya Uruga², Tomonari Takeuchi³, Toyoki Okumura³, Mizuki Tada^{4,5}, Yoshiharu Uchimoto⁶ and Koji Amezawa¹; ¹Tohoku Daigaku, Japan; ²Kokido Hikari Kagaku Kenkyu Center, Japan; ³Sangyo Gijutsu Sogo Kenkyujo Kansai Center, Japan; ⁴Nagoya Daigaku, Japan; ⁵RIKEN Spring-8 Center, Japan; ⁶Kyoto Daigaku, Japan

Solid state batteries (SSBs) are one of the emerging options for next-generation energy storage systems because they could exhibit improved safety and high power/energy densities. In the composite SSB electrodes, particles of active material (AM) and solid electrolyte (SE) form intricate and three-dimensional (3D) ionic/electronic pathways. Furthermore, large interfacial resistances often occur in SSBs due to poor solid-solid contacts. Such complicated mass transport pathways with high resistance can locally cause a shortage of the ion- and/or electron- supplies in the electrode, especially at high current densities, leading to a 3D mesoscopic inhomogeneous reaction distribution involving a large number of AM particles as well as a microscopic reaction distribution within each single AM particle. Such inhomogeneous reactions can significantly deteriorate the capacity/power output of SSBs. Therefore, an understanding of the origin of the inhomogeneous reactions is important for the development of high-performance SSBs. However, the majority of existing techniques for analyzing such inhomogeneous reactions are based on one- or two-dimensional observations, and hence they provide only limited information regarding the 3D reaction distribution.

Herein, we developed an advanced imaging technique enabling 3D *operando* visualization of both meso- and microscopic inhomogeneous electrochemical reactions in electrodes with high resolution (~100 nm) based on our previously reported technique using computed-tomography with X-ray absorption fine structure spectroscopy (CT-XAFS) [1], and performed the *operando* observation of composite SSB electrodes. Furthermore, using the large dataset of both chemical and microstructural information (over 10^7 voxels and hundreds of AM particles) obtained by the 3D imaging, we quantitatively analyzed the origin of the reaction distribution formation.

As a model SSB, we prepared a bulk-type SSB with the configuration of 50 μm -thick LiCoO_2 (LCO)- $\text{Li}_{2.2}\text{C}_{0.8}\text{B}_{0.2}\text{O}_3$ (LCBO) composite cathode |LCBO electrolyte|PEO-based polymer electrolyte|Li metal anode. To achieve high spatial resolution, we performed the imaging CT-XAFS measurements near Co-K edge, employing an imaging optics consisted of a conical-shape mono-capillary beam condenser and an objective Fresnel zone plate. The 3D charging state distribution in the electrode was evaluated from the peak top energy of Co-K edge at each voxel.

We three-dimensionally visualized the electrochemical reactions in more than 200 LCO particles in the region of $50 \times 50 \times 50 \mu\text{m}^3$ in the composite SSB electrode during (dis)charge with the spatial resolution of ~100 nm. The electrochemical reaction was found to proceed inhomogeneously both in the entire LCO particle ensemble and in each single particle. To reveal the origin of the reaction distribution formation, we statistically analyzed the relationship between the electrochemical reaction and geometric features (*e.g.* coordinates, volume, and shape) of LCO particles. We found that the electrochemical reaction proceeded more inhomogeneously in LCO particles with larger volume and lower sphericity. These results were in sharp contrast to the (dis)charge behavior of LCO particles in liquid electrolyte, which is reported to exhibit the capacity close to the theoretical one even at high rates (~30 C) [2], *i.e.*, no reaction distribution is formed in single particle in liquid electrolyte. Therefore, the reaction distribution formation in LCO particles observed in this study could be a unique phenomenon caused by the use of solid electrolytes, which we will discuss further in the presentation. Our technique can provide deeper insights into inhomogeneous electrochemical reactions and enables us to rationally optimize composite electrodes.

Acknowledgements: This project was supported by JST-ALCA SPRING, Japan.

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5:05 PM ES05.10

$\text{Li}_{10}\text{GeP}_2\text{O}_{12}$ Electrolyte for All-Solid-State Batteries [Giuliana Materzanini](#)¹, Leonid Kahle^{2,3}, Aris Marcolongo^{2,3}, Tommaso Chiarotti^{4,2} and Nicola Marzari^{4,2}; ¹Universite catholique de Louvain, Belgium; ²National Centre for Computational Design and Discovery of Novel Materials, Switzerland; ³IBM RSM Zurich Research Laboratory, Switzerland; ⁴Ecole Polytechnique Federale de Lausanne, Switzerland

Superionic materials are ideal candidates to replace the conductive but flammable liquid organic electrolytes currently used, leading to prospectively safer all-solid-state batteries. Aiming to find highly conductive candidates that have the appealing electrochemical properties of an oxide, we study here extensively LGPO, the oxide analogue of LGPS, one of the best conducting solid-state electrolytes. We find that for LGPO a hypothetical tetragonal phase mirroring that of LGPS would be highly conductive. We thus employ isobaric-isothermal simulations to explore phase stability and phase transitions, while extracting from the trajectories the relevant elastic moduli.

5:20 PM ES05.11

Engineering Ion Migration at Cathode Electrolyte Interfaces for High Performance All-Solid-State Batteries [Yuxuan Zhang](#)¹, Thomas Kivevele², Han Wook Song³ and SungHwan Lee¹; ¹Purdue University, United States; ²Nelson Mandela African Institution of Science and Technology, Tanzania, United Republic of; ³Research Institute of Standard and Science, Korea (the Republic of)

Recent metal-ion batteries with liquid electrolytes still suffer from issues regarding inflammability and insufficient lifetime.¹ All-solid-state batteries (ASSBs) have promising potentials for the improved safety, higher energy density, and longer cycle life than conventional Li-ion batteries.² The nonflammable solid electrolytes (SEs) could prevent battery combustion and explosion since the side reactions that cause safety issues as well as degradation of the battery performance are largely suppressed. However, their practical application is hampered by the high resistance arising at the electrode–electrolyte interface.³ Several methods such as protection layer for metal anode and liquid phase metal have been introduced to optimize the contact capability as well as the electrochemical/chemical stability between the metal anode (typically Li or Na) and the SE, which exhibited decent results in decreasing the charge transfer resistance and broadening the range of the stable energy window.⁴ Nevertheless, mitigation for the cathode in ASSB is tardily developed because: (1) the porous structure of the cathode is hard to be infiltrated by SEs;⁵ (2) High charge state would oxidize and decompose SEs due to the high valence state elements at the surface of the cathode.⁵

Herein, we demonstrate a universal cathode design strategy to achieve superior contact capability and high electrochemical/chemical stability with SEs. Stereolithography is adopted as a manufacturing technique to realize a hierarchical three-dimensional (H3D) electrode architecture with micro-size channels, which is expected to provide larger contact areas with SEs. Then, the manufactured cathode is sintered at 700 °C in a N₂ atmosphere to accomplish the carbonization of the resin, delivering sufficiently high electronic conductivity. To avoid the direct exposure of the cathode active materials to the SEs, oxidative chemical vapor deposition technique (oCVD) is leveraged to build conformal and highly conducting poly(3,4-ethylenedioxythiophene) (PEDOT) on the surface of the H3D cathode.⁶ To demonstrate our design strategy, both NCM811 and Na₃V₂(PO₄)₃ are selected as active materials in the H3D cathode, then each cathode is paired with organic (polyacrylonitrile-based) SEs assembled into two batteries (i.e., with each of NCM811 and Na₃V₂(PO₄)₃). SEM and TEM reveal the micro-size H3D structure with built-in channels. Featured by the H3D architecture, the intrinsic kinetic and thermodynamic conditions are expected to be enhanced by larger surface contact areas, more active sites with improved infusion and electrolyte ion accessibility as well as larger volume expansion capability. Disclosed by X-ray CT, the interface between the cathode and SE in the four modified samples demonstrates higher homogeneity than that of all other pristine samples. Atomic force microscopy is employed to measure the potential image of the cross-sectional interface by the peak force tapping mode. The average potential of modified samples is lower than that of pristine samples, which confirms a weakened space charge layer by the enhanced contact capability. In addition, through electron energy loss spectroscopy coupled with scanning transmission electron microscopy, the preserved interface between H3D cathode and SE is identified. In addition, Finite element method simulations validate that the diffusion dynamics of lithium ions is favored by H3D structures. Such a demonstrated universal strategy provides a new guideline to engineer the cathode electrolyte interface by uniquely designing electrode structures that can be applicable to all solid-state batteries in a wide range of chemical conditions.

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5:35 PM ES05.12

Thermodynamic Aspects of LiCoO₂ Grain Growth on Li-Garnet Electrolyte Thin-Film for All-Solid-State Batteries Anatolii Morozov¹, Haemin Paik², Anton O. Boev¹, Dmitry A. Aksyonov¹, Svetlana A. Lipovskikh¹, Keith J. Stevenson¹, Jennifer Rupp² and Artem M. Abakumov¹; ¹Skolkovskij institut nauki i tehnologii, Russian Federation; ²Massachusetts Institute of Technology, United States

LiCoO₂ (LCO) is a commonly used cathode material for Li-ion batteries due to its high capacity and good cycling stability. Preparing desired phase and crystal orientation is particularly important for layered structure LCO to design a solid-state battery due to its confined Li ion diffusion pathway. Here, the atomic structures of thin (~500 nm) film of LCO grown on top of polycrystalline Ta-doped Li₇La₃Zr₂O₁₂ (Ta-LLZO) solid electrolyte by pulsed laser deposition (PLD) technique was investigated. Scanning transmission electron microscopy, electron diffraction and electron tomography demonstrated that the LCO film is formed by columnar elements with the shape of inverted cones. The film appears to be highly textured, with the (003) LCO crystal planes parallel to the LCO/Ta-LLZO interface and with internal pores shaped by the {104} and {102} planes. According to DFT calculations, this specific microstructure is governed by a competition between free energies of the corresponding crystal planes, which in turn depends on the oxygen and lithium chemical potentials during the deposition indicating that thermodynamics plays an important role in the resulting LCO microstructure even at non-equilibrium PLD conditions. Based on the thermodynamic estimates, the experimental conditions within the LCO stability domain are proposed for the preferential {104} LCO orientation, which is considered as favorable for enhanced Li diffusion in the cathode layers of all-solid-state batteries.

5:50 PM ES05.13

Ultrathin LLZO-Polymer Composite Solid Polymer Electrolytes for Solid-State Batteries P. Sivaraj, Sagar A. Joshi and Seema Agarwal; Universitat Bayreuth, Germany

The solid-state electrolytes play a crucial role in reducing the dendrite growth during the charge-discharge process and enable to use of Li metal as a superior anode material which also enhances the specific capacity and energy density of the solid-state batteries (SSBs). The design of low interface resistance without Lithium dendrite growth is a big challenge in the prototype SSBs. In this concern, a novel strategy has been employed to decrease the interfacial resistance by direct integration of garnet LLZO-porous polymer matrix on the electrode, which can eliminate the pore defects on the electrode surface and improve the electrode/electrolyte interface contact. The Lithium dendrite growth is reduced by crafting the ultrathin highly wetting polymer matrices on both sides of composite solid electrolytes, which can also prevent the electrolyte from being oxidized by the cathode during the charge-discharge process under high voltage. The influence of inorganic filler on ionic conductivity has been demonstrated. The LLZO-polymer electrolyte is exhibited an excellent ionic conductivity in the order of 10⁻³ S cm⁻¹ at 25 °C. The electrochemical stability of the composite solid electrolyte has been explored with LiFePO₄/C cathode and Li metal as anode. The LLZO-polymer composite would be well worth designing high-capacity/energy density batteries, especially for power batteries in EVs, to alleviate the greenhouse effect and improve the environment quality.

SESSION ES06: Poster Session II: Energy Storage II

Tuesday Afternoon, July 19, 2022

6:00 PM - 8:00 PM

Mezzanine Level, Second Floor, Stadler

Cycling Property of High-Crystalline $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ Cathode Tatsuya Nakamura¹, Takayuki Konya¹, Mitsuharu Tabuchi² and Yo Kobayashi³; ¹Hyogo Kenritsu Daigaku - Himeji Kogaku Campus, Japan; ²National Inst of AIST, Japan; ³Denryoku Chuo Kenkyujo Denryoku Gijutsu Kenkyujo, Japan

We successfully prepared $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ particles with high-crystallinity, high-purity and the stoichiometric composition, which were confirmed with X-ray diffraction, scanning electron microscopy and low-temperature magnetic measurement [1,2]. Additionally, the structural evolution of the high-voltage spinel compound was studied using the operando X-ray diffraction [2]. In this work, the electrochemical results about the charge-discharge cycling were presented and discussed, where three different anode materials were used to compare the cycling property. The electrochemical properties were measured using the cathode films (material loading of 10 mg/cm² and thickness of 30 μm), which were prepared by coating of NMP suspension containing cathode particle/carbon black/PVDF=86/7/7 (by weight ratio). 1.0M LiPF₆/EC-DMC (volume ratio of 3:7) was used as electrolyte solution. Various anode materials coupled with the cathode were applied: Li metal, MCMB graphite and $\text{Li}_4\text{Ti}_5\text{O}_{12}$. In the case of MCMB and $\text{Li}_4\text{Ti}_5\text{O}_{12}$ anode, the capacity ratio of anode/cathode was adjusted to 1.2. For Li metal anode, the discharge capacity during three formation cycles at 0.1C was attained to 141mAh/g. On the redox cycling under CCCV-charge/CC-discharge mode at 1C rate, the capacity retention after 100th cycle was 96%, where the CV charge capacity gradually increased (13 to 15mAh/g) with the cycle number, and the polarization also continuously increased (150 to 218mV). The kinetic limitation was thought to be one of the main reason for the capacity fading. For graphite anode, the charge/discharge capacity in the initial formation cycle was 148/124mAh/g; a large irreversibility due to the SEI formation. But on the cycling, the capacity retention after 100th cycle was 89%, where both the CV charge capacity and the polarization remained almost constant (13mAh/g and 170mV). The voltage profile analysis implied that the capacity slippage was a significant influence on the cycle degradation. And for $\text{Li}_4\text{Ti}_5\text{O}_{12}$ anode, the charge/discharge capacity in the initial formation cycle was 149/138mAh/g. On the cycling, the capacity retention after 100th cycle was 97%, where both the CV charge capacity and the polarization remained almost constant (12mAh/g and 170mV). X-ray diffraction analysis after the 100th cycling and cell impedance growth during the cycling are being carried out, and the results will be presented at the conference for discussion.

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ES06.02

Superior Lithium Dendrite Suppression Ability and Air Stability of Sc_2O_3 Substituted Li-Argyrodites Superionic Conductor and Admirable Cyclability in Lithium Solid-State Batteries Yuvaraj Subramanian and Kwang-Sun Ryu; University of Ulsan, Korea (the Republic of)

The lithium-ion battery is an inevitable energy storage device in our regular life that has been utilized in mobile phones, laptops, electric vehicles, and hybrid electric vehicles due to its excellent properties such as high cell voltage and energy density. Despite, commercially used Li-ion batteries working with the aid of flammable non-aqueous organic electrolyte thus makes an explosion of battery during the internal short circuit. Recently, the solid-state electrolyte contained lithium batteries can be considered as an effective energy storage system instead of non-aqueous Li-ion batteries because it possesses excellent properties such as non-flammable nature, good thermal stability at high temperature, large potential window, simplicity in battery design, low manufacturing cost and high compatibility with high cell voltage cathode materials. Nevertheless, sulfide solid electrolyte has a low critical current density that makes a failure of the battery within a few cycles due to fast lithium dendrite formation. So the metal oxide substitution on P and S-site argyrodite has been considered as an excellent strategy to enhance the interface stability and air stability. In this work, we enhance the interface stability of the Li-argyrodites using Sc_2O_3 substitution in P and S-site and evaluate their structural, atmospheric stability and, electrochemical performances. Here, the Sc_2O_3 substituted argyrodite and Li_2S deficient Sc_2O_3 substituted argyrodite are synthesized using high-energy ball milling followed by a calcination process. The structural analysis of the prepared argyrodite is examined using Rietveld refinement and NMR analysis. The prepared metal oxide substituted argyrodite shows the ionic conductivity of 3.80 mS cm⁻¹ which is slightly low (3.80 mS cm⁻¹) compared to bare argyrodites (4.91 mS cm⁻¹). However, it enhances the interface stability with lithium metal that exhibits a high critical current density of 0.6 mA cm⁻² than $\text{Li}_6\text{PS}_5\text{Cl}$ (0.2 mA cm⁻²). Also, it demonstrates the excellent DC cyclability at 0.2 and 0.3 mA cm⁻² after 200 cycles without a short circuit. Moreover, the air stability test reveals that the prepared solid electrolyte indicates sluggish reaction kinetics when exposed to dry air. In addition, the assembled solid-state battery delivers the high initial discharge capacity of 182.9 mAh g⁻¹, and the discharge capacity was retained over 97.5 % after 100 cycles and also demonstrates the high discharge capacity of 139.9 mAh g⁻¹ at 1C rate. The overall result confirms that the prepared electrolyte can be considered as a promising solid electrolyte candidate for Lithium solid-state batteries.

ES06.04

On the Electrochemical Stability of the Li-Electrolyte $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ Joseph R. Ring¹, Andreas Bumberger¹, Andreas Nanning¹, Markus Kubicek¹, Sergey Volkov², Vedran Vonck², Thomas Schachinger³ and Herbert Hutter¹; ¹Technische Universität Wien, Austria; ²Deutsches Elektronen-Synchrotron, Germany; ³Technische Universität Wien Institut für Festkörperphysik, Austria

Cubic $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZO) based garnet electrolytes are promising for solid state batteries, due to their high conductivity and stability towards Li-metal anodes. The stability of LLZO towards high voltage cathodes, however, is less clear. According to DFT calculations, the thermodynamic stability window of LLZO ranges only up to 3-3.3 V vs. Li⁰ [1], whereas experimental studies with ion blocking electrodes report a stability window up to 5-6 V vs. Li⁰ [2]. The practically usable voltage range of LLZO electrolytes is therefore an important unresolved question.

Recent studies have shown that LLZO undergoes electrochemical decomposition when a voltage of 5 V vs. Li metal is applied to an inert Au-electrode at 300 °C [3]. This decomposition happens via loss of oxygen evolution and Li-depletion. Subsequent structural instability results in the formation $\text{La}_2\text{Zr}_2\text{O}_7$ and La_2O_3 . At the cathode, Li-ions and electrons react with the atmosphere forming Li-salts such as LiOH, Li_2O or Li_2CO_3 . These studies clearly show the instability of LLZO at high potentials, but the detailed decomposition mechanism is still only partly understood.

For this, we conducted in-situ synchrotron XRD experiments to further elucidate the structural changes during degradation of LLZO. Direct voltages were applied between microstructured working electrodes and macroscopic counter electrodes to observe time-resolved structural changes caused by the electric field stress. Afterwards, O¹⁸-tracer exchange experiments with subsequent secondary ion mass spectroscopy (SIMS) analysis was performed to gain information about possible changes of oxygen vacancy concentration. Furthermore, by means of transmission electron microscopy (TEM) and electron energy loss spectroscopy (EELS), more detailed structural and chemical information about the decomposed LLZO was obtained. These findings contribute to a better understanding of the electrochemical decomposition of LLZO and show that an amorphization is taking place before the formation of a $\text{La}_2\text{Zr}_2\text{O}_7$ phase.

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15237.

ES06.05

Interpreting Impedance Spectra of Li-Intercalation Thin Films [Andreas Bumberger](#), Claudia Schrenk, Matthias Kogler, Andreas Nennung and Juergen Fleig; Technische Universitat Wien, Austria

Solid-state diffusion in lithium intercalation compounds is one of the most fundamental processes determining the overall kinetics in lithium-ion cells and placing practical constraints on the composition and morphology of composite electrode coatings. Thin films of lithium intercalation compounds offer a suitable platform for the extraction of the underlying intrinsic material properties from electrochemical impedance spectra. However, the equivalent circuit models commonly applied to extract solid-state diffusion parameters from impedance spectra rely on the so-called open Warburg element [1] that is derived from Fick's law under the limiting assumption of negligible electronic resistance. This Warburg element is incorporated into the intuitively derived Randles equivalent circuit [2] to describe the impedance behavior of lithium intercalation electrodes.

In this work, we apply the generalized transmission line model proposed by Jamnik and Maier [3] to the specific case of lithium intercalation materials and thus also go beyond the assumptions underlying the traditional Randles model by considering both electronic and ionic resistances in the material. It is shown how in the absence of electrical potential gradients, the transmission line model explicitly maps ionic resistance, chemical capacitance, charge transfer resistance and interfacial double layer capacitance onto an equivalent circuit that is identical to the Randles circuit. Upon the introduction of electrical resistances, the circuit not only transforms beyond the assumptions of the Warburg element, but also requires the consideration of four distinct interfacial terminals instead of the simplified two-terminal connectivity in the classical Randles model. We further discuss the relationship between ionic and electronic resistances, chemical capacitance and the ambipolar diffusion coefficient with regard to impedance spectra and charge/discharge curves of common intercalation electrode materials.

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ES06.06

Enhanced Ionic Conductivity and Electrochemical Stability of poly(ethylene oxide) Electrolyte by Multiple-Functional Metal-Organic-Framework Fillers for Solid-State Lithium Batteries [Jeong Jae Kim](#), Cheol Hyoun Ahn, Won Seok Yang and Hyung Koun Cho; Sungkyunkwan University, Korea (the Republic of)

Abstract

Rechargeable lithium-ion batteries are widely used in the predominant energy storage technology, owing to their high specific energy, good capability, good cycle performance and environmentally friendly property. With the growing demand of smart electronics and electric vehicle, developing high energy-density batteries without flammable and explosive issue come into request. The replacement of conventional carbonate based liquid electrolytes with solid state electrolyte have been accepted to be one good approach. [1]

Among solid-state electrolyte, polymer-based solid electrolytes such as poly(ethylene oxide) (PEO) are now becoming increasingly attractive for lithium-ion batteries, because of their excellent properties such as safety, mechanical properties, and flexibility. However, polymer-based electrolyte cannot meet the commercial requirements due to their inherent issues, such as low electrochemical window, high interface impedance, and low ionic conductivity. The compositing with inorganic filler and PEO has been received to promising approach, as they show a high ionic conductivity and are stable under relative high voltage.

Recently, metal-organic frameworks with permanent porosity and highly ordered structures have emerged as promising materials for many applications, including catalyst, energy storage technologies. In addition, MOFs as fillers in polymer-based solid-state electrolyte have emerged with improved ionic conductivity and stability. [2]

In this work, we report the effects of metal-organic-framework (MOF) fillers in PEO-based solid electrolytes. Interestingly, MOF@PEO solid state electrolytes showed the enhanced ionic conductivity, electrochemical window, lithium-ion transference, and long-term stability, that of PEO electrolyte. We found that the multi-functional MOF provides numerous functional groups, which can enable to modulation on structural/chemical properties of PEO.

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ES06.07

The Influence of Mg and Li Substitutions on Structural, Transport and Electrochemical Properties of Sodium-Manganese Layered Oxide as a Cathode for Na-Ion Batteries [Gabriela K. Wazny](#), Katarzyna Walczak and Janina Molenda; Akademia Gorniczo-Hutnicza imienia Stanislaw Staszica w Krakowie Wydział Energetyki i Paliw, Poland

In the perspective of continuous search of high energy density cathode materials for Na-ion batteries, agents activating oxygen redox seem to be especially promising. Here we present a complex investigation of two substitutions that affect crystal and electronic structure in layered $\text{Na}_{0.67}\text{MnO}_2$ significantly: Mg and Li.

The samples were synthesized via the sol-gel method using acetates and sucrose as a fuel. The crystal structure was determined using X-Ray diffractometry, and transport properties were investigated by electrochemical impedance spectroscopy. The most promising compositions were used as active materials and mixed with carbon black and PVDF to prepare cathode layers. Then, the CR2032-type coin cells were assembled in an argon glovebox with high purity, using metallic sodium as an anode and 1M NaPF₆ in EC:DEC as an electrolyte. The electrochemical performance was tested using cyclic voltammetry and cyclic charge/discharge techniques. Cyclic voltammetry allowed also to calculate chemical sodium diffusion coefficient using the Randles-Sevcik equation. Changes in the crystal structure in selected samples during cell performance were inspected via ex-situ and in-situ XRD measurements. X-ray absorption spectroscopy allowed us to determine oxidation states of transition metal in selected samples and take a look at the changes in oxygen behavior during cycling.

All investigated materials crystallize in a P2-type layered structure, described as P6₃/mmc or P6₃/mcm space groups. X-ray diffraction measurements of cathode materials in the batteries showed that Mg substitution stabilizes the crystal structure significantly, preventing phase transition during cycling. Mg substitution allows for better capacity retention than Li substitution, reaching 112% of theoretical capacity for $\text{Na}_{0.67}\text{Mg}_{0.25}\text{Mn}_{0.75}\text{O}_2$ in the first discharge, followed by 105% in the next one. XAS measurements of $\text{Na}_{0.67}\text{Mg}_{0.2}\text{Mn}_{0.8}\text{O}_2$ samples confirmed changes in oxygen K-edge spectra during the charging/discharging processes. The characteristic plateau on the first charge on charge/discharge plots can be associated with the activation of oxygen-related electrochemical processes. The first charge suggests the irreversible character of the anionic redox process, which is confirmed by the cyclic voltammetry. This behavior applies to the whole $\text{Na}_x\text{Mg}_y\text{Mn}_{1-y}\text{O}_2$ system with various amounts of Mg, to a greater or lesser extent. The mechanism, however, is different for Li-substituted Na_xMnO_2 . It is because alkali metal in transition metal sublattice affects the electronic structure differently. To some extent, this phenomenon is visible in cyclic voltammetry and cyclic charge/discharge plots: cyclic voltammetry shows plenty of irregular peaks,

which reflect irregular charge/discharge curves.

A complex analysis of Mg- and Li-substituted Na_xMnO_2 system properties gives a huge insight into the work mechanisms induced by such different elements. This approach can have a great impact on designing and understanding advanced cathode materials for Na-ion batteries as eco-friendly and safe post-lithium batteries generation.

ES06.08

Unrevealing the Mechanism of Antimony-Based Anodes Sodiation Through the Operando and Ex Situ Measurements in Na-Ion Batteries [Justyna Plotek](#), Andrzej J. Kulka and Janina Molenda; Akademia Gorniczo-Hutnicza imienia Stanislawia Staszica w Krakowie Wydział Energetyki i Paliw, Poland

The market of energy storage systems has been dominated by Li-ion batteries since their commercialization in 1991. However, the limited resources in the earth's crust of used elements intensify the search for an alternative technology. Na-ion batteries appear as a very promising solution to this problem. They are characterized by a lower energy density, but, on the other hand, they can be successfully used for large-scale energy storage, the technology required for renewable energy production. One of the biggest bottlenecks in the commercialization of Na-ion batteries is the lack of appropriate anode material. Quite recently, the novel concept of anode materials based on alloying-type Na-storage mechanism has emerged. This electrochemical process is characteristic for elements of 14 and 15 groups of the periodic table which form various Na-Me (Me- metal, metalloid) alloys reversibly. Among them, antimony stands out with its high electrical conductivity and also the high theoretical capacity of 660 mAh/g. However, it is not flawless: with volume changes up to 293% and severe microstructure degradation, poor cyclability is inevitable. The prospective strategy to overcome these obstacles is to synthesize sub-micron and nanosized composites of antimony with carbon.

This work aims to elucidate the sodiation and desodiation mechanism of the antimony-carbon composite synthesized via solvothermal reaction. The composite enables good reversibility of the electrochemical reaction in comparison to material without carbon additive. Operando and ex-situ measurements revealed processes hidden during the discharge and charge processes.

The structure of the material was characterized through X-ray diffraction with Rietveld refinement and Raman spectroscopy. The main phase in the as-obtained sample was found to be rhombohedral antimony (R-3m space group), with the second monoclinic phase of $\text{Sb}_4\text{O}_5\text{Cl}_2$ (P21/a space group). However, this impurity is not detrimental from a point of view of electrochemical performance. Scanning electron microscopy revealed the presence of an extraordinary branch-like microstructure with sub-micron particles size, which has not been previously reported in the literature. The as-obtained material was mixed with carbon additive and eco-friendly carboxymethyl cellulose (CMC) binder to prepare an electrode. To get a deep insight into the (de)sodiation mechanisms, operando X-ray diffraction and Raman spectroscopy measurements were conducted. The qualitative change of the X-ray absorption spectra for the L_3 -edge for Sb and the K-edge for Na as a function of sodium content (ex-situ measurements) in total electron and total/partial fluorescence yields is also presented. Comparison of the three above-mentioned techniques allowed providing the detailed description of the processes occurring during first sodiation and desodiation into the antimony characterized by remarkable microstructure. Moreover, numerous electrochemical measurements were performed: charge and discharge cycling, cycling voltammetry, and electrochemical impedance spectroscopy as a function of the state of charge.

The results confirm that during the alloying reaction, despite the application of a novel synthesis method resulting in a previously unobserved microstructure, the Na_3Sb phase was formed, similarly as in commercial antimony. Application of a broad range of different operando and ex-situ characterization methods revealed the structural changes in the electrode depending on the stage of the reaction.

ES06.09

Neural Ordinary Differential Equations and Recurrent Neural Networks for Predicting the State of Health of Batteries [Simona Pepe](#) and Francesco Ciucci; The Hong Kong University of Science and Technology, Hong Kong

Battery management systems require efficient battery prognostics so that failures can be prevented, and efficient operation guaranteed. In this work, we develop new models based on neural networks and ordinary differential equations (ODE) to forecast the state of health (SOH) of batteries and predict their end of life (EOL). Governing differential equations are discovered using measured capacities and voltage curves. In this context, discoveries and predictions made with neural ODEs, augmented neural ODEs, predictor-corrector recurrent ODEs are compared against established recurrent neural network models, including long short-term memory and gated recurrent units. The ODE models show good performance, achieving errors of 1% in SOH and 5% in EOL estimation when predicting 30% of the remaining battery's cycle life. Variable cycling conditions and a range of prediction horizons are analyzed to evaluate the models' characteristics. The results obtained are extremely promising for applications in SOH and EOL predictions.

ES06.10

Understanding the Na-Ion Diffusivity for $\text{P2-Na}_{2/3}\text{Mn}_{1-x}\text{Fe}_x\text{O}_2$ ($x = 0, 1/3, 1/2$) Sodium-Ion Battery Cathode Material [Priyanka Gupta](#)¹, Sujatha Pushpakanth², Madhulika Gupta³, M. Ali Haider¹ and Suddhasatwa Basu^{1,4}; ¹Indian Institute of Technology Delhi, India; ²Bharat Forge Ltd, India; ³Indian Institute of Technology, India; ⁴CSIR- Institute of Minerals and Materials Technology, Bhubaneswar, India

Rechargeable lithium-based batteries are being extensively deployed as energy storage devices for rendering electric vehicle applications. With non-uniform disposition and large-scale demands of lithium reserves, exploration of suitable alternatives is inevitable. Though sodium-ion batteries (SIBs) based on earth-abundant elements appear as an apt substitute yet inefficient electrodes particularly cathodes impede its commercialization. Out of all, layered transition metal oxide (LTMO) Na_xMO_2 (M= transition element) serve as a promising cathode owing to their facile synthetic approach and 2D Na^+ ion transport channels yielding decent specific capacity. The oxide compounds could further be classified as O3 and P2 configurations depending on Na-ion octahedral and prismatic coordination environment respectively. Here "3", "2" depict the number of transition metal layers with distinct oxygen stacking. Generally, P2- phase reveals a higher reversible capacity and lower diffusion barrier than its counter O3 due to the direct migration of sodium ions from one prismatic site to the adjacent. To analyse the diffusion of these ions, we have performed molecular dynamics simulation for $\text{P2-Na}_{2/3}\text{Mn}_{1-x}\text{Fe}_x\text{O}_2$ ($x=0, 1/3, 1/2$) cathode material as it is based on economically viable environmentally benign Mn and Fe elements. The preliminary calculation results showcased the increasing and further decreasing trend in Na-ion self-diffusivity at room temperature with the enhancement of Fe^{+3} dopant onto $\text{P2-Na}_{2/3}\text{MnO}_2$ material which might be attributed to the phase stabilization aspect of Mn element and the redox couple of $\text{Fe}^{3+}/\text{Fe}^{4+}$ and $\text{Mn}^{3+}/\text{Mn}^{4+}$ for charge compensation mechanism.

ES06.11

Computational Design of Sustainable and Low-Cost High-Entropy Disordered-Rocksalt Li-Ion Cathode Materials [Alex G. Squires](#)^{1,2} and David O. Scanlon^{1,2,3}; ¹University College London, United Kingdom; ²The Faraday Institution, United Kingdom; ³Thomas Young Centre, United Kingdom

Disordered rock salt cathode materials are perceived as excellent candidates for application as future lithium-ion cathode materials enabling chemistries beyond commercial Ni-Mn-Co technologies [1]. Suppressing short-range order (SRO) in disordered rocksalt cathode materials is crucial to maximising their performance. Disordered rocksalt cathodes can possess long-range "0-TM" percolation networks, which allow for fast and facile lithium diffusion, ensuring a good rate capability and high capacity [2]. SRO is typically associated with a reduced connectivity of these 0-TM networks [3]. Alloying many transition metals together across the cation sublattice in a rocksalt structure, creating so-called high entropy rocksalts, has been proposed as a method for minimising

SRO [4, 5]. This approach is expected to improve Li transport through the bulk by suppressing the formation of a single dominant SRO type by increasing competition between a larger number of transition metal species [6]. While the high-entropy cathode concept has been shown to have initial promise, typically studies on these materials have not gone far beyond “proof of concept” stages, identifying optimal compositions remains an open question. When designing new energy materials which contain many component elements, working within sustainability and cost constraints becomes even more important. Many transition metals with favourable electrochemical properties are subject to high and volatile prices, with supply chain issues, precluding their use in truly sustainable cost-effective energy storage technologies [7].

Taken together, this poses an exciting design challenge in identifying low-cost, high-entropy rocksalt compositions which can remain insensitive to market fluctuations and supply chain issues, while retaining excellent electrochemical performance. In this work we use cluster-expansion parameterised Monte Carlo simulations to examine the connectivity of the Li percolation network when varying the number and concentration of different transition metals. We then assess the electrochemical properties and stability of these systems using first principles approaches. Also included in our cathode design is an analysis of time-series data for the cost and availability of the component elements to ensure that not only are any proposed compositions excellent candidate cathode materials, but also should represent cost-effective potential future cathodes. Our most promising candidate compositions identified will be passed to our experimental collaborators for follow-up study.

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ES06.12

Amorphization of Germanium Selenide Driven by Chemical Interaction with Carbon and Realization of Reversible Conversion-Alloying Reaction for Superior K-Ion Storage [Kwang Kim](#); Yonsei University, Korea (the Republic of)

Chemical interaction with carbon has been employed to establish electron conduction pathways through intimate contact with anode materials. It is highly plausible that the strong chemical interaction can change the crystallinity as well as bonding nature of anode materials. This highlights the importance of chemical interaction with carbon and its effects on the material and electrochemical properties of anode materials. However, this is not yet investigated. This study is the first report on the amorphization of layered structured GeSe induced by the chemical interaction and its implications on the electrochemical properties for K-ion batteries. The charge storage mechanism of GeSe/CNT composite, investigated using *ex-situ* X-ray diffraction, indicates that reversible conversion-alloying reaction of GeSe is realized by the amorphization, which is closely linked with weakening of Ge–Se bonds derived from the strong chemical interaction and a concomitant increase in K-ion diffusion. As a result, the GeSe/CNT composite exhibits excellent electrochemical properties. Similar amorphization driven by chemical interaction is also observed for other layered structured anode materials. This study provides new insights on the chemical interaction of layered anode materials with carbon. Our findings could effectively be used to realize reversible conversion reaction for other anode materials for advanced secondary batteries.

SESSION ES07: Solid State Batteries V

Session Chair: Jeuan Seymour

Wednesday Morning, July 20, 2022

Lobby Level, Avenue 34, The Loft

9:10 AM **ES07.01

Electrochemical-Mechanical Coupling at a Li Metal / Solid Electrolyte Interface [Paul Albertus](#); University of Maryland at College Park, United States

Mechanical forces can play an important role in the performance and degradation at an interface between Li metal and a solid electrolyte. This presentation will focus on recent experimental and modeling work that seeks to advance the quantitative understanding of electrochemical-mechanical coupling at metal/solid electrolyte interfaces, and how these couplings relate to the design and performance potential of Li metal batteries that use a solid-state separator. A particular emphasis will be placed on the importance of mechanical boundary conditions and how they influence the mechanical stress at the electrochemical interface, as well as the specific conditions in which mechanical stresses lead to a shift in the electrochemical potential that is significant for battery performance and degradation. Another highlight will be that the plastic and creep behavior of Li metal are of great importance for determining the stresses at a solid electrolyte interface. Remaining experimental and modeling research needs will also be addressed.

9:40 AM *ES07.02

Synthesis, Characterization and Processability of Oxide- and Phosphate-Based Ceramic Lithium-Ion Conductors [Montse Casas Cabanas](#); Centro de Investigación en Energías Alternativas, Spain

Solid-state batteries (SSBs) are considered as a realistic mid-term approach to enhance the safety and energy density of current Li-ion batteries as they will enable the use of metallic lithium as anode and the replacement of flammable electrolytes by solid ionic conductors. However, the selection of a suitable solid electrolyte still remains one of the main challenges for the wide development of solid-state batteries. For the last years, intense research efforts from both academy and industry have indeed been aimed at developing solid electrolytes that present a high ionic Li⁺ conductivity, that are easily processable and that form to stable interphases with both metallic lithium and high-voltage electrodes.

Inorganic solid electrolytes stand out for their high Li-ion conductivity but mainly fail in terms of rigidity (oxides) or low electrochemical stability (sulfides). Cold and hot-pressing techniques are generally employed to densify these electrolytes, although high temperature sintering steps are generally required for complex oxide electrolytes. These sintering steps have important implications in the SSB fabrication flow, since most common cathode active materials do not stand the required sintering temperatures. Alternatively, lithium phosphorous oxynitride (LiPON) represents an interesting alternative owing to its large electrochemical stability window (0–5 V against Li/Li⁺) and its compatibility with a wide range of electrode materials. However, the

synthesis of amorphous LiPON is generally carried out by reactive magnetron sputtering starting from a Li₃PO₄ target source and using N₂ as background gas, thereby limiting its use to thin film batteries.

In the present work a new bulk LiPON crystalline form prepared by mechano-synthesis from low-cost precursors will be presented. Dense pellets were obtained for characterization with the use of an alternative sintering method based on the combination of high-pressure (5.5 GPa) and low temperatures (300-500°C), exhibiting a conductivity similar to its thin film amorphous form. The application of this method to other oxide-based electrolytes will also be discussed, together with the integration and compatibility between components (electrolyte, electrode and conducting additives) in ceramic-based cathode composites.

10:00 AM ES07.03

Automated Rapid Screening of Fast-Ion Conducting Solids and Interfaces [Stefan Adams](#); National University of Singapore, Singapore

Identifying new materials that combine fast ionic conductivity with structural and electrochemical stability so far remains a slow trial and error search process. To rationally accelerate the design of battery materials and their interfaces, dependable rapid screening tools are required so that promising structures can be shortlisted for higher level computational as well as experimental characterization. Here we report on the progress of our softBV bond-valence site energy-based automated pathway analysis software suite that is available free for academic use from <http://www.dmse.nus.edu.sg/asn/software.html>.

Combined with a graphical user interface our software suite provides rapid and simple visualization of pathways [1,2], to provide experimentalists with meaningful approximate predictions of ion transport pathways from experimental or computed crystal structure models within seconds or minutes, i.e. about four orders of magnitude faster when compared to DFT-based methods. This aims to enable experimentalists to quickly identify candidate solid electrolyte materials as well as insertion electrode materials with high rate capability. We also aim to integrate the pre-screening into an automated workflow for subsequent more detailed DFT characterization [3]. Results are benchmarked against both experimental and DFT NEB migration barriers. While migration barrier predictions are useful, the final goal is in most cases a prediction of absolute (room temperature) predictions. Starting from a comparison of different approaches to predict absolute conductivities from static energy landscape analysis, bond-valence based empirical MD simulations and ab initio molecular dynamics (AIMD) simulations, it is discussed under which circumstances fast static approaches can yield meaningful approximations and in which cases computationally more expensive dynamic approaches are inevitable. While for small fast-ion conductor structures at sufficiently high temperatures AIMD appears to be the gold standard, the less reliable but computationally empirical approaches have an advantage in modelling complex disordered interfaces at low temperatures over longer periods. This eliminates hazards involved in extrapolations down to room temperature properties for the frequent cases of order-disorder phase transitions at intermediate temperatures. As an example, we will discuss lithium and sodium compounds containing multiple (poly)anions, in particular the combination of thiophosphate and halide anions or various MS₄ polyanions [4, 5] as well as garnet-type solid electrolytes. To assist experimentalists in not only explore but also rationally engineer transport properties by exploring favorable substitutional dopants, the softBV-GUI software suite now also comprises an AI-based dopant predictor focusing on bond-valence-based crystal chemical descriptors.

We also explore tools that simplify the prediction of functional interface properties. The current version already contains an extension of our bond-valence based approach by computationally efficient (embedded atom-type) multibody terms to optimize their accuracy in rapid simulations of interfaces and surfaces [6]. This will be integrated with a machine-learned predictor of interfacial stability on the way to a computational design of entire solid-state batteries.

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10:15 AM ES07.04

Structure-Mechanics Correlation in Amorphous Oxynitride Lithium Ionic Conductor (Lipon) [Sergiy Kalnaus](#)¹, [Andrew Westover](#)¹, [Mordechai Kornbluth](#)², [Erik Herbert](#)³ and [Nancy Dudney](#)¹; ¹Oak Ridge National Laboratory, United States; ²Robert Bosch LLC, United States; ³Michigan Technological University Department of Materials Science and Engineering, United States

Solid electrolyte is the critical component in a solid-state cell as it is responsible not only for fast ionic transport but also for maintaining functioning interface with the electrodes for efficient charge transfer. In case of a solid-state battery with lithium metallic anode, the electrolyte should also be able to support uniform cyclic deposition and stripping of lithium and resist growth of the lithium filaments (often called dendrites) through the electrolyte. During the charge and mass transport the cell components experience dimensional changes resulting in local instabilities in stress, especially at the contact points with the electrolyte. It is therefore essential for the electrolyte to provide the means of the stress relief without fracture. We discuss such mechanism in lithium phosphorous oxynitride amorphous electrolyte, Lipon. We experimentally demonstrate Lipon's remarkable ability to resist fracture at micro- and nanoscale. Using molecular dynamics simulations, we show partitioning of deformation in Lipon into densification and isochoric shear – the mechanisms that mitigate stress without resorting to fracture. We discuss the findings in a broader prospect of designing ductility in solid electrolytes to withstand stresses and strains in a solid-state battery.

10:30 AM ES07.05

Exploration of Li-P-S-O System for Discovery of New Solid Electrolyte [Audric Neveu](#)¹, [Vincent Pele](#)², [Christian Jordy](#)² and [Valerie Pralong](#)¹; ¹Laboratoire de Cristallographie et Sciences des Matériaux, France; ²SAFT, France

With the aim of making lithium batteries safer, the scientific community is looking in recent years to replace the liquid solvents used as electrolytes with a solid ionic conductor compound. Several families of materials have been developed, leading to major improvements in this technology (NASICON, perovskites, Garnets). In addition, the thio-phosphate family is widely explored and several compounds have been discovered in the pseudo-binary Li₂S-P₂S₅ diagram such as Li₃PS₄, Li₇P₃S₁₁, or Li₇PS₆. In 2011, R. Kanno and al. had discovered a new phase: Li₁₀GeP₂S₁₂ showing ionic conduction of 12 mS/cm. Unfortunately, this structure is unstable towards lithium metal and germanium remains a very expensive element. In order to improve the stability of this structure, a partial substitution of sulfur by oxygen has been successfully obtained and shown better cycling capability. Very recently, the germanium-free phase Li_{9,6}P₃S₁₂ has been obtained and exhibits better stability towards lithium despite a lower conductivity. Here, we will present the effect of anionic substitution inside the structure of this new material and we will review the effect on the ionic conductivity, the stability versus lithium, and the performance in all-solid-state battery.

10:45 AM BREAK

11:00 AM ES07.06

Structural Investigation of LAGP/PEO Composite for Solid-State Batteries Using Vibrational and Nuclear Magnetic Resonance Spectroscopies L. J. Deiner¹, Kalle Levon², David Clarkson³, Mounesha Garaga³ and Steve Greenbaum³; ¹New York City College of Technology, United States; ²New York University, United States; ³Hunter College, United States

Solid state lithium batteries have the potential to meet increasingly stringent safety and power density requirements in the transportation and consumer electronics sectors. Realizing the promise of solid state lithium batteries will require development of composite solid electrolytes that combine the compliance and processability of polymers with the ruggedness, temperature flexibility, and ionic conductivity of ceramics. In this work, we present a simple one-pot mechanochemical method for preparation of a high inorganics composite comprised of lithium aluminum germanium phosphate (LAGP) and polyethylene oxide (PEO). Products can be tuned by changing the polymer/inorganic ratio, milling speed, and milling time. This is the first step toward development of electrolyte films that exhibit high conductivity even in the absence of elevated temperature post-deposition processing. Fourier transform infrared (FTIR) analysis of LAGP after combination with PEO shows the growth of a band assigned to the deformation/bending mode of surface bound water. The growth of this band suggests that PEO may attach to the LAGP surface through a condensation reaction. Standard high resolution magic angle spinning (MAS) solid state multinuclear magnetic resonance (⁷Li, ²⁷Al, ³¹P), which is sensitive to even small changes in short-range structure of the bulk phase, reveals both a well-defined crystalline phase and a relatively minor amorphous phase, with little apparent difference between LAGP and the LAGP/PEO composite. However cross polarization (CPMAS) measurements, which rely on spatial correlation between nuclei near the surface of the LAGP particles and protons in PEO, demonstrate that the amorphous LAGP phase resides on the surface and that both ³¹P and to a lesser extent ⁷Li nuclei are proximal to the PEO protons. Comparison with non-milled physical mixtures of LAGP and PEO demonstrates chemical binding of the polymer with the LAGP surface in the milled materials. Ionic conductivity results for these materials, including the effect of added Li salt, will also be presented.

11:15 AM ES07.07

High Cell Level Energy Density of Metal Sulfide Based All-Solid-State Batteries Hongli (. Zhu; Northeastern University, United States

Sulfide solid-state electrolytes (SEs) featured with nonflammability and superior ionic conductivity ($>10^{-3}$ S cm⁻¹) enable all-solid-state lithium batteries (ASLBs) to deliver safer and more reliable energy storage. However, current sulfides-based ASLBs exhibit far below expected energy densities at the cell level (<50 Wh kg⁻¹, <100 Wh L⁻¹), due to the employment of SE membranes with extreme high thickness (>500 μm), large weight (>80 mg cm⁻²), and limited ion conductance. The high sensitivity to polar solvent and natural brittleness of sulfide SE challenge the fabrication of thin light-weight SE membranes with no sacrifice in ionic conductivity.

The binder-assisted solution method is a promising strategy to fabricate a thin and robust sulfide SE membrane. A critical step to is to select a binder satisfying following requirements: 1) Excellent solubility and stability in nonpolar solvent; 2) High stability with sulfide SE; 3) High thermal stability; 4) High binding strength. In this work, for the first time, we employed and studied ethyl cellulose as a binder. Attributing to ethyl cellulose's unique amphipathic molecular structure, the obtained freestanding SE membrane possesses ultralow thickness (<50 μm), high ionic conductivity (>1.0 mS cm⁻¹), high robustness, excellent stability. The ASLB employing this thin SE membrane delivers exceedingly high energy densities at the cell level.

11:30 AM ES07.09

The Mechanism of Lithium Dendrite Formation and Propagation Under Pulsed Charging Conditions in Solid-State Lithium Batteries Florian Flatscher¹, Verena Reisecker², Lukas Porz¹, Cole Fincher³, Maria de las Mercedes Linares Moreau⁴, Paolo Falcaro⁴, Sigurd Wenner⁵, Juergen Fleig⁶, Yet-Ming Chiang³ and Daniel Rettenwander¹; ¹Norges teknisk-naturvitenskapelige universitet, Norway; ²Technische Universität Graz, Austria; ³Massachusetts Institute of Technology, United States; ⁴Technische Universität Graz Fakultät für Technische Chemie Verfahrenstechnik und Biotechnologie, Austria; ⁵SINTEF Industri, Norway; ⁶Technische Universität Wien, Austria

To this date lithium dendrites remain one of the key challenges in solid-state Li-batteries (SSLB).^{1,2} The formation and growth of these dendrites cause an inevitable failure at charge rates far below the threshold set by industry (>3 mA/cm²) and are believed to be driven by stress accumulation stemming from the deposited lithium itself. Upon reaching a critical pressure, the solid-state electrolyte (SSE) starts to crack, which propagates until the cell short-circuits.³ Herein, we propose that this fracturing is not of purely mechanical origin but can rather be related to an increased Li activity in the SSE near the protrusion, caused by the diffusion-controlled Li deposition. This destabilizes the local structure of the SSE and weakens it within a certain time frame. If current is applied for shorter durations than is required for the Li activity to reach critical values, as is with high frequency pulses, the structural destabilization of the SSE can be delayed, and higher critical current densities (CCD) can be reached. Applying 1 MHz current pulses, a sixfold increase of the CCD, compared to DC operation and a maximum value of around 6.3 mA/cm² was reached in this work. Since an adaption of the applied current waveform can be combined with other reported measures like interlayers, alloys or structured interfaces, the fast-charging goal set for electric vehicles, appears to become feasible.^{4,5,6} Hence, the application of pulsed currents represents a crucial step toward realization of SSLBs for electric vehicles and other emerging applications.

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11:45 AM ES07.10

Nasicon Structured Li_{1.3}Al_{0.3}Ti_{1.7}(PO₄)₃ Dispersed Solid Polymer Electrolytes and Their Applications in Electric Double Layer Supercapacitors [Shrishti Sharma](#) and Anshuman Dalvi; Birla Institute of Technology & Science Pilani, India

Composite solid polymer electrolyte membranes (conductivity $\sim 10^{-4} \Omega^{-1} \text{cm}^{-1}$) have been prepared by a novel milling-assisted synthesis route by reinforcing NASICON structured Li_{1.3}Al_{0.3}Ti_{1.7}(PO₄)₃ (LATP) in the PEO (polyethylene oxide)-salt (Salt: LiClO₄, LiCF₃SO₃, and LiTFSI) matrix. Using membranes of thickness ~ 200 microns (containing a range of $\sim 36\text{-}67$ wt % of reinforced LATP) and high surface area ($\sim 850 \text{ m}^2 \text{g}^{-1}$) activated charcoal, the all-solid-state electric double layer supercapacitors were prepared by hot-roll lamination technique. The EDLC behavior is confirmed by nyquist plots, linear galvanostatic discharge curves, and featureless CV scans. For various CSPE membrane compositions, these EDLCs display appreciable specific capacitance of $\sim 40\text{-}180 \text{ Fg}^{-1}$ at 40 oC at $\sim 1 \text{ Ag}^{-1}$, 2V and stability at least up to ~ 16000 cycles. Further, these cells exhibit specific energy and specific power of 20-50 WhKg⁻¹ and 1500 WKg⁻¹, respectively. The conductivity of solid polymer electrolyte exhibits an interesting correlation with EDLC performance. LATP as well as salt content affect the membrane conductivity, thus influence the EDLC performance. These all-solid-state cells could glow the LEDs of $\sim 2\text{ W}$ for approximately 5-10 mins at 30oC, thus found to be useful for low power applications.

12:00 PM ES07.11

All-Solid-State Li Batteries with NCM-LLZO Based Composite Cathodes [Christoph Roitzheim](#)^{1,2}, Martin Finsterbusch¹, Olivier Guillon^{1,3} and Dina Fattakhova-Rohlfing^{1,2}; ¹Forschungszentrum Julich GmbH, Germany; ²Universitat Duisburg-Essen, Germany; ³Rheinisch-Westfalische Technische Hochschule Aachen, Germany

Garnet-based all-solid-state lithium batteries (ASBs) featuring a thick composite cathode, composed of a solid-state electrolyte (SSE) and a high-capacity active material (CAM), are promising candidates for the next generation energy storage systems. They address several challenges of conventional lithium-ion batteries (LIBs) by promising higher energy densities and intrinsic safety. However, the fabrication of such ceramic batteries is challenging due to the necessary high temperature processing leading to material compatibility issues. High capacity CAMs, like LiNi_xCo_yMn_{1-x-y}O₂ (NCM), show insufficient material compatibility towards the solid electrolyte Li_{6.45}Al_{0.05}La₃Zr_{1.6}Ta_{0.4}O₁₂ (LLZO:Ta) during co-sintering, leading to the formation of detrimental interphases. Thus, the thermodynamic stability of NCM towards LLZO:Ta, at elevated temperatures, needs to be increased. Here, we investigated two NCM compositions (NCM111 and Ni-rich NCM811), to assess the impact of the transition metal composition on the compatibility with LLZO:Ta. Additionally, we investigated B-doping of the NCM host structure, since Li₃BO₃ (LBO) is often used as a sintering additive in garnet based composite cathodes and can eventually diffuse in the NCM structure. Surprisingly, the Ni-rich NCM811 was found to be the most promising CAM for the combination with garnet type LLZO:Ta in composite cathodes of ceramic ASBs. During Co-sintering up to 1000 °C, NCM811/LLZO:Ta mixtures form only small amounts of secondary phases and B-doping does not negatively affect the thermodynamic stability. Therefore, a fully inorganic ASB based on a Li-metal anode, a LLZO:Ta separator and a composite cathode, consisting of Ni-rich NCM811, LBO and LLZO:Ta, could be successfully manufactured by conventional sintering. This ceramic ASB, exhibits one of the highest active material loading reported so far and delivers significant higher specific areal capacities (0.7 mAh cm^{-2}) than comparable ceramic ASBs based on LLZO:Ta and NCM811.

SESSION ES08: Li-ion Batteries I
Session Chair: M Rosa Palacin
Thursday Morning, July 21, 2022
Lobby Level, Avenue 34, The Loft

9:10 AM **ES08.01

Rational Concentration Gradient Designs and Morphology Control Stabilizing Ni-rich NMC Cathodes [Khalil Amine](#) and Tongchao Liu; Argonne National Laboratory, United States

Performance improvement of cathode materials represents one of the most critical technological challenges for lithium-ion batteries (LIBs), as existing Li(Ni_xMn_yCo_z)O₂ layered oxide cathode materials (NMC) exhibit poor performance when operating at a voltage higher than 4.4V. Efforts to solve these issues have to start with an understanding of what causes NMC cathode, especially Ni-rich NMC, to degrade quickly. In this talk, the fundamental linkage between compositions, structure, and electrochemical properties of Ni-rich NMC cathodes will be discussed. We will share our understanding of the roles of Ni, Co and Mn on electrochemical performance, structural stability, and mechanical properties of Ni-rich NMC cathodes. With these fundamental discoveries, we will demonstrate how to utilize rational gradient concentration designs and morphology control to effectively improve the structural stability and electrochemical performance of the Ni-rich NMC cathodes at high voltage. Finally, we will focus on our newly designed concentration gradient cathode that utilizes the different mechanical properties of Mn and Co to simultaneously achieve improved mechanical stability and maintain high capacity and excellent abuse tolerance.

9:40 AM *ES08.02

Processing Thin But Robust Electrolytes for Solid-State Batteries [Moran Balaish](#)^{1,1}, Juan Carlos Gonzalez-Rosillo², Kun Joong Kim³, Zachary D. Hood⁴ and Jennifer Rupp^{3,1,1}; ¹Technische Universitat Munchen, Germany; ²Institut de Recerca en Energia de Catalunya, Spain; ³Massachusetts Institute of Technology, United States; ⁴Argonne National Laboratory, United States

The widespread adoption of high-energy-density solid-state batteries (SSBs) requires cost-effective processing and the integration of solid electrolytes of about the same thickness as the polymer-membrane separators found in conventional lithium-ion batteries. Here we critically discuss the current status of research on SSB processing as well as recent cost calculations and compare SSB oxide electrolyte material and processing options in terms of performance parameters for thick versus thin ceramics. We identify as critical for future SSB design the need to capture the thermal processing budget and the stability of the phase of interest for oxide solid electrolytes, namely lithium phosphorus oxynitride, sodium superionic conductors, perovskites, and garnets, in addition to the classic plots of Arrhenius lithium transport and the electrochemical stability window. Transitioning to SSB oxide electrolyte films with thicknesses close to the range for lithium-ion battery separators could provide ample opportunities for low-temperature ceramic manufacture and potential cost reduction.

10:00 AM ES08.03

Parameter Identification of Lithium-Ion Batteries by Coupling of Electrochemical Spectroscopy and a Physics-Based Model [Xinfang Jin](#) and Xiting Duan; University of Massachusetts Lowell, United States

Lithium-Ion batteries (LIBs) have an unmatched combination of high energy and power density, high round-trip efficiency and low cost, making it the technology of choice for portable electronics, power tools and electric vehicles (EVs) [1]. With a 85% cost reduction of LIBs in the past 10 years, a 50-fold growth in market penetration of the technology has been projected through 2030 to aggressively electrify the transportation and electricity sectors[2]. For many years, researchers focus on discovering new materials to improve LIBs' energy density, lifetime, and safety. With the massive adoption of LIBs for EVs and stationary energy storage, increasing researchers are exploring fast, efficient, and accurate diagnostic tools to evaluate battery performance so the battery packs could be managed properly to achieve safe operation and elongated lifetime.

Electrochemical impedance spectroscopy (EIS) is well-known as a significant technique to investigate electrical properties of LIBs in association with electrochemical processes without destruction. It can make measurements in a wide frequency range, which provides the possibility to separate the elementary reaction steps from an overall electrochemical spectra, and to extract numerical values of rate constants and other kinetic parameters characterizing those reaction steps[4].

In this study, we will collect EIS data of an in-house assembled $\text{Li}[\text{Ni}_{0.5}\text{Mn}_{0.3}\text{Co}_{0.2}]\text{O}_2$ /Lithium metal coin cells under different state of charges (SOCs) and different charge/discharge cycles. We will also build a physical impedance model in frequency domain to estimate nonlinear transport and kinetic parameters of the LIB coin cells using a nonlinear optimization procedure. The nonideality effect is caused by interaction among high concentration Li ions[3] based on concentrated solution theory[5]. Parameters including ohmic resistance (high frequency), solid/liquid interface reaction (intermediate frequency), Li-ion diffusion (low frequency) will be extracted from experimental EIS data. Their confidence levels and accuracy dependence on the initial guesses will be discussed extensively. To validate the fidelity of the parameters, they will be compared against the parameters obtained from traditional GITT technique and EIS-Equivalent Circuit Method. Results show the exchange current density, electronic conductivity and diffusion coefficients of solid $\text{Li}[\text{Ni}_{0.5}\text{Mn}_{0.3}\text{Co}_{0.2}]\text{O}_2$ (NMC532) particles are greatly dependent on the Lithium content or SOC. The proposed impedance model to deconvolute the EIS data (~2.5 hours) is less time consuming than GITT technique (>200 hours); at the same time, the obtained parameters are physically meaningful and ~10 times more precise than those obtained from EIS-Equivalent Circuit Method.

Keywords: NMC532; GITT; EIS; Physical impedance model

References:

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10:15 AM ES08.04

Measuring Full Sets of Electrochemical Transport Parameters in Thin Films of Lithium Intercalation Compounds Andreas Bumberger, Claudia Schrenk, Matthias Kogler, Joseph R. Ring, Andreas Nening and Juergen Fleig; Technische Universitat Wien, Austria

With the proceeding development of all solid-state batteries and the ever-increasing demands placed on lithium-ion batteries in terms of power density and charging speed, solid-state diffusion kinetics in lithium intercalation compounds are shifting back into focus. The three archetypal cathode material classes of spinel, layered oxide and olivine all belong to the class of mixed ionic and electronic conductors (MIECs) and as such all exhibit ionic, electronic, and chemical capacitive contributions to the ambipolar solid-state diffusion process. Moreover, these elementary material parameters depend on the state of charge of the cathode. Measuring all these properties in dependence of the Li content is far from trivial and data are often deduced from porous and geometrically complex electrode systems relying on simplifying assumptions.

In this work, we study the electrochemical properties of thin film cathode materials by using a complementary combination of in-plane and cross-plane impedance measurements with selectively blocking electrodes. For epitaxial LiCoO_2 and LiMn_2O_4 thin films prepared by radio-frequency magnetron sputtering, full sets of material parameters are extracted at various states of charge, including both electronic and ionic conductivity, chemical capacitance and interfacial charge transfer resistance. For this purpose, we adapt the transmission line model by Jamnik and Maier [1] for the most general case of four distinct terminals and analyze the validity of the simplified Randles circuit [2, 3]. The evolution of all material parameters along the charge curve is discussed and their separate contributions to the total electrode resistance are evaluated. We compare the structure-property relationships that govern the differing transport properties of layered oxide and spinel materials. Finally, the study is extended to the structurally homologous cathode materials $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ and $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ and the implications of the solid-state diffusion resistances for thin film devices and bulk electrodes are evaluated.

- [1] J. Jamnik and J. Maier, *Phys. Chem. Chem. Phys.* **2001**, 3, 1668-1678.
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10:30 AM ES08.05

Origins of Excellent Cycling Stability in the Sn-Rich Spinel-Structured High Entropy Oxide Anode Materials for Li-Ion Cells Maciej Mozdziej¹, Konrad Swierczek¹, Juliusz Dabrowa², Marta Gajewska³ and Jakub Cieslak⁴; ¹Akademia Gorniczo-Hutnicza imienia Stanislaw Staszica w Krakowie Wydzial Energetyki i Paliw, Poland; ²Akademia Gorniczo-Hutnicza imienia Stanislaw Staszica w Krakowie Wydzial Inzynierii Materialowej i Ceramiki, Poland; ³Akademia Gorniczo-Hutnicza imienia Stanislaw Staszica w Krakowie, Poland; ⁴Akademia Gorniczo-Hutnicza imienia Stanislaw Staszica w Krakowie Wydzial Fizyki i Informatyki Stosowanej, Poland

From the point of view of further growth of the Li-ion battery market, new applications, i.e. distributed electrical energy storage systems, next generation electric vehicles, as well as improved power tools and portable electronics, all require cells with extended lifespan, safety, and higher energy and/or power density. To achieve this goal, one of the most significant objectives is to replace the conventional intercalation-based anode material, graphite, with compound having better electrochemical properties. Recent advances in this field come from the use of anodes with different chemistries. Among promising alternatives, there are those working on a basis of alloying/dealloying and reversible conversion mechanisms. Although much higher capacities are obtained for various compounds from both groups, many new challenging issues have emerged, with the main being poor cycling stability. From another perspective, the most recent literature reports show that a novel group of materials, the so-called high-entropy oxides (HEOs), exhibits very interesting electrochemical characteristics as an anode in Li-ion cells. HEOs can be defined as multi-principle component materials (with five or more elements) in an equimolar or near-equimolar ratio, characterized by extraordinary properties emerging from synergistic effects, beyond a simple rule of mixing. Interestingly, excellent capacity retention during cycling is typical for all HEO-based anodes, regardless of the chosen synthesis method and (at least to some degree) chemical composition. Up to date, the nature of this behavior has not been fully understood yet. Consequently, elucidation of the phenomena occurring during (de-)lithiation of HEO anode materials, explaining their great performance in Li-ion cells, was the main goal of this research.

Several Sn-rich HEOs from the Sn-Co-Mg-Mn-Ni-Zn-O system, previously not reported in the literature, were successfully synthesized using a facile solid-state route. All materials were found to exhibit the inverse spinel-type structure (Fd-3m space group), with Sn occupying mainly octahedral sites, and the rest of the cations being distributed in both spinel sublattices, as proven by the X-ray diffraction (XRD), Raman spectroscopy, and high-resolution transmission electron microscopy measurements (HR-TEM). The elemental distribution, was confirmed to be homogeneous through both, scanning and transmission electron microscopy techniques, combined with chemical composition analysis. The materials were investigated in terms of the electrochemical properties in half-cells against metallic Li electrode using galvanostatic charge/discharge, cyclic voltammetry, and impedance spectroscopy techniques. High reversible capacities (exceeding 600 mAhg⁻¹) with coulombic efficiencies in a range of 60-70% in the initial cycle, and above 99% during further cycling were recorded, showing that the HEO materials significantly outperform their conventional counterparts (e.g. Zn₂SnO₄). Additionally, the observed excellent cyclability proved that application of the high entropy approach indeed results in the improved stability. Noteworthy, those remarkable properties were achieved for samples obtained by a low cost and facile solid-state method. To uncover reasons for the observed improved behavior, extensive characterization is provided, based on numerous operando and ex-situ studies, including XRD, HR-TEM, Raman, X-ray absorption, X-ray photoelectron, and Mössbauer spectroscopy methods. It was found that the samples combine both alloying/dealloying and reversible conversion reactions with Li during the battery work, while the multicomponent complex and distorted structure contributes to the enhanced cycling stability. Overall, a model explaining reactivity of the HEO anode materials in Li-ion cells can be presented for the first time.

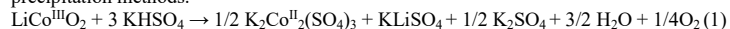
10:45 AM BREAK

11:00 AM ES08.06

Investigation of the Conversion Mechanism of Positive Electrode Materials into Water-Soluble Sulfates for Easier Metals Recycling of Spent Li-Ion Batteries Lydia Hamitouche; Sorbonne Université Faculté des Sciences et Ingénierie, France

Li-ion batteries (LIBs) containing lithium and transition metals (e.g. Co, Ni, Mn, and others) are the powerhouse of digital electronics. The growing demand for such batteries has led to an impact on the environment. The investigation of new recycling methods for spent Li-ion batteries (LIBs) is mandatory to meet these problems. The pyrometallurgical and hydrometallurgical processes have been developed to recycle spent LIBs^{1,2}. In our project, we propose a pyrochemical approach using molten salt as a reagent to chemically convert lithium transition metal oxides LMO₂ (M = Co, Ni, Mn or mixture of metals) into water-soluble sulfate-based products. This process involves a solid-state reaction between a cathode material of LIBs and a hydrogen potassium sulfate molten salt.

The investigation of the reaction mechanism of LiCoO₂ (LCO) and KHSO₄ mixture in stoichiometric quantity *i.e.* 1 LiCoO₂ with 3 KHSO₄, was performed using X-ray absorption spectroscopy and in situ temperature-programmed XRD. The results showed that the reaction mechanism implicated during the conversion of the oxide LiCoO₂ into a sulfate-based product was complex. At room temperature, Li⁺/H⁺ ionic exchange has occurred. This ionic exchange was noticed through the increase in C parameters of LiCoO₂ phase due to the delithiation and the formation of a potassium hydrogen lithium sulfate phase K₄LiH₃(SO₄)₄. The follow-up of the reaction mechanism during the heat treatment of LiCoO₂ and KHSO₄ mixture revealed that around the melting point of KHSO₄, *i.e.* 200°C, an intermediate phase Co₃(SO₄)₂(OH)₂ appears before the total conversion to langbeinite K₂Co₂(SO₄)₃ and potassium/lithium sulfates at 400°C under air (eq1). The obtained sulfate-based products are soluble in water, allowing for the recovery of the targeted elements by selective precipitation methods.



As mentioned in the literature, the langbeinite structure³ can accommodate different metal cations, including nickel, Manganese, and cobalt mainly used in the cathode materials of Li-ion batteries. Allowing the extension of our approach to other layered cathode materials Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O₂ (NMC) and Li(Ni_{0.82}Co_{0.15}Al_{0.03})O₂ (NCA) and also spinel structure LiMn₂O₄. The reaction of LMO with KHSO₄ leads to the formation of langbeinite K₂M₂(SO₄)₃ (M = Co, Ni, Mn or mixture of metals) and potassium/lithium sulfates.

In conclusion, a new pyrochemical approach was investigated to convert lithium transition metal oxide materials LiMO₂ into water-soluble sulfate products. The treatment of LMO with potassium hydrogen sulfate KHSO₄ leads to the formation of water-soluble sulfate products. This approach was successfully applied to layered structure LCO, NMC, and NCA and also spinel structure LiMn₂O₄. During the treatment of LMO with potassium hydrogen sulfates, the reaction involves Li⁺/H⁺ ion exchange between LMO and KHSO₄ leading to the formation of the Li_{1-x}MO₂ delithiated phase. Thereafter, the melting of KHSO₄ induces the appearance of the intermediates phase before the full conversion to K₂M₂(SO₄)₃.

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11:15 AM *ES08.07

Convection-Enhanced Electrochemical Energy Storage—Design Guidelines from Simulation Weiran Gao, Javit Drake and Fikile Brushett; Massachusetts Institute of Technology, United States

Ubiquitous in portable electronics and emergent in transportation and grid applications, lithium (Li)-ion batteries represent the state-of-the-art in electrochemical energy storage technology due to their energy density, efficiency, and cycle life [1]. However, their performance is frequently limited by diffusive transport losses in the electrodes and electrolyte, which are overcome by using thin electrodes and separators at present [2]. This in turn leads to inactive components occupying a substantial fraction of the battery weight and volume, leading to higher subsequent energy storage costs [3] and persistent charge and discharge rate capability limitations.

Here, I will present on convection-enhanced electrochemical energy storage as a means of enabling battery architectures and operating conditions that can reduce system costs. In this configuration, diffusive losses are overcome by forced convection of the electrolyte through the electrodes which is predicted to promote uniform concentration throughout the porous structure. This approach has several important advantages over more traditional battery formats including: (1) electrodes with an increased and controllable range of operation, (2) improved battery safety and maintenance, (3) simplifications to manufacturing, and, ultimately, (4) reduced system costs. Given the novelty of this approach and the breadth of the parameter space involved, this presentation will focus on MATLAB-based mathematical models to simulate dynamic behavior of the battery over a range of conditions to elucidate the fundamental relationships that govern electrochemical performance and provide design guidelines for prototype construction.

References

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11:35 AM ES08.08

Complex Phase Evolution in Fast Charging Lithium-Ion Battery Electrodes from *Operando* Synchrotron Diffraction and Complementary Techniques [Kent Griffith](#); Northwestern University, United States

Complex early transition metal oxides have emerged as leading candidates for fast charging lithium-ion battery anode materials. Framework crystal structures with frustrated topologies are good electrode candidates because they may intercalate large quantities of guest ions with minimal structural response. Starting from the empty perovskite (ReO_3) framework, shear planes and filled pentagonal columns are examples of motifs that decrease the structural degrees of freedom. As a consequence, many early transition metal oxide shear and bronze structures do not readily undergo the tilts and distortions that lead to phase transitions and/or the clamping of lithium diffusion pathways that occur in a purely corner-shared polyhedral network.

In this work, we focus on advanced characterization techniques to explore the relationship between composition, crystal structure, and reduction pathway in a variety of mixed transition metal and alkali or main group oxides. The electrochemical properties of a series of sodium and lithium niobates are studied as new fast-charging lithium-ion battery electrode materials. High-resolution neutron diffraction is used to resolve structural questions in the host materials related to sodium disorder, space group subtleties, lithium positions, and second-order Jahn–Teller distortions of the $d^0 \text{Nb}^{5+}$ redox centers. Structural evolution is followed in real-time at rapid discharge/charge rates with *operando* synchrotron X-ray diffraction, collecting high-resolution diffraction patterns in a few seconds. The structure models from diffraction are informed by the local structure perspective from solid-state NMR spectroscopy and *operando* X-ray absorption spectroscopy (XANES and EXAFS), while the structural (meta)stability and ionic properties are probed through density functional theory (DFT) calculations. A comprehensive picture of the charge storage mechanisms in these complex oxides are described. Prospects for tunability and implications for charge rate and structural stability will be discussed.

11:50 AM ES08.09

Mathematical Design of Intercalation Materials [Ananya Renuka Balakrishna](#); University of Southern California, United States

Today, we have a need to not only discover materials with enhanced properties but to do them urgently—there is a need to establish a quantitative design framework to accelerate materials development. Finding these design principles is the focus of my research group. In this talk, I'll share our recent findings to enhance the lifespans of intercalation cathodes. First, I will show how film straining of intercalation electrodes can circumvent its structural degradation upon repeated cycling. While suppressing chemo-mechanical degradation has been a longstanding problem, our paper [1] initiates a new line of research by using mechanical stress states to regulate the energy landscape in intercalation materials and to thus improve their lifespans. Second, I will share our ongoing work on understanding and engineering structural transformation pathways of intercalation materials. We draw inspiration from phase transformation materials, such as shape memory alloys, to crystallographically engineer self-accommodating and highly-reversible microstructures in intercalation cathodes. Overall, our research aims to establish a theoretical and computational framework to accelerate the discovery and development of intercalation materials.

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12:05 PM ES08.10

Searching for Polyanionic Cathode Materials for Li-Ion Batteries in Underexplored Chemical Spaces [Bonan Zhu](#)^{1,2}, Chris J. Pickard^{3,4} and David O. Scanlon^{1,2}; ¹University College London, United Kingdom; ²The Faraday Institution, United Kingdom; ³University of Cambridge, United Kingdom; ⁴Tohoku Daigaku, Japan

The discovery of materials suitable as Li-ion battery cathodes have led to significant advances in the field historically. Coming up with new cathode systems is an experimentally challenging task, which can be accelerated by combination with computational searches. Polyanion-based materials, such as LiFePO_4 , typically have lower theoretical capacities than their oxide-based counterparts, yet the richness in charge and geometry among different polyanions allows tuning key cathode parameters through structural-property relationships. Higher capacities are achievable if multi-electron redox (such as in $\epsilon\text{-VOPO}_4$) or anionic redox can be incorporated. We have developed procedures for mining polyanionic units from databases of inorganic structures, and subsequently evaluating their potential as building blocks for cathode materials. The focus on unexplored chemical spaces mean traditional database-centric structure prediction approaches are less applicable. Instead, *ab initio* random structure searching (AIRSS)²⁻⁴ is employed to locate the lower energy structures in underexplored chemical spaces from only the desired compositions and polyanion units as the inputs. Several new phases identified using our approach and their predicted electrochemical properties will be discussed.

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12:20 PM ES08.11

Nickel Niobate Anodes for High Rate Lithium-Ion Batteries Rui Xia, Daniel Cunha, Sizhao Huang, Jie Zheng, Bernard Boukamp, Johan E. ten Elshof and [Mark Huijben](#); Universiteit Twente Faculteit Technische Natuurwetenschappen, Netherlands

Fast charging is one of the key requirements for next-generation lithium-ion batteries, however, lithium-ion diffusion rates of typical electrode materials are limited. Nanosizing of active electrode material is a common strategy to increase the effective lithium-ion diffusion transport rate, but it also decreases the volumetric energy/power density and stability of the battery. In this work, nickel niobate NiNb_2O_6 is demonstrated for the first time as a new intrinsic high-rate anode material for lithium-ion batteries without the requirement of realizing nano-architectures.^[1] The NiNb_2O_6 host crystal structure exhibits only a single type of channel for lithium-ion intercalation and can be fully lithiated with a capacity of about 244 mAh g^{-1} at low current densities. Interestingly, a high diffusion coefficient of $10^{-12} \text{ cm}^2 \text{ s}^{-1}$ at 300 K enables fast (dis)charging at high current densities resulting in high capacities of 140 and 50 mAh g^{-1} for 10 and 100 C respectively. The minimal volume change during lithiation is the origin of the stable reversible lithiation process in NiNb_2O_6 and leads to 81% capacity retention after 20,000 cycles at 100 C. Finally, full cell systems against LiFePO_4 and $\text{Li}[\text{Ni}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}]\text{O}_2$ (NCM811) cathodes demonstrate the promising energy storage performance of nickel niobate anodes in practical battery devices.

[1] R. Xia et al., *Adv. Energy Mater.*, 2021, 2102972.

12:35 PM ES08.12

How to Thermodynamically Describe Massive Stoichiometric Change in Battery Electrodes? Application to Nano-LiFePO₄ Yue Zhu and Joachim Maier; Max-Planck-Institut für Festkörperforschung, Germany

The understanding of a battery material's theoretical charge/discharge curves based on defect chemical modeling is a prime example of the achievements of solid state ionics [1]. However, conventional models either concentrate on dilute situations (e.g. semiconductors) or are restricted to incorporation of neutral species (e.g. lattice gas models). Storage in a battery material involves both ions and electrons which are perceived as defects at particularly high concentrations, thus advanced models are needed to adequately describe the interplay between compositional changes and outer electrical potential variations.

Here we put forward a defect chemical model to consider such a high defect concentration scenario that is important for insertion materials or nanosized phase change materials. Using LiFePO₄ as an example, we model the incorporation of Li in nanocrystalline FePO₄ where no phase transformation occurs for the whole range from FePO₄ to LiFePO₄ [2]. In this simplest ideal case, the electrode potential is the sum of chemical potential contributions from the ions and the electrons. For both constituents treated as defects, the Fermi-Dirac statistics has to be applied for ions occupying lattice vacancies and electrons filling conduction band. Furthermore, interactions between the two are considered in terms of defect association and attraction. Despite being mathematically simple, our modeling results in the best match to the experimental discharge curve of nanosized LiFePO₄ [3]. The present defect chemical model can be applied to other insertion materials, and it could also serve as the basis for further development of more sophisticated models involving high defect concentrations and complicated defect interactions.

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SESSION ES09: Li-ion Batteries II
 Session Chair: Ieuan Seymour
 Thursday Afternoon, July 21, 2022
 Lobby Level, Avenue 34, The Loft

2:00 PM ES09.01

Chemo-Mechanical Deformations in Lithium Cobalt Oxide Cathode During Li-Ion Intercalation Bertan Özdoğru and Ömer Ö. Çapraz; Oklahoma State Regents for Higher Education, United States

The overall energy density of the Li-ion batteries depends on the operation voltage and the theoretical capacity of the electrodes. Theoretical capacity of layered lithium cobalt oxide (Li_{1-x}CoO₂) cathode is 274 mAh/g, which is higher than the many other commercially available cathode materials, including lithium manganese oxide (148 mAh/g) and lithium iron phosphate (170 mAh/g). However, the irreversible chemo-mechanical deformations at deep charge condition (x>0.5) at high voltages (>4.2V) presents harvesting its full theoretical capacity. Previous XRD and NMR studies demonstrated the structural collapse of the material at deep charge condition [1]. A various material-based strategies such as doping and surface coating have been utilized to improve the stability of the LCO cathodes at deep charge conditions [2]. However, the governing forces behind the chemo-mechanical instabilities in LCO cathodes at high voltages are still poorly understood.

In this study, our goal is to elucidate the electrochemically-driven mechanical deformations in the LCO cathode during Li-ion intercalation. To achieve it, we performed in situ curvature measurement and digital image correlation measurements to probe stress and strain evolution in the electrode while cycling the battery. The combination of these techniques previously provided information about the interfacial and structural deformations in LiFePO₄ and LiMn₂O₄ [3,4]. Here, free-standing composite LCO electrodes were fabricated for strain measurements. Thin film LCO electrode was prepared using chemical vapor deposition method on a silicon wafer for stress measurements. The electrodes were cycled in 1 M LiClO₄ in 1:1 EC:DMC electrolyte against Li counter electrode. The upper limit of the charge voltage were varied from 4.2 to 4.5V periodically in order to investigate the deformations at deep charge state. Strain and stress derivatives were calculated with respect to applied potential in order to understand the potential-dependent mechanical deformations in the LCO electrode. In this talk, we will present the impact of the structural and interfacial deformations on the chemo-mechanical instabilities of LCO cathodes.

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2:15 PM ES09.02

2D Titanoniobate-Titaniumcarbide Nanohybrid Anodes for Ultrafast Lithium-Ion Batteries Jie Zheng, Rui Xia, Johan E. ten Elshof and Mark Huijben; Universiteit Twente Faculteit Technische Natuurwetenschappen, Netherlands

Mixed titanium-niobium oxides are considered to be promising anode candidates due to the high theoretical capacity based on the presence of multiple redox couples (Nb⁵⁺/Nb⁴⁺, Nb⁴⁺/Nb³⁺ and Ti⁴⁺/Ti³⁺). Among them, layered titanoniobates with a two-dimensional (2D) nanosheet structure are expected to expose most surface and near-surface active sites and a minimal Li⁺ diffusion pathway, and thus could exhibit ultrafast pseudocapacitive dominated lithium storage performance. This work presents the synthesis of 2D HTiNbO₅/H-Ti₃C₂T_x nanohybrid anodes via a combined exfoliation and co-flocculation

strategy taking advantage of the ultrathin 2D structure of HTiNbO₅ nanosheets and the high electronic conductivity of H-Ti₃C₂T_x nanosheets [1]. This leads to the random restacking of these two nanosheets and the formation of plane-to-plane contact, insuring excellent transfer kinetics of electrons as well as Li⁺ ions. Benefitting from such unique 2D lamellar structure, the HTiNbO₅/H-Ti₃C₂T_x nanohybrid anode with an optimized (3:1) mass ratio is able to exhibit fast lithium storage process by delivering a high capacity of 111.5 mAh g⁻¹ at a current density of 5 A g⁻¹ (~20.6 C). Our results demonstrate the feasibility of such co-flocculation strategy for designing new high-rate anode material, which outperforms the original bulk HTiNbO₅ compound, making it a promising candidate for application in ultrafast lithium-ion batteries.

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2:30 PM ES09.03

Probing Parasitic Gas Evolving Reactions in Nickel-Rich LiNi_xMn_yCo_zO₂ Lithium-Ion Battery Cathodes with On-Chip Electrochemistry Mass Spectrometry Daisy Thornton^{1,2}, Bethan Davies^{1,2}, Soren Scott¹, Zonghao Shen^{1,2}, Ainara Aguadero¹, Mary Ryan¹ and Ifan Stephens¹; ¹Imperial College London, United Kingdom; ²The Faraday Institution, United Kingdom

Performance improvements in electric vehicle batteries are needed in order to reduce their cost and encourage greater use.¹ This improvement is dependent on the properties (e.g. specific capacity and stability) of the cathode active material in the electric vehicle's lithium ion battery.¹ Lithium Nickel Cobalt Manganese Oxide (NMC) is a layered transition metal oxide that shows great promise as an electrode in lithium ion batteries for electric vehicles, with a high theoretical specific capacity and good stability in the layered structure.² As the nickel content of the cathode material increases, so does the discharge capacity, however this increase comes at the cost of significantly decreased capacity retention.¹ The mechanisms that contribute to this degradation are complex and interlinking and many of them are accompanied by some form of gas evolution. For example, the solid electrolyte interphase formation at the cathode evolves CO₂, which is able to crossover and contribute to solid electrolyte interphase formation at the anode.¹ Similarly, upon electrochemical cycling a reactive form of oxygen can be evolved from the NMC lattice, resulting in a cascade of parasitic reactions within a lithium-ion battery.²

These gas evolving degradation mechanisms are probed by the development and use of a novel type of electrochemistry mass spectrometry (EC-MS) with unprecedented time resolution and sensitivity.^{3,4} The new technique, known as on-chip EC-MS, employs a microfabricated membrane chip to precisely control the transfer of volatile species from an electrochemical cell to a mass spectrometer. Its design also allows instantaneous gas exchange, particularly useful to simulate cross talk phenomena. This work demonstrates the first application of this technique to the study of lithium-ion batteries; this study uses a new cell design to facilitate *operando* measurements of gas evolution in lithium-ion batteries to provide important insight into these complex mechanisms.⁴ We use isotopic labelling of ¹⁸O and ¹³C in CO, CO₂ and NMC to probe degradation processes involving evolution and consumption of gases produced from cross talk. Complementary and correlative ex situ surface sensitive analysis (such as x-ray photoelectron spectroscopy and secondary ion mass spectrometry) are carried out in order to develop a holistic understanding of the complex reactivity and chemistry evolution of lithium-ion batteries during operation.

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2:45 PM ES09.04

Impact of the Li/Mn Superstructure Rearrangement on the O Redox Reaction in Li-Rich NMC Electrodes Andrzej J. Kulka, Anna Plewa, Katarzyna Walczak, Justyna Plotek and Katarzyna Redel; Akademia Gorniczko-Hutnicza imienia Stanislawia Staszica w Krakowie, Poland

In modern Li-ion batteries, intercalation compounds are electrode of choice since they exhibit high potential vs Li^{+/}Li⁰ and broad range of Li intercalation process, which accounts for high energy density while their high mixed ionic-electronic conductivities contributes to high ampacity of the electrodes. However, the high mass taken up by a TM redox-active (TM – transition metal) host lattice in intercalation positive electrodes limits the capacity of the cathodes, which is considerable lower comparing with a graphite anode being a benchmark negative electrode. Thus, in order to overcome the intrinsic drawbacks of current Li-ion batteries related to the limited capacity of their positive electrodes, novel cathodes materials with excess Li within the TM layers Li(Li_xNi_aMn_bCo_c)O₂ (Li-rich NMC) are extensively investigated. Li-rich NMC are capable to deliver capacity beyond standard TM redox processes due to ability to additionally utilize the redox reaction of its lattice oxygen. The O redox reactions involve depopulation of the unhybridized O 2p orbitals from the Li–O–Li configurations¹ which, depending on the crystal and electronic structure of the materials may lead to the bonds reorganization and stabilization of the peroxy-like O–O dimers through covalent interactions². The superstructure of the electrode materials was found to have pronounced impact on the mechanism of O redox reactions facilitating formation either O₂ or O^{•-} species (n<2) depending on the honeycomb and ribbon type ordering of Li within TM layers³. Within this study, with intention to contribute to better understanding of the O redox reaction in Li-rich NMC, we present detailed investigation of the structural and electrochemical properties of several Li(Li_xNi_aMn_bCo_c)O₂ compositions with different TM elemental compositions leading to different Li rearrangements within TM layers. Using *operando* XRD techniques coupled with *operando* XAS of Mn K – edge we monitor the crystal structure changes and variations of the electronic environment for selected compositions in order to elucidate the high valency of the Mn species appearing during Li-NMC operation. The detailed XAS investigations of the ex situ O K-edge showed that for particular compositions we were able to observe during charging repetitively appearing signature coming from, most likely O₂ molecules formed in the materials and rigidly caged within TM vacancy clusters in the materials. After the slight TM elemental composition change we observed that the O K-edge showed characteristics assigned to the formation of the reduced surface layers, which was associated with the reversible spinel-type structure formation. Further electrochemical investigation enable us to correlate the observed different O behaviors with voltage and capacity fade registered during long-term cycling and contribute to the optimizing of the electrodes reactions involving anionic redox.

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3:00 PM ES09.05

Physics-Based Transmission Line Model for Impedance Analysis of Lithium-Ion Batteries—Case Studies on Manganese-Rich and Nickel-Rich Layered Oxide Cathodes Thuy Linh Pham¹, Thi Ngoc Tran Tran¹, Aqsa Nazir¹, Eui-Chol Shin¹, Namsoo Shin², Chan-Jin Park¹, Jaekook Kim¹ and Jong-Sook Lee¹; ¹Chonnam National University, Korea (the Republic of); ²Deep Solutions Inc., Korea (the Republic of)

Constant phase elements (CPEs) of impedance ($Z_C = 1/(Q(j\omega)^\alpha)$) are known as “magic elements” essential in fitting most, if not all, impedance spectroscopy data but a good curve fitting with arbitrarily adjusted frequency power exponents α should not be considered scientifically justified parameterization. Currently, CPEs are mostly employed in equivalent circuit modeling (ECM) as generalized capacitor elements with α close to 1 whereas R elements remain ideal and well-defined and connected in series. Originally, however, Cole and Cole introduced CPE replacing R ($\alpha = 0$) or the deviation from the ideal Debye response, where capacitor elements are well-defined and additive in parallel connection [1]. In fact, the additive capacitive effects are far superior to the additive impedance effects for the multiple processes in the bulk and associated interfaces [2]. CPE with $\alpha = 0.5$ corresponds to RC transmission line which can be physics-based modeling for diffusion-related process and also percolating network as in porous electrodes. However, generalization of shunt capacitors to CPEs is being made and the trouble persists in more obscure way [3]. In this study, we propose a comprehensive transmission line model (TLM) developed from the original suggested by Barsoukov [4] for lithium-ion batteries which is 1-dimensional TLM for porous electrodes with percolating ionic and electronic networks comprising solid-state diffusion and intercalation into the dispersed active particles where only ohmic resistance of the electrolyte is considered. We have confirmed the exact matching between Barsoukov’s model circuit parameters and the parameters of governing equations of finite element COMSOL simulation [5]. Ambipolar diffusion processes in liquid electrolyte in porous separator and electrodes in finite element simulation according to Newman’s theory remain yet unsatisfactorily modeled by R and C parameters. For the real battery data we modeled the separator separately as Nernst-Planck solution which results in liquid phase diffusion process overlapped with solid state process in the low frequency range. Liquid phase diffusion in porous electrodes is suggested to be represented by the interfacial open Warburg impedance added in parallel to well defined shunt capacitances of TLM [6]. In a similar spirit, SEI layer of lithium anode can be successfully modeled by the ideal Debye circuit for the capacitance relaxation without affecting other processes, rather than additional RC or R-CPE parallel components. Following Barsoukov’s suggestion [4] final capacitive effects at low-frequency region are obtained by the open-circuit voltage from a galvanostatic intermittent titration technique (GITT) titration curve and fixed. The physics-based modeling has been applied to analyze experimental data of different layer cathode materials, such as manganese-rich oxide $0.3\text{Li}[\text{Li}_{0.33}\text{Mn}_{0.67}]\text{O}_2$ - $0.7\text{Li}[\text{Ni}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}]\text{O}_2$, nickel-rich oxides $\text{Li}[\text{Ni}_{0.6}\text{Mn}_{0.2}\text{Co}_{0.2}]\text{O}_2$ (NMC622) and $\text{Li}[\text{Ni}_{0.8}\text{Mn}_{0.1}\text{Co}_{0.1}]\text{O}_2$ (NMC811).

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3:15 PM ES09.07

Real Time Crystallization of LiCoO₂ from β -Co(OH)₂ and Co₃O₄—Synthetic Pathways and Structural Evolution Marie Duffiet¹, Damian Goonetilleke¹, François Fauth², Torsten Brezesinski¹, Jürgen Janek^{1,3} and Matteo Bianchini^{1,4,5}; ¹Karlsruher Institut für Technologie, Germany; ²CELLS-ALBA, Spain; ³Justus Liebig Universität Giessen, Germany; ⁴BASF SE, Germany; ⁵Universität Bayreuth, Germany

Layered LiCoO₂ (LCO) remains today one of the most prominent positive electrode materials in Li-ion batteries, especially for portable electronics applications. Even for automotive applications, where low-Co materials are targeted, LiCoO₂ is still investigated as a protective coating material: recent papers have reported¹⁻⁶ on the use of various Co-precursors to coat high Ni-content NCMs (lithium Ni-Co-Mn oxide cathodes) and LiNiO₂ (LNO) in the [500 – 650°C] range, believed to react with residual Li species at its surface and ensuring a stable long term cycling. In this temperature range, various ordered or disordered Co-phases such as LiCo₂O₄ (or so-called low-temperature LCO, “LT-LCO”), Li₃Co_{3-y}O₄, or Co₃O₄ may be expected to form, depending on the synthetic conditions and the choice of initial Co- and Li-precursors. The composition and the crystallinity of the coating is then believed to affect the electrochemical performance of the Co-coated NCM materials. However, understanding the composition and crystallinity of a material used as coating (hence present in small amounts) requires insight onto its thermodynamic crystallization pathway as a function of temperature and choice of precursors.

While the synthesis of LCO has been reported using several methods such as solid-state synthesis, sol-gel, spray-drying, hydrothermal synthesis, among others⁷, the *in situ* resolution of the intermediate phases which form during the heat treatment of cobalt precursors and lithium salts has only been reported for the reaction of Li₂CO₃ with Co₃O₄ or for the acetates^{8,9}.

Here, the solid-state reactions of LiOH.H₂O with both β -Co(OH)₂ and Co₃O₄ have been investigated through the combined use of high resolution *in situ* synchrotron XRD and Raman spectroscopy, with a special focus on the low temperature range (RT – 600°C). We show that several spinel structures (LiCo₂O₄, Co₃O₄) are formed in the [300 – 500 °C] range, whose clear identification is only possible through the use of Raman spectroscopy, as their XRD patterns are almost identical. The relative proportions and crystallinity of the different spinels change as a function of both the temperature and the Co-precursor.

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3:30 PM BREAK

3:45 PM *ES09.08

Zintl Chemistry in Batteries—Comparative Study of Lithium and Sodium Electrochemical Reactions with Lead Christopher Johnson¹, Jehee

Park^{1,2}, Jinyup Han¹, Shabbir Ahmed¹, Seong-Min Bak³, Seoung-Bum Son¹, Jiyeon Gim¹, Youngsik Kim² and Eungje Lee¹; ¹Argonne National Laboratory, United States; ²Ulsan National Institute of Science and Technology, Korea (the Republic of); ³Brookhaven National Laboratory, United States

Low cost batteries require abundant and readily available elements that can be easily dry-room processed into high-performance electrodes. In this paper, I will discuss a new mechanistic description of the electrochemical reaction occurring between either lithium (Li) or sodium (Na) with lead (Pb), represented as an engineered structural anode. The chemistry, which is defined in terms of the formation of various Zintl compounds (with distinct ionic-like compositions) or binary alloys (solid solution of the metals) is gleaned from a careful analysis of the X-ray absorption spectra as a function of state-of-charge (SOC). Increased charge is localized on the Pb atom (anionic character) with increasing lithiation or sodiation. This information is not readily obtained from high-energy X-ray diffraction methods. Results have implications on the reaction mechanisms at play in Group-14 elements (i.e. Si, Sn).

4:05 PM ES09.09

Self-Discharge of Layered Oxide Cathodes Induced by Carbonate-Mediated Hydrogenation Gang Wan^{1,2}, Travis P. Pollard³, Lin Ma³, Marshall Schroeder³, Hans-Georg Steinrück⁴, Chia-Chin Chen⁵, Zihua Zhu⁶, Steve Harvey⁷, Yingge Du⁶, Christopher Tassone², Zhenxing Feng⁸, Joseph Franklin^{9,10}, Kang Xu³, Oleg Borodin³ and Michael Toney¹¹; ¹Stanford University, United States; ²Stanford Linear Accelerator Center, United States; ³US Army Research Laboratory, United States; ⁴Universitat Paderborn, Germany; ⁵National Taiwan University, Taiwan; ⁶Pacific Northwest National Laboratory, United States; ⁷National Renewable Energy Laboratory, United States; ⁸Oregon State University, United States; ⁹E O Lawrence Berkeley National Laboratory, United States; ¹⁰University College London, United Kingdom; ¹¹University of Colorado Boulder, United States

Significant efforts are being made to improve the energy and power characteristics of cathodes in Li-ion batteries, while the research into cathode self-discharge has lagged behind. Self-discharge is the voltage drop experienced by all rechargeable batteries while stored in the charged state. The voltage drop becomes more problematic with increased cathode voltage and temperature. The physicochemical nature of internal reactions leading to cathode self-discharge is hardly understood and seldom discussed.

To tackle this challenge, the structure and redox evolution of commercial $\text{LiNi}_{0.5}\text{Mn}_{0.3}\text{Co}_{0.2}\text{O}_2$ electrodes and single crystal cathode thin films upon the self-discharge in carbonate-based electrolyte is revealed by surface-sensitive X-ray scattering, spectrometric and electrochemical characterizations in conjunction with thermodynamic analysis. As evidenced by the interfacial toolkits and theoretical calculations, there is an evolution and growth of cathode surface reduction layer in LP57 electrolyte after self-discharged from different potentials. Structural and chemical characterizations as well as the elemental depth profiles within cathode thin film confirms proton-insertion-induced layered cathode hydrogenation. Calculation shows that such process is both thermodynamically and kinetically favorable and is triggered by the interfacial hydrogen atom abstraction of methylene group in carbonate solvent on delithiated cathode surface. A combination of experimental and theoretical studies reveals the carbonate-mediated cathode hydrogenation mechanism accounting for the voltage drop in the self-discharge. This offers additional understanding regarding defect generation and the degradation mechanism in layered cathodes beyond the traditional behaviors of lithium-diffusion-induced self-discharge and rock-salt phase induced cathode degradation. This study offers foundational knowledge of the interfacial degradation of cathode that can be translated to the rational design of improved cathodes and electrolytes, and the self-discharge mechanism studies in other electrochemical ion insertion materials and devices.

4:20 PM ES09.10

The Interplay Between Thermodynamics and Kinetics in the Solid-State Synthesis of Layered Oxides Wenhao Sun; University of Michigan, United States

The voltages, ion diffusion rates, and storage capacities of electrode materials strongly depend on which structural polymorph they are synthesized as. Unfortunately, the complicated solid-state synthesis routes to these multicomponent oxides often yield non-equilibrium intermediates, resulting in poor phase purity in the final reaction products. To better understand the mechanisms of structure-selection during materials formation, we combine *ab initio* thermodynamics with *in situ* synchrotron X-ray scattering to elucidate the origins of metastable O3' and P3 phases in the synthesis of layered Na_xCoO_2 and Na_xMnO_2 ,¹ as well as metastable spinel $\text{Li}_2\text{Co}_2\text{O}_4$ and disordered $\text{Li}_{1-x}\text{Ni}_{1+x}\text{O}_2$ in the formation of layered LiCoO_2 and LiNiO_2 . Structural motifs that arise during low-temperature reactions are found to often template and persist as metastable phases during high-temperature calcination. By engineering which metastable intermediates form during the early stages of crystallization, we can achieve better control over the structural polymorphism and interlayer defects of these important cathode materials.

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4:35 PM ES09.11

Controlled Synthesis and Integration of Energy Materials by Lithiation-Assisted Epitaxy Le Wang¹, Zhenzhong Yang², Hua Zhou³ and Yingge Du¹; ¹Pacific Northwest National Laboratory, United States; ²East China Normal University, China; ³Argonne National Laboratory, United States

Epitaxial growth is a powerful tool for synthesizing heterostructures and integrating multiple functionalities. Interfacial mixing can readily occur at temperatures required for complete film crystallization and can significantly modify the properties of layered structures, particularly for those containing energy storage materials with smaller cations, such as Li^+ . Here, we report that lithiation-assisted epitaxy, a two-step sequence involving the growth of an epitaxial LiCoO_2 cathode layer followed by the deposition of a binary transition metal oxide, is a highly controllable way to synthesize model solid-state heterostructures of energy materials. The Li concentration can be controlled by the cathode layer thickness and over-lithiation is mitigated as excess Li can be stably stored in the underlying cathode layers. The examples we present here are $\text{WO}_3/\text{LiCoO}_2 \rightarrow \text{Li}_2\text{WO}_4$ (a solid-state electrolyte) and $\text{TiO}_2/\text{LiCoO}_2 \rightarrow \text{Li}_4\text{Ti}_5\text{O}_{12}$ (an anode) with controlled structures and orientations. Additionally, we argue that this approach can be extended to other transition metal oxides such as MoO_3 and Fe_2O_3 , among others. Our study highlights that lithiation-assisted epitaxy can be a broadly applicable synthesis technique for solid-state energy materials discovery and epitaxial design of relevant model heterostructures. Furthermore, the resulting high-quality heterostructures and well-defined interfaces are ideal model systems for fundamental studies of performance and degradation mechanisms in solid-state Lithium-ion batteries.

4:50 PM ES09.12

Incorporation of Sodium Into Layered-Spinel Nanoparticles as Promising Cathode for Lithium-Ion Batteries Nerly L. Mosquera and Jorge A. Calderón Gutierrez; Universidad de Antioquia, Colombia

The usage of lithium ion batteries (LIBs) have received worldwide attention as power sources for transport applications in electric vehicles (EVs) and hybrid electric vehicles (HEVs) and massive energy storage facilities¹. Many efforts have been directed toward development of new cathode materials that present high energy density, high rate capability, cycling performance, environmental friendliness, low cost and higher enhanced safety to make a post-

transition possible. Nowadays, different cathode materials have been explored, specially, the layered-spinel structure. The incorporation of Ti^{4+} in the LiMn_2O_4 spinel phase is performed with the purpose of improving its stability by averting the Jahn-Teller effect of the Mn^{3+} and decreasing Mn^{2+} dissolution towards the electrolyte during cycling since Ti-O provides a higher binding energy (662 kJ/mol) than for Mn-O (402 kJ/mol)². Besides, the cation substitution based on monovalent atoms have been used to improving the cycling performance and high rate capability. Na^+ doping on the layered structure cathode could be create a pinning effect that it stabilizes structure, and facilitates Li^+ -ion diffusion³.

In the present study, we varied the concentration of Na^+ in the $(1-x)\text{Li}_{1-x}\text{Na}_x\text{M}_{1-z}\text{Ti}_z\text{O}_2 \times \text{LiM}_{2-z}\text{Ti}_z\text{O}_4$ layered-spinel and to study the effect of the Na^+ addition in the cycling stability and specific capacity of the active material. A facile sol-gel method is presented as alternative to develop new composite materials for LIBs.

Analysis of XRD patterns confirmed the existence of a spinel-layered composite where the peaks can be indexed to the cubic spinel structure (space group) and layered structure (C 12 - m1; R-3m and P 63-mmc space group)⁴. Cycling was performed typically between 4.8 and 2.0V vs. Li|Li^+ at a constant current of 29.0 mA g^{-1} , equivalent to 0.1 C-rate. The stoichiometry $0.5\text{Li}_{0.8}\text{Na}_{0.2}\text{Mn}_{0.4}\text{Ni}_{0.5}\text{Ti}_{0.1}\text{O}_2 - 0.5\text{LiMn}_{1.4}\text{Ni}_{0.5}\text{Ti}_{0.1}\text{O}_4$ showed an initial specific capacity, ca. 204 mAh g^{-1} and maintained near 80% of charge retention after 50 cycles. Moreover, the stoichiometry $0.5\text{Li}_{0.9}\text{Na}_{0.1}\text{Mn}_{0.4}\text{Ni}_{0.5}\text{Ti}_{0.1}\text{O}_2 - 0.5\text{LiMn}_{1.4}\text{Ni}_{0.5}\text{Ti}_{0.1}\text{O}_4$ showed an initial specific capacity, ca. 141 mAh g^{-1} but later it presented increasing of the specific capacity, ca. 180 mAh g^{-1} at 15th cycling exhibiting 98% of its charge capacity after 50th cycles compared with pristine $0.5\text{Li}_1\text{Mn}_{0.4}\text{Ni}_{0.5}\text{Ti}_{0.1}\text{O}_2 - 0.5\text{LiMn}_{1.4}\text{Ni}_{0.5}\text{Ti}_{0.1}\text{O}_4$ which was ca. 148 mAh g^{-1} . Therefore, it can be concluded that by adding dopant cations like Na^+ the active material shows significant increasing of the specific capacity and enhanced cycling stability of the system. Thus, by possessing interesting properties electrochemical we believe Na-Layered/Spinel heterostructured could be a potential cathode for the development of high-power rechargeable Li-ion batteries.

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5:05 PM ES09.13

Real-Time Measurements of Young's Modulus and Partial Molar Volume of Commercial Graphite Electrodes During Electrochemical Cycling Dawei Li¹, Yikai Wang² and Junqian Zhang³; ¹University of Shanghai for Science and Technology, China; ²University of Kentucky, United States; ³Shanghai University, China

In situ measurements of Lithium concentration-dependent mechanical properties in energy storage materials are crucial to improve the performance and durability of LIBs. Here, we report a real time measurement of the elastic modulus and partial molar volume of commercial graphite electrodes. A physical model is developed to analyze the relationship between bending curvature and materials properties. Composite graphite electrodes with different thickness ratios are chosen as the working electrode, and its deformation are captured using a CCD camera during electrochemical cycling. The results show that the elastic modulus increases with the insertion of lithium ions, while the partial molar volume shows a stage change corresponding to the phase change of graphite materials. These results are important for the mechanical modeling and provide basic information for the commercial graphite electrodes.

5:20 PM ES09.14

Quantifying Variability Between Individual Battery Particles Using Single-Particle Electrochemistry Lindsay Gubow, Jinhong Min and YiYang Li; University of Michigan College of Engineering, United States

Standard Lithium-ion batteries contain micron-sized redox-active materials and liquid electrolytes. Active materials are assembled into heterogeneous composites with $>10^6$ particles and electrochemically charged and discharged. There are many reports that show certain battery particles have faster electrochemistry than others in the electrode¹⁻³; however, the electrochemical variability between different particles have not been quantified due to the difficulty in measuring the single-particle current. Quantifying the variability between particles and understanding their physical origins can be used to identify structure-property relationships and engineer better battery materials.

We develop a high-throughput platform to electrochemically cycle many individual battery particles simultaneously. We assembled the NMC 532 cathode particles on a microfabricated multi-electrode array; this array electrically isolates individual particles from each other, thus enabling the ability to independently charge and discharge individual particles. Non-aqueous liquid electrolyte and a counter-electrode is added to complete the electrochemical circuit. We have successfully conducted single-particle charge and discharge on many isolated particles using both galvanostatic (DC) and impedance spectroscopy (AC). We observed substantial variability in the reaction rates of individual battery particles. We conduct materials characterization on the same particles to correlate variabilities in electrochemical performance to differences in microstructure and chemistry to understand structure-property-composition relationships.

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SESSION ES10: Poster Session III: Energy Storage III
Thursday Afternoon, July 21, 2022
6:00 PM - 8:00 PM
Mezzanine Level, Second Floor, Stadler

ES10.01

Ultrafast Sintering and Application as a Solid-State Electrolyte of LAGP Glass-Ceramic Antonino Curcio¹, Antonio Gianfranco Sabato², Albert

Tarancón² and Francesco Ciucci¹; ¹The Hong Kong University of Science and Technology, Hong Kong; ²Institut de Recerca en Energia de Catalunya, Spain

Sintering of ceramics typically requires the intensive use of energy resources and long processing times, resulting in high costs and limited throughput. Recently, less time- and energy-consuming rapid sintering techniques such as microwave sintering, spark plasma sintering, cold sintering, flash sintering, and ultrafast high-temperature sintering (UHS) have attracted significant attention. Among the mentioned techniques, UHS stands out for being independent of the material's properties, and for requiring a relatively simple setup, whose core consists of a power source and graphite felt strips. However, as the UHS is a novel technique, further studies are needed to fully disclose the potential of such a technique. To this purpose, we investigate, for the first time, the sintering by UHS of a glass-ceramic material, namely $\text{Li}_{1.5}\text{Al}_{0.5}\text{Ge}_{1.5}(\text{PO}_4)_3$ (LAGP). LAGP, at temperatures above $\sim 600^\circ\text{C}$, crystallizes in a Na super ionic conductor (NASICON) structure, which makes it a suitable electrolyte for all-solid-state batteries. Pellets of LAGP are sintered by UHS in minutes. In contrast, the conventional treatment in a muffle furnace requires a total of ~ 50 hours. Thus, UHS enables ~ 1000 faster crystallization and sintering than a conventional furnace. Preliminary results show that the UHSed and conventionally sintered samples have comparable ionic conductivity at room temperature (1.03×10^{-4} S/cm vs 2.11×10^{-4} S/cm, respectively). Further, differential scanning calorimetry (DSC) characterizations suggest that the high heating rate of UHS ($\sim 10^4$ – 10^5 °C/min) unlocks the possibility of distancing the glass transition (T_g) and crystallization (T_c) temperatures of LAGP. Such a feature enables to sinter dense glassy-state LAGP pellets, which, besides possibly implying interesting applications, enables the study of the crystallization and sintering processes of LAGP and their influence on its ionic conductivity. This work demonstrates the potential of applying UHS to processing glass-ceramics and obtaining functional materials for electrochemical applications.

ES10.02

Structurally Reinforced Silicon/Reduced Graphene Oxide Microspherical Composite for Lithium-Ion Battery Anodes—Carbon Anchor as a Conductive Structural Support Kwang Kim¹, Byung Hoon Park¹ and Yong Gil Choi²; ¹Yonsei University, Korea (the Republic of); ²SVOLT Energy Technology Company LLC, Korea (the Republic of)

Herein, we report a Si/reduced graphene oxide (rGO)/C microsphere composite in which sucrose-derived carbon binds Si nanoparticles (NPs) and rGO to act as a carbon anchor and links neighboring rGO sheets to reinforce the composite structure. In this structurally reinforced Si/rGO/C composite, the electron conduction pathways between rGO and the Si NPs are maintained even under large volume changes during repeated charge–discharge processes. Consequently, the Si/rGO/C composite anode exhibits an initial discharge capacity of 1209 mAh g⁻¹ as well as superior cyclability (92% retention at 100 cycles), initial coulombic efficiency of 80.5%, and high-rate capability even at high C rate (6 C). Furthermore, the anode thickness changes negligibly after repeated cycling, confirming the structural stability imparted by the sucrose-derived carbon binder. A full cell assembled with a LiCoO₂ cathode and the Si/rGO/C composite anode remains stable over 200 cycles.

ES10.03

Effects of Li Vapor Overpressure on the Microstructure, Composition and Ion Conductivity of Perovskite $\text{Li}_{3-x}\text{La}_{1/3-x}\text{TaO}_3$ Ion Conductors Jan A. Brummel¹, Harlan J. Brown-Shaklee², William Lanford³, Kevin Wynne³ and Jon Ihlefeld¹; ¹University of Virginia, United States; ²Sandia National Laboratories, United States; ³SUNY The State University of New York, United States

A combustion synthesis methodology for the preparation of perovskite $\text{Li}_{3-x}\text{La}_{1/3-x}\text{TaO}_3$ lithium-ion conductors with $x=0.033$ is presented. Bulk ceramic specimens were prepared under different lithium vapor overpressure conditions governed by combinations of burial powder and cover crucibles. Specimens were batched with a nominal lithium excess of 20 at%, to account for losses during sintering. All specimens were observed to exhibit tetragonal symmetry as a result of La ordering along the c-axis. The lithium content was determined using nuclear reaction analysis with the $^7\text{Li}(p,\alpha)^4\text{He}$ reaction. Room temperature lithium-ion conductivity varied depending upon lithium over-pressure during sintering and a maximum of 6.0×10^{-6} S/cm was observed for pellets sintered with a cover crucible sealed with parent powder. Both the inter- and intra-granular ion conductivities were maximized under the same condition. Schottky barrier effects at grain boundaries were explored by impedance spectroscopy using differing DC biases. The ion conductivity was found to be independent of applied DC bias, implying grain boundary conductivity effects are not governed by Schottky barriers. Grain sizes determined from backscatter SEM micrographs showed no correlation to the observed trend in ion conductivity.

ES10.05

Li-Conduction in Gallium and Scandium Doped NASICON Compound Dharmesh H. Kothari; The Maharaja Sayajirao University of Baroda, India

We report the electrical conductivity results of Li-conducting Li-Al-Ti-P (LATP) compound doped with cations of increasing ionic radii. All the samples viz. $\text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3$ (LATP), $\text{Li}_{1.3}\text{Al}_{0.29}\text{Ga}_{0.01}\text{Ti}_{1.7}(\text{PO}_4)_3$ (LAGTP) and $\text{Li}_{1.3}\text{Al}_{0.29}\text{Sc}_{0.01}\text{Ti}_{1.7}(\text{PO}_4)_3$ (LASTP) and $\text{Li}_{1.3}\text{Al}_{0.29}\text{Ga}_{0.005}\text{Sc}_{0.005}\text{Ti}_{1.7}(\text{PO}_4)_3$ (LAGSTP) were prepared via solid state reaction method. The samples were characterized by X-ray diffraction (XRD), X-ray Photoelectron Spectroscopy and Nuclear Magnetic Resonance (NMR) spectroscopy. From XRD, $\text{LiTi}_2(\text{PO}_4)_3$ (LTP) was determined to be the parent phase in all compounds. Further, it was found that the larger cations replace host Ti^{4+} in the LTP lattice. ^{27}Al NMR revealed two positions (Al_{01} and Al_{02}) at the octahedral site. The electrical properties were determined by Electrochemical Impedance Spectroscopy (EIS) exhibited a bulk Li^+ ion conductivity to be in the range of 10^{-4} S/cm for LAGSTP. The transport number study indicated a 75% Li^+ conductivity for the doubly doped LAGSTP compound which makes it an ideal candidate for cathode material in solid state lithium ion batteries.

ES10.06

Structure Changes of Li_4SnS_4 Electrolytes in Humidified Atmosphere Takuya Kimura, Takumi Nakano, Kota Motohashi, Atsushi Sakuda, Masahiro Tatsumisago and Akitoshi Hayashi; Osaka Prefecture University, Osaka Furitsu Daigaku, Sakai, Osaka, JP, academic, Japan

The development of sulfide electrolytes with high ionic conductivity and chemical stability is indispensable for applying to all-solid-state lithium batteries. Sulfide electrolytes have the advantage of high conductivity and high ductility but have a disadvantage in releasing H₂S gas upon exposure to air and moisture. We have previously reported Li_4SnS_4 and Li_3SbS_4 electrolytes by a mechanochemical process to suppress the generation of H₂S gas [1,2]. In particular, Li_4SnS_4 has crystal polymorphs of metastable hexagonal phase and stable orthorhombic phase. The metastable hexagonal phase shows higher ionic conductivity of 10^{-4} S cm⁻¹ than the stable orthorhombic phase. In addition, Li_4SnS_4 generates significantly less H₂S gas than Li_3PS_4 , which generates the least H₂S among $\text{Li}_2\text{S-P}_2\text{S}_5$ electrolytes [3]. Using sulfide electrolytes generating no H₂S in a low dew point environment is advantageous in battery assembly. However, the structural changes at a commercial dew point have not been clarified in detail.

This study focused on Li_4SnS_4 electrolytes and the X-ray diffraction (XRD) measurements with flowing humidified N₂ gas. The crystal structure analysis and characterization for crystals of the exposed Li_4SnS_4 were performed.

The starting materials Li₂S and SnS₂ were weighed to a given composition ratio in a dry argon atmosphere and then mechanochemically treated with a planetary ball mill apparatus. Subsequently, obtained powder was heated at 260°C for 2 hours. The structure changes of Li_4SnS_4 during humid air exposure were evaluated by *in-situ* X-ray diffraction measurements. Furthermore, the exposed samples were dried under vacuum. The XRD measurements, thermogravimetric-differential thermal analyses (TG-DTA), and ionic conductivity measurements by the AC impedance method were performed for the

obtained powder sample. The crystal structure of the Li_4SnS_4 hydrate was determined using Rietveld refinement.

When Li_4SnS_4 was exposed to the atmosphere at a dew point of -20°C for 1 hour, the *in-situ* XRD patterns during air exposure showed the peaks attributed to the hexagonal phase. After 2 hours, the XRD pattern changed significantly, and peaks attributable to a new phase were observed. In the XRD pattern of the vacuum-dried sample, only peaks attributable to the new phase were observed.

The peaks of the new phase were indexed in the tetragonal system. The Rietveld refinement of the model structure showed that the crystal structure of the new phase had the SnS_4 units at the body-center position and the water molecules corresponding to the formula amount in the spaces among the units.

In the TG-DTA curves of the hydrate, a large endothermic peak and weight loss were observed around 120°C . The amount of weight loss was about 21%, corresponding to 4 mol equivalents of water.

The ionic conductivity of the hydrate is $3.3 \times 10^{-9} \text{ S cm}^{-1}$ at 25°C , and the activation energy is 110 kJ mol^{-1} . The hydrate was not suitable for ionic conductors.

By heating at 260°C , the tetrahydrate was dehydrated to the hexagonal phase. The anhydrate showed the ionic conductivity of $10^{-4} \text{ S cm}^{-1}$ at 25°C , suggesting that Li_4SnS_4 reversibly absorbed and released water molecules.

ES10.07

Elemental Inhomogeneity, the Cause of Ga-Doped LLZO Failure? [Nomaan Nabi](#); Imperial College London, United Kingdom

Currently, a vast amount of research into fast lithium-ion conductors is taking place for application into solid electrolytes. The most attractive compositions are from the garnet family with the chemical composition of $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ [1]. LLZO has high lithium-ion mobility at room temperature, a large electrochemical window that allows high voltage cathodes to be employed and good stability with lithium metal anodes. Typically, LLZO is doped at the lithium position with donor cations these include Al^{3+} and Ga^{3+} which provide stability of the cubic crystal phase thus allowing Li^+ mobility in three dimensions. The mobility for Ga-LLZO has been reported to be above $10^{-3} \text{ S.cm}^{-1}$ [2], [3] this is the composition that will be mainly focused on in the poster.

Preliminary investigations have shown that due to lithium loss during high processing temperatures oxygen vacancies are formed because of the charge compensation mechanism[4]. The quantification of oxygen vacancies as an effect of the processing conditions and its effect on the conductivity of oxygen and lithium ions have been investigated in this work using electrochemical impedance spectroscopy and cell cycling.

The effect of different densification atmospheres (Ar, Vac, and O_2) on oxygen vacancies are measured using ^{18}O isotopic labelling coupled with the Time of Flight Secondary Ion Mass Spectrometer (ToF-SIMS) to assess which results in a higher degree of oxygen defects and elemental segregation. This work will be correlated with lithium defect chemistry and mobility to understand the lithium critical current density for dendrite growth which are detrimental to battery life.

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ES10.08

The SEI of "LiPON" in Contact with the Lithium Metal Anode – A Quantitative Assessment [Matthias Geiss](#), [Thomas Leichtweiss](#), [Joachim Sann](#) and [Jürgen Janek](#); Justus Liebig Universität Giessen, Germany

Solid-state batteries (SSB) currently attract large interest due to their expected stability, inherent safety and the intrinsic separator function of the solid electrolyte (SE). Combined with a high-voltage material as cathode the SE may enable the use of lithium metal anodes which are necessary to achieve competitive energy densities. One of the remaining key challenges is the electrochemical stability of both electrodes in contact with the SE: Due to the highly oxidizing potential of the cathode and the highly reducing conditions on the lithium anode side, chemical decomposition of the SE may deteriorate both contacts. The transport properties of thereby formed solid electrolyte interphases (SEI) then determine the device performance.

Here [1], we present a detailed study on the direct observation of such interphases between lithium metal and thin-film "LiPON" (lithium phosphorous oxide nitride, $\text{Li}_x\text{PO}_y\text{N}_z$) solid electrolyte as model system. By applying a novel technique, we follow the chemical reactions during contact formation *in situ* by photoelectron spectroscopy (XPS) and discuss the underlying reaction mechanisms. [2] In addition to a quantitative chemical analysis of the reaction products for different "LiPON" compositions, we also demonstrate that the thickness of the SEI on thin-film solid electrolytes can be directly measured by this method.

We find that "LiPON" reacts in contact with lithium metal and the binary compounds Li_2O , Li_3P and Li_3N are formed in a two-step reaction with Li_3PO_4 as intermediate product. Moreover, the thickness of the formed interphase depends on the composition of the "LiPON" films and is found to be less than 5 nm.

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ES10.09

Studies on Spinel-Layer Composite Cathode for Lithium-Ion Battery [Nischal Oli](#); Universidad de Puerto Rico Recinto de Rio Piedras, Puerto Rico

The development of rechargeable lithium-ion batteries with higher energy density is of technological importance for applications. In this context, the use of active spinel cathode LiMn_2O_4 and $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ materials has attracted attention due to its robust stable structure and layer cathode Li_2MnO_3 materials known due to high capacity at moderate rates during intercalation of the lithium ions. We report studies on compound of $x\text{LiMn}_2\text{O}_4 - (1-x)\text{Li}_2\text{MnO}_3$ composite cathode, where ($x = 0.1, 0.2, 0.3, 0.4$ and 0.5) for high energy density and high-capacity retention for hybrid applications. Sol-gel route has been employed for synthesis of the layer and spinel compound for cathode composite and Intimate mixing of two compound materials was achieved by a ball milling for a cathode paste. The key challenges and corresponding strategies for these materials will be discussed, with an emphasis placed on the intrinsic structural properties and energy storage electrochemistry with respect to the redox reactions. The gravimetric energy density of our composite cathode materials will carry out in comparison with the LiMn_2O_4 and Li_2MnO_3 electrodes used in lithium-ion batteries and provide a new alternative material for applications where weight, rather than volume is a critical factor. Preliminary data of electrochemical studies revealed high capacity and cycle

retentions of composites.

ES10.11

Influence of Li_2MnO_3 Content on Structure and Electrochemical Properties of $x\text{Li}_2\text{MnO}_3-(1-x)\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ for Li-Ion Batteries Kuan-Zong Fung, Shu-Yi Tsai and Wei-Zhi Lin; National Cheng Kung University, Taiwan

Recently, lithium-rich layered oxides have become attractive cathode materials for high storage energy applications. Lithium rich layered oxides materials, represented by the general formula $x\text{Li}_2\text{MnO}_3-(1-x)\text{LiMO}_2$ in which M is Mn, Ni and Co are of interest for both high-power and high capacity lithium ion cells. In this study, a series of cathode materials with molecular notation of $x\text{Li}_2\text{MnO}_3-(1-x)\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ ($x = 0, 0.3, 0.5, 0.7$ and 1.0) were synthesized by sol-gel method to investigate their structure and electrochemical properties. The crystal structure of the samples were examined by X-ray diffraction. It is show that the structure of $x\text{Li}_2\text{MnO}_3-(1-x)\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ possessed the composite characteristic. Its electrochemical performance is examined with galvanostatic charge/discharge. Increasing Li_2MnO_3 content may stabilize Li rich structure to increase capacity but the irreversible reaction of Li_2MnO_3 would reduce capacity. These factors resulted that $0.5\text{Li}_2\text{MnO}_3-0.5\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ cathode exhibited best electrochemical performance with discharge capacity 250 mAh/g.

ES10.12

Theoretical Understanding of the Deposition and Growth of Lithium in a Solid State Lithium-Ion Conducting Electrolyte Yudong Wang, Xingwen Yu and Xiao-Dong Zhou; University of Louisiana at Lafayette, United States

All-solid-state lithium batteries have been extensively pursued for next-generation energy storage, in which the state electrolyte (SSE) is a key component. While the use of an SSE may suppress the formation of dendrites observed in a conventional lithium ion battery, recent research has revealed that the deposition of lithium exists at the electrode-electrolyte interface in an all-solid-state lithium battery. Furthermore, the deposition of lithium has been observed inside an SSE during the cell cycling, which may lead to the loss of capacity and induce safety issues. In this work, we first present a thermodynamic model that is built based on a local equilibrium while taking consideration of the electronic conduction in an SSE. The electronic conductivity is a key variable to determine the chemical potential of lithium. The distribution of chemical potential of lithium is then calculated based on transport properties of an SSE. When the lithium chemical potential is higher than the sum of the elastic energy and surface energy, the change of Gibbs free energy for lithium formation is less than zero, which is the thermodynamic criterion for the deposition of lithium in an SSE. We will present our ongoing experimental research, as well as the electrochemical and materials characterization, to elucidate the approaches to control the deposition of lithium in an all-solid-state battery.

ES10.13

Binder-free High Temperature Stable Polymer-Inorganic Hybrid Separator for Improved Safety, Thermal, Mechanical and Electrochemical Performance of Li-Ion Battery Sagar A. Joshi¹, P. Sivaraj¹, Josef Breu² and Seema Agarwal¹; ¹University of Bayreuth, Germany; ²Universitat Bayreuth, Germany

Layered inorganic materials with inherent ion exchange properties are the promising component for improving the safety and performance of rechargeable batteries. A separator combining the high-temperature stable polymer matrix and the layered inorganic sheets has been developed. Here, an effective strategy has been designed to prepare the separator containing high-temperature stable polymer and layered inorganic sheets using a simple binder-free and filtration approach. The composite membrane shows excellent properties, such as superior wettability (Solvent uptake- 413%), thermostability (>600 °C), flame resistance, and interfacial compatibility, resulting from the interconnected porous network structure formed by the synergistic porous structure of polymer membrane and inorganic nano-sheets. Compared with the commercial separators, our separator shows excellent Li-ion conductivity (4.09×10^{-3} S/cm), Li-ion transference number (0.44) (Celgard- 0.27), cycling stability, and rate performance. The Li-ion exchange capability of our separator provides broader prospects for the application of the separator towards advanced-safety and high-performance of Li-ion batteries.

SESSION ES11: Beyond Li-ion I
Session Chairs: Montse Casas Cabanas and Mir Mehraj Ud Din
Friday Morning, July 22, 2022
Lobby Level, Avenue 34, The Loft

9:10 AM **ES11.01

Calcium Based Batteries—Lessons Learnt and Challenges Ahead M Rosa Palacin; Institut de Ciencia de Materials de Barcelona, Spain

The aim to develop batteries based in multivalent metal anodes has recently reemerged as part of the worldwide quest for new energy storage technologies with high energy density. Amongst these, calcium concepts have been less explored than their different counterparts despite exhibiting interesting prospects. Indeed, figures of merit attainable at the cell level computed using simple models indicate that the theoretical energy densities could easily top the state-of-the-art Li-ion, with costs being potentially much lower.

The achievement of reversible plating/stripping of calcium in organic electrolytes prompted the screening of suitable positive electrodes. Both traditional intercalation hosts and alternative inorganic materials have been investigated with diverse success. Electrochemical extraction of calcium in some ternary transition metal ions is feasible but the reversibility of the process is more difficult to achieve, which is likely related to strong solvation of calcium ions, with reactions sometimes involving solvent co-intercalation and high cell overpotential.

Overall, there is a long and winding road to follow before reliable proof-of-concept can be achieved and technological prospects evaluated. Development of reliable experimental setups, including reference and counter electrodes, coupled to complementary characterization techniques, as well as computational tools, is mandatory if steady progress is to be achieved.

9:40 AM *ES11.02

Interplay of Chemistry and Function at Lithium and Calcium Metal Anode Interfaces Betar Gallant; Massachusetts Institute of Technology, United States

Metal anodes such as lithium (Li) and calcium (Ca) offer significantly higher capacities than graphite and are therefore compelling alternatives to meet

range and performance targets for electric vehicles if key issues can be addressed. However, their interfacial reactivity with electrolyte solvent and salt upon electroplating leads to evolution of a solid electrolyte interphase (SEI) that governs cycleability and leads to capacity losses. While the SEI can be minimized or mitigated through judicious electrolyte selection, the field is still searching for rational design principles to identify the properties, composition, morphology and functionality that define an ideal SEI, such that electrolytes and additives can be designed to form improved interfaces and maintain them over long cycle life.

In an attempt to inform such efforts, our work has developed model SEI that allow for phase-wise experimental interrogation and extraction of properties such as ionic conductivity, diffusivity, microstructure and electrochemical/chemical reactivity and performance. Early efforts focused on synthesizing ionic phases relevant to the native Li SEI at nanoscale thickness directly on Li metal, including lithium oxide (Li₂O) and lithium fluoride (LiF). These interfaces have been interrogated *via* targeted electrochemical and spectroscopy techniques to reveal their transport properties, chemical reactivity and most recently, Li⁺ exchange kinetics in different electrolytes. The results provide insight into how such model phases may function in a native SEI. I will then discuss more recent efforts looking at organic phases of the SEI, including those using titration-based chromatography to quantify the evolution of organic phases during initial SEI formation and over cycling. By applying these tools to high- and low-CE electrolytes alike, we are identifying descriptors that can support continued development of advanced electrolytes and additives.

Recently, we are also translating these efforts to study Ca metal anodes, which exhibit exacerbated reactivity towards most electrolytes and severely interface-dominated electrochemical behaviors. I will describe some of our early findings that reveal how Ca²⁺ coordination can dramatically influence the activity – or lack thereof – of Ca plating/stripping, which directly relates to the nature of the formed interface.

10:00 AM ES11.03

From Simple to High Entropy Transition Metals Oxides—Applications in Electrochemical Energy Storage Janina Molenda; Akademia Gorniczno-Hutnicza imienia Stanisława Staszica w Krakowie, Poland

The author of this work basing on her own investigations of A_xMO₂ cathode materials (A=Li, Na; M=Ni, Co, Mn, Fe, Ti, Cu) has demonstrated that the electronic structure of these materials plays an important role in the electrochemical intercalation process [1]. The paper reveals correlation between crystal and electronic structure, chemical disorder, transport and electrochemical properties of layered Li_xCoO₂, Na_xCoO_{2-y}, Li_xNi_{1-y-z}Co_yCu_zMn_{0.1}O₂ and Na_xNi_{1/5}Co_{1/5}Fe_{1/5}Mn_{1/5}Ti_{1/5}O₂ high entropy cathode materials and explains of apparently different character of the discharge/charge curve in those systems. The complex studies, including experimental as well as theoretical parts (electronic structure calculations performed using the Korringa-Kohn-Rostoker method with the coherent potential approximation KKR-CPA to account for chemical disorder), showed a strong correlation between structural, transport and electrochemical properties of these materials.

The battery on the base on the developed high entropy oxides NaNi_{1/5}Co_{1/5}Fe_{1/5}Mn_{1/5}Ti_{1/5}O₂ cathode materials are characterized by high potential, high capacity and high rate capability guaranteeing high energy and power densities. The quickly appearing of O3-P3 phase transformation in this oxide leads to metallic conductivity and better kinetics of Na|Na⁺|Na_xMn_{0.2}Fe_{0.2}Co_{0.2}Ni_{0.2}Ti_{0.2}O₂ cell. By using the structural analysis methods (*operando* XRD, XAS and Mossbauer spectroscopy) we described the mechanism that governs the sodium deintercalation/intercalation processes in Na_xMn_{0.2}Fe_{0.2}Co_{0.2}Ni_{0.2}Ti_{0.2}O₂ cathode with indicating the valence state of transition metals. Our investigation indicated that only titanium is electrochemically inactive during the cell operation, while Mn, Fe, Co, Ni undergo reduction and oxidation processes [2].

The detailed analysis presented in this work provides a strong proof that the high-entropy Na_xMn_{0.2}Fe_{0.2}Co_{0.2}Ni_{0.2}Ti_{0.2}O₂ oxide with reduced content of cobalt and nickel, might be applicable in sodium batteries technology, especially in terms of large-scale energy storage units.

Acknowledgements

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10:15 AM ES11.04

Phenomena of Multi-Way Sodium Storage in Transition Metal Dichalcogenides- MoS₂ vs. MoSe₂ Anna F. Plewa¹, Andrzej J. Kulka¹, Emil Hanc², Katarzyna Walczak¹ and Janina Molenda¹; ¹Akademia Gorniczno-Hutnicza imienia Stanisława Staszica w Krakowie Wydział Energetyki i Paliw, Poland; ²Instytut Gospodarki Surowcami Mineralnymi i Energia Polskiej Akademii Nauk, Poland

Sodium-ion batteries have recently gained a lot of research interest as a cheaper alternative to lithium-ion batteries. However, one of the bottlenecks of them is the lack of anode materials with appropriate electrochemical performance, including high specific charge, good rate capability, and high capacity retention.

Generally, the anode materials may be classified according to three distinct charge storage mechanisms: alloying, conversion, and intercalation. Among them, Na⁺ storage occurring via intercalation is the most common process which covers Ti-based and carbonaceous anodes. These materials exhibit good reversibility and relatively small volume changes. Nonetheless, the reversible intercalation of Na⁺ is mainly limited by the deformations that the crystal structure can withstand and the limited redox activity of the transition metals. This type of anode has intrinsic limitations in terms of capacity, thus further increase of the energy density can be expected using different storage mechanisms. The extremely high values can be achieved from alloying reactions between Na and Sn or P to form, for example, Na₁₅Sn₄ or Na₃P. However, the practical utilization of these reactions has been severely limited by the huge volume changes (even 400%) associated with the (de)sodiation process. The discovery of the third type of Na storage reaction referred as conversion mechanism brought a compromise between high capacity and small volume changes. The key to the reversibility of the conversion reactions lies in the formation of metal nanoparticles with a large interfacial surface embedded in sodium compounds. Conversion-based anodes mainly include the compounds of transition metals with oxygen, nitrogen, phosphorous, sulfur, or selenium. Among them, transition metal dichalcogenides (TMDs) gained special popularity since their sodium storage mechanism is a unique combination of alloying, conversion, and intercalation reactions.

In this work, we elucidate the sodiation mechanism of two leading members of TMDs family (MoS₂ and MoSe₂), which recently have gained increased research attention. The sodium storage processes in MoS₂ and MoSe₂ remain under intensive discussion. Since the *ex-situ* approach turned out to be an insufficient tool in in-depth investigation of the (de)sodiation mechanism of MoS₂ and MoSe₂ electrodes, within this work we applied a comprehensive approach of using combined Raman spectroscopy, *operando* X-ray diffraction (XRD), *operando/ex-situ* X-ray absorption spectroscopy (XAS), and X-ray photoelectron spectroscopy (XPS) techniques.

The novel concept of MoS₂ (de)sodiation mechanism is proposed based on repetitive disintegration and rearrangement of Na₂S, Na₂S₂ and Mo accompanied by the formation of new well-crystallized phase Na_xMo₃S₄. Since Na_xMo₃S₄ crystallizes by rapid electrochemically driven congruent crystallization from an amorphous matrix, it contributes to the high Na⁺ diffusion, thus its formation is crucial for the high-performance MoS₂ anode. The

presented iterative conversion and electrochemical type crystallization reactions provide new insight into the electrochemical (de)sodiation process of MoS₂.

Moreover, an anomalous multi-way mechanism in MoSe₂ electrode, including all three scenarios (intercalation, conversion, and alloying), is reported. The intercalation product of the discharge/charge process is a mixture of Se, Mo, and 1T-structured Na_xMoSe₂. An unexpected phenomenon of Se precipitation leads to the additional alloying reaction, which is exclusive among all chalcogenides and runs together with conversion and intercalation reactions in the same cycle. This new concept of the sodium storage process includes two models, previously seemed to be mutually exclusive.

10:30 AM ES11.05

A Ternary Metal Fluoride Pb₂CuF₆ as a Cathode Material for Fluoride-Ion Batteries Takeshi Tojigamori^{1,2}, Hiroshi Nakajima³, Hidenori Miki¹, Naoki Matsui², Tomotaka Nakatani⁴, So Fujinami⁴, Kousuke Noi^{4,1}, Hirofumi Tsukasaki³, Kota Suzuki², Masaaki Hirayama², Shigeo Mori³, Takeshi Abe⁴ and Ryoji Kanno²; ¹Toyota Jidosha Kabushiki Kaisha Higashifuji Kenkyujo, Japan; ²Tokyo Kogyo Daigaku, Japan; ³Osaka Furitsu Daigaku, Japan; ⁴Kyoto Daigaku, Japan

Abstract

All-solid-state fluoride-ion batteries are promising next-generation batteries due to their high energy densities. CuF₂, which is one of the promising candidates for cathode materials, has a high theoretical capacity (527 mAh g⁻¹) due to its two-electron reaction per Cu atom [1, 2]. However, the ionic conductivity of CuF₂ is very low (10⁻¹¹ S cm⁻¹ at 140°C) [3] and charging/discharging reactions are possible only at low rates [2]. Here, we report Pb₂CuF₆ as a cathode material, exhibiting high-rate capability of the all-solid-state fluoride-ion batteries. Pb₂CuF₆ was synthesized by a mechanical milling method and evaluated for electrochemical properties at 140°C.

Pb₂CuF₆, which has fluorite-related structure [4], exhibited a high ionic conductivity of 3 × 10⁻⁵ S cm⁻¹ at 140°C. Therefore, Pb₂CuF₆ cathode composite reacted to charging and discharging without the addition of solid electrolyte. The initial discharging capacity of Pb₂CuF₆ cathode was 78 mAh g⁻¹. Subsequently, the charge capacity decreased to 44 mAh g⁻¹, after which a reversible charge/discharge reaction was observed. Pb₂CuF₆ cathode exhibited Cu utilization of 24% even at 1 mA cm⁻² discharge (corresponding to 0.77 C), which is four times higher than that of CuF₂ cathode. To investigate the origin of the high rate capability, the charge-discharge reaction products of Pb₂CuF₆ were investigated. Synchrotron X-ray diffraction measurements revealed that ion-conductive β-PbF₂ [5] and metallic Cu were formed in Pb₂CuF₆ cathode after discharging, and Pb₂CuF₆ was reversibly formed after charging. Transmission electron microscopy confirmed that all the products of the charge-discharge reaction were present in nanoparticle form. The high fluoride ion conductivity of the charge-discharge reaction products and the short fluoride-ion diffusion length in the active material due to the nanoparticle shape may have contributed to the high-rate characteristics of Pb₂CuF₆.

Acknowledgement

This work is based on results obtained from two projects (JPNP16001 and JPNP21006) commissioned by the New Energy and Industrial Technology Development Organization (NEDO). The synchrotron radiation experiments were performed at the BL28XU beamline of SPring-8 with the approval of the Japan Synchrotron Radiation Research Institute (JASRI) (Proposal Nos. 2020A7613 and 2021A7618).

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10:45 AM BREAK

11:00 AM *ES11.07

Sustainability of Sodium-Ion Batteries Emma Kendrick; University of Birmingham, United Kingdom

Sustainability in batteries needs to be considered at a holistic level, from materials source, manufacturing, lifetime and if there is value in the materials what happens to the batteries at end of life. Sustainability needs to consider the full lifetime of the materials. In this work we discuss three different aspects of sustainable considerations within a sodium-ion technology development. Materials developments, cell lifetime and optimisations, and design for recycling. The cell type is focused upon nickel based layered oxide material cathode with hard carbon anodes. We discuss a facile method for manufacturing a stabilised O3- type layered oxide via simultaneous doping and surface coating. A higher average voltage is obtained, which stabilised the high voltage phase transition to higher voltages, and results in longer-cycle life.

The lifetime and performance properties of the cell are also considered. Electrolyte additives which show enhanced performance properties in electrodes and full cell configurations are discussed. In particular those which remove small molecules such as water from the electrolyte during use. ZSM-5 has been utilised as a water scavenger in both an electrode and an electrolyte, and both methods of addition show significant improvement in lifetime of the cell and the electrodes with less SEI build up over time.

Finally design for remanufacture is also discussed, utilising water-based binder systems we show differences in delamination and material recovery.

Utilising different recycling schemes through shredding and physical processing through to disassembly processes improvements in recovery rates are required. Particularly for low value materials, where the techno-economics of the processes do not currently work. Direct recycling of materials reclaimed from the batteries, wherever possible allows value within the material design to be maintained, rather than relying directly upon elemental value. Aspects of direct loop recycling and short loop recycling are discussed with respect to current lithium-ion technologies, and the ability to directly translate this to sodium-ion.

In conclusion three aspects for sustainability considerations are discussed with respect to the materials life-cycle; active material optimisation, longevity and life-time when in use and electrode developments for recycling.

11:20 AM ES11.10

Tailoring High Capacity NASICON Cathodes for Sodium-Ion Batteries Premkumar Senguttuvan and Subham Ghosh; Jawaharlal Nehru Centre for Advanced Scientific Research, India

The development of high voltage and high capacity Na-ion cathodes is one of the key challenges for the successful realization of high energy density sodium ion batteries.¹ Whilst layered Na-ion transition metal oxides are the frontrunners for practical application, their poor air stability and cycling performances are still required to be addressed.² On the other hand, phosphate cathodes offer high structural stability and insertion voltages as well rich structural diversity.³ Among them, NASICON-Na₃V₂(PO₄)₃ cathode is attractive because of its high intercalation voltage (3.45 V vs. Na⁺/Na⁰), moderate capacity (~120 mAh g⁻¹) and excellent rate capability.⁴ The sodium (de)intercalation process in the NVP cathode proceeds via a two-phase mechanism and the corresponding redox activity is ascribed to the operation of V⁴⁺/V³⁺ couple. Further, other cations are substituted in the place of vanadium of the NVP

lattice to seek the participation multiple redox centres, thereby enhancing intercalation capacities. Particularly, the NASICON end member $\text{Na}_4\text{VMn}(\text{PO}_4)_3$ has garnered significant attention due to its reduced cost, improved insertion voltage and the participation of $\text{V}^{5+}/\text{V}^{4+}$, $\text{V}^{4+}/\text{V}^{3+}$ and $\text{Mn}^{3+}/\text{Mn}^{2+}$ redox couples.⁵ Recently, our group has developed a series of $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ -type cathode in which vanadium cations are partially replaced by different cations such as Mn^{2+} , Mg^{2+} , Al^{3+} and In^{3+} .⁶⁻⁸ The Mn-rich $\text{Na}_{3.75}\text{V}_{1.25}\text{Mn}_{0.25}(\text{PO}_4)_3$ cathode has displayed highest capacity and rate performances (100 and 89 mAh g^{-1} at 1 and 5C rates, respectively) due to its modulated V- and Mn-redox centers and optimum bottleneck size. The substitution of Mg^{2+} and Al^{3+} into the $\text{Na}_3\text{VMn}(\text{PO}_4)_3$ -type cathode has enhanced its rate performances and cycling stability. The In-substituted $\text{Na}_3\text{VIn}(\text{PO}_4)_3$ cathode has exhibited asymmetric multi-redox $\text{V}^{5+}/\text{V}^{4+}/\text{V}^{3+}$ operation during Na-ion (de)intercalation reaction. During this talk, we will highlight the importance of chemical tuning to enhance the electrochemical performances of NASICON cathodes.

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SESSION ES12: Flow Batteries
 Session Chair: Mir Mehraj Ud Din
 Friday Morning, July 22, 2022
 Lobby Level, Avenue 34, Studio 2

9:10 AM *ES12.01

Strategies for Addressing Crossover in Non-Aqueous Redox Flow Batteries [Shelley Minteer](#); The University of Utah, United States

Redox flow batteries (RFBs) are a class of devices in which the decoupling of the power and energy provide great potential in grid-scale energy storage. Non-aqueous all-organic redox flow batteries have been suggested as an alternative to aqueous vanadium RFBs due to the potential to achieve higher energy density at a lower cost. Nevertheless, their value is countered by the insufficient rapid electrolyte crossover in the membranes compatible with these organic electrolytes. Bipolar redox-active molecules (BRMs), single molecules that undergo both positive and negative redox reactions, suggest an interesting way of addressing this challenge. The unique redox chemistry of BRMs is commensurate to vanadium species, but enable greater design flexibility and potentially more favorable properties that are otherwise unattainable. However, there are complex tradeoffs in their properties. Balancing these properties have been incredibly challenging. As such, we employed crystallography, quantum chemistry, and molecular dynamics to develop a fundamental rubric for BRM rational design and uncovered the likely origins of these complex tradeoffs. Our studies revealed that the oscillating properties observed are a result of conformation-related interactions, suggesting the critical role of structural order in BRM systems. Knowledge of these structural factors will allow more rational design of BRMs for organic RFBs for grid-scale energy storage. This talk will also discuss ion exchange polymer strategies for minimizing crossover in RFBs.

9:30 AM *ES12.02

High Performance and Low Cost Flow Batteries for Large Scale Grid Storage [Hongli \(. Zhu\)](#); Northeastern University, United States

As the number of generation sources from intermittent renewable technologies on the electric grid increases, the need for large-scale energy storage devices is becoming essential to ensure grid stability. Aqueous redox flow batteries (AORFB) are the most promising choice as they can improve the efficiency of the existing grid infrastructure by providing cost-effective storage together with a long life. Although the RFBs have been recognized as a viable technology for large-scale energy storage, the extensive utilization of the RFBs has been limited by the high cost. In our lab, several strategies have been published to reduce the cost of the RFB.

One effective way is to reduce the cost of the flow battery components by reducing the chemical cost of the electrolyte, the cost of electrode treatments, and finally, the cost of the ion exchange membrane. The work presented in the first part of the presentation aims to reduce the cost of the electrolyte by developing anolyte utilizing an organic crystal indigo carmine (IC-Na), a water-soluble derivative of the naturally occurring dye indigo. The 5,5'-indigodisulfonic acid (IC-H) is obtained through the substitution of sodium ions in IC-Na with protons (H^+). The aqueous solubility of IC-H was increased dramatically from 0.035 M to 0.760 M (1.52 M electron concentration) in protic solvents. The highly soluble and affordable IC-H with fast redox kinetics was used as a sustainable anolyte by pairing with different catholytes. Moreover, computational study was also conducted which signifies the prospect of further improvements in solubility and voltage window by tuning the structure.

The second part demonstrates an energy-efficient, affordable, and scalable surface modification method of graphite felt (GF) electrode based on the electrochemical exfoliation to enhance the mass and charge transfer of the electrode. Exfoliation of the GF was conducted in ammonium sulfate ($(\text{NH}_4)_2\text{SO}_4$) aqueous solution by breaking the weak van der Waals forces between the graphitic layers. The exfoliation incorporated sufficient oxygen functional groups that increase the active surface area, resulting in enhanced reaction kinetics at the electrode-electrolyte interface and improved hydrophilicity. Benefitting from the sufficient oxygen groups and superior wettability, the exfoliated GF (E-GF) shows brilliant electrocatalytic activity with minimized overpotential, higher volumetric capacity, and improved energy efficiency.

Finally, the last part of the talk introduces our works to develop stable and highly ion-selective membrane by both utilizing proton conductive groups or porous structures. For example, the cellulose nanocrystals (CNCs) incorporated in semicrystalline hydrophobic poly (vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) matrix was investigated. The high hydrophobicity of the PVDF-HFP matrix mitigates crossover of the electrolytes, whereas, the abundant and low-cost CNCs derived from wood provide high proton conductivity. The fundamental contributors for CNCs' excellent proton conductivity are the hydroxyl (-OH) functional groups, highly acidic sulfonate (-SO₃H) functional groups, and the extensive intramolecular hydrogen bonding network. The obtained membrane possesses excellent flexibility, high mechanical tensile strength, and superior selectivity.

9:50 AM ES12.03

Composite Lithium-Conductive LATP+PVDF Membranes—Development, Optimization and Applicability for Hybrid Redox Flow Batteries [Keith J. Stevenson](#); Skolkovskij institut nauki i tehnologij, Russian Federation

The redox flow batteries (RFBs) are energy storage devices enabling to rationalize energy distribution from renewable sources. The lithium metal hybrid flow batteries (Li-HFBs) represent a very promising type of RFBs distinguished by improved energy and power density and simplified configuration. Unfortunately, the absence of a highly conductive and stable membrane hinders the next Li-HFBs generation. Current research describes the development of $\text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3$ -poly(vinylidene fluoride) composite membrane and shows its applicability for Li-HFBs for the first time. The easily fabricated membranes demonstrate high ionic conductivity of $3.4 \times 10^{-4} \text{ S cm}^{-1}$ (in contrast with 0.74 and $0.16 \times 10^{-4} \text{ S cm}^{-1}$ of commercially available Nafion and Neosepta, correspondingly) and improved stability towards metallic lithium. The hybrid Li-TEMPO cell with composite membrane shows stable coulombic and energy efficiency (over 95 and 73%, respectively), moderate capacity decay from 2.5 to 1.4 Ah L^{-1} (preliminarily associated with membrane's permeability), and no membrane degradation after 100 charge/discharge cycles. The combination of functional features established for the proposed composite membranes makes them promising for Li-HFBs, as well as for other energy storage devices, and can potentially accelerate their introduction to the energy storage market.

10:05 AM ES12.04

Synthesis of Freestanding 3D N-Doped Graphene Nanoflower for High Performance BSH Devices Rebti Bhushan and AK Thakur; Indian Institute of Technology, India

Battery-Supercapacitor Hybrid (BSH) devices based on a battery-type negative and a supercapacitor-type positive electrode offers a promising solution for future advanced energy storage devices. An ever challenging task of fabricating a device with high energy density without compromising the power density and rate capability has been accomplished by designing a 3D flowerly shaped N-doped graphene (3D-NGNF) electrode, synthesized via a novel microwave assisted strategy, based BSH device with organic (LiPF_6) and aqueous electrolytes. The as prepared device consists 3D-NGNF as negative electrode exhibiting improved Li^+ ion diffusion coefficient $\sim 5.37 \times 10^{-9} \text{ cm}^2/\text{s}$ and graphene electrode as supercapacitor positive electrode. Benefiting from specially designed atomic doping (N~26.8 at%) and defect creation, 3D-NGNF BSH device exhibits a high energy density of 128.7 WhKg^{-1} and power density of 15.3 kWKg^{-1} with superior rate capability upto 48 Ag^{-1} . A capacity retention of 87% up to 12000 cycles at a rapid rate of 32 Ag^{-1} indicates its potential prospect as future generation electrode material for powering high performance electric vehicles and portable electronic devices.

10:20 AM ES12.05

Evaluation of the Polarization Resistance using Gaussian Processes and the Hilbert Transform Baptiste D. Py, Adeleke Maradesa and Francesco Ciucci; The Hong Kong University of Science and Technology School of Engineering, Hong Kong

Introduction

In the current context of global warming, batteries and fuel cells play a paramount role as they enable to store electricity from intermittent renewable sources and to replace combustion engines with electric cars. Understanding the physicochemical processes that govern their behavior is therefore crucial in order to improve these electrochemical systems. The electrochemical impedance spectroscopy (EIS) has emerged as a promising technique to investigate the properties of such systems [1]. EIS is now widely implemented to evaluate the polarization resistance, which is a highly-relevant parameter related to the internal resistance [2]. To analyze EIS spectra, the deconvolution of relaxation times (DRT) has emerged as a highly-accurate tool. In this work, we apply a model we previously developed with Gaussian processes (GP) to effectively calculate the polarization resistance of different batteries and fuel cells using the DRT [3].

Method

By leveraging the GP-Hilbert Transform (GP-HT) model, we are able to express the real part of the impedance both for the frequency 0 and the frequency increasing to +infinite given the condition that the real and imaginary parts of the experimental impedance are known [4]. This provides a mean value for these two real impedances, which then leads to the polarization resistance defined as the difference between both quantities [3]. Besides this direct application, the previous GP-HT model is also improved by including in the negative marginal log likelihood (NMLL) the two bounds that were used to define the band-limited kernel. Traditionally, the NMLL is minimized to optimize the experimental evidence, which leads to more accurate results compared to the previous work [4]. The limits of each kernel for equal frequencies, frequencies equal to 0 or increasing to + infinite is also investigated to ensure the finiteness of each quantity involved.

Results

We validated this extension with synthetic and real EIS data. Regarding the former, we considered the 1xZARC and 2xZARC models with different levels of noise; as for the latter, we used EIS spectra derived from real EIS experiments involving batteries and fuel cells. This opens the venue for new applications of GPs in the field of the DRT to analyze batteries, fuel cells, and possibly even supercapacitors more accurately.

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10:35 AM BREAK

SESSION ES13: Beyond Li-ion II
Session Chair: Juan Rosillo
Friday Morning, July 22, 2022
Lobby Level, Terrace

11:00 AM ES13.01

On the Thermodynamic Origin of the Formation of Li-Dendrites in an Electrochemical Cell Yudong Wang, Anil Virkar and Xiao-Dong Zhou;

University of Louisiana at Lafayette, United States

The direction of growth of neutral species in batteries and electrolyzers differs significantly. In a battery, dendrites can be formed during the charging process and are perpendicular to the interface between electrode and electrolyte. We will address the origin of the growth orientation of the neutral metal and elucidate the factors that govern the dendrite growth by using the concept of chemical potential of neutral lithium and the electronic current in the electrolyte. With the consideration of the electronic conductivity in the ionic conductive phases, the chemical potential difference of lithium could be calculated across the cell, and predicts lithium deposition in the solid-electrolyte interphase (SEI) layer. The electronically conducting metal precipitate could work as a part of electrode and allow further growth along the current direction, resulting in the formation of dendrites. During growth, the ionic conductivity and the thickness distribution of the SEI layer determine the growth kinetics and the dendrite shape. A lower ionic conductivity and a nonuniform SEI layer lead to a sharp lithium dendrite. On the other hand, a low electronic conductivity and a high ionic conductivity of the electrode/electrolyte interface are in favor of suppressing the formation of a neutral species.

11:15 AM ES13.03

High-Rate Long-Lifespan Lithium-Sulfur Batteries via Stereolithography Technique and Oxidative Chemical Vapor Deposition Yuxuan Zhang¹, Thomas Kivevele², Han Wook Song³ and SungHwan Lee¹; ¹Purdue University, United States; ²Nelson Mandela African Institution of Science and Technology, Tanzania, United Republic of; ³Research Institute of Standard and Science, Korea (the Republic of)

Enhancing battery energy storage capability and reducing the cost per average energy capacity is urgent to satisfy the increasing energy demand in modern society. The lithium-sulfur (Li-S) battery is especially attractive because of its high theoretical specific energy (around 2600 Wh kg⁻¹), low cost, and low toxicity.¹

Despite these advantages, the practical utilization of lithium-sulfur (Li-S) batteries to date has been hindered by a series of obstacles, including low active material loading, shuttle effects, and sluggish sulfur conversion kinetics.² The traditional 2D planer thick electrode is considered as a general approach to enhance the mass loading of the Li-S battery.³ However, the longer diffusion length of lithium ions, which resulted in high tortuosity in the compact stacking thick electrode, decreases the penetration ability of the electrolyte into the entire cathode.⁴ Although an effort to induce catalysts in the cathode was made to promote sulfur conversion kinetic conditions, catalysts based on transition metals suffered from the low electronic conductivity and some elements (i.e.: Co, Mn) may even absorb and restrict polysulfides for further reaction.⁵

To mitigate the issues listed above, herein we propose a novel sulfur cathode design strategy enabled by additive manufacturing and oxidative chemical vapor deposition (oCVD).^{6,7} Specifically, the cathode is designed to have a hierarchical hollow structure via a stereolithography technique to increase sulfur usage. Microchannels are constructed on the tailored sulfur cathode to further fortify the wettability of the electrolyte. The as-printed cathode is then sintered at 700 °C in a N₂ atmosphere in order to generate a carbon skeleton (i.e.: carbonization of resin) with intrinsic carbon defects. The intrinsic carbon defects are expected to create favorable sulfur conversion conditions with sufficient electronic conductivity. In this study, the oCVD technique is leveraged to produce a conformal coating layer to eliminate shuttle effects. Identified by scanning electron microscopy and energy-dispersive X-ray spectroscopy mapping characterizations, the oCVD PEDOT is not only covered on the surface of the cathode but also the inner surface of the microchannels. High resolution x-ray photoelectron spectroscopy analyses (C 1s and S 2p orbitals) between pristine and modified sample demonstrate that the high concentration of the defects have been produced on the sulfur matrix after sintering and posttreatment. In-operando XRD diffractograms show that the Li₂S is generated in the oCVD PEDOT-coated sample during the charge and discharge process even with a high current density, confirming an eminent sulfur conversion kinetic condition. In addition, ICP-OES results of lithium metal anode at different states of charge (SoC) verify that the shuttle effects are excellently restricted by oCVD PEDOT.

Overall, the high mass loading (> 5 mg cm⁻²) with an elevated sulfur utilization ratio, accelerated reaction kinetics, and stabilized electrochemical process have been achieved on the sulfur cathode by implementing this innovative cathode design strategy. The results of this study demonstrate significant promises of employing pure sulfur powder with high electrochemical performance and suggest a pathway to the higher energy and power density battery.

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7 Zekoll, S. *Energy & Environmental Science* **11**, 185-201.

11:30 AM ES13.05

Devising Cathodes for Lithium Sulfur Batteries Doped with Ferroelectric Materials Yielding Sustainable High-Capacity Performance Claudia C. Zuluaga-Gomez¹, Christian Plaza², Gerardo Morell¹, Margarita Correa³, Yi Lin⁴ and Ram Katiyar¹; ¹Universidad de Puerto Rico Recinto de Rio Piedras, Puerto Rico; ²Massachusetts Institute of Technology, United States; ³Universidad del Atlantico, Colombia; ⁴National Institute of Aerospace, United States

Lithium-Sulfur (Li-S) batteries have been vigorously revisited in recent years due to the need of advanced energy storage technologies which can be more efficient and cost effective. Li-S batteries have been considered promising for high energy density batteries to be used in electronic devices such as electric vehicles and aircrafts which are becoming more prevalent. The discharge capacity of current Lithium-Ion Batteries (LIBs) technology is reaching its theoretical limit, which is far from enough to keep up with current and growing portable energy needs. The research on Li-S batteries is promising, since they have a high theoretical gravimetric energy density of 2,600 Wh/kg, compared to the energy density of the LIBs which is lower than 200 Wh/kg. In addition, Li-S batteries have a high theoretical capacity of 1,675 mAh/g versus 300 mAh/g in LIBs. Although Li-S batteries are in great demand, their development is still plagued by rapid capacity fading mainly stemming from polysulfide shuttle. The coupling of a highly polarized ferroelectric nanoparticles layer is an approach that can be used to reduce the characteristic polysulfide shuttling in Li-S batteries. This coupling helps to build up an internal electric field and induce macroscopic charges separation on the surface of the cathode of Li-S batteries. To improve the electrochemical performance of the cathode in Lithium-Sulfur batteries, holey graphene and carbon-based materials are employed. This allows for a dry compression manufacturing process to facilitate the bonding between the Sulfur and the ferroelectric nanoparticles layer to generate a more stable cathode. The result is less polysulfide shuttling to achieve the high-capacity storage required for the Li-S batteries to become the power source of today. The current research has the desired preliminary results of cathode composition S_{47.5}(BiFeO₃)₃hG_{47.5} in discharge specific capacity as a function of the cycle number: a reversible capacity of ~1,388 mAh/g was achieved with high coulombic efficiencies (> 87%) and active sulfur mass loading of 6.908 mgs/cm².

11:45 AM *ES13.06

Argyrodite-Type Solid State Ion Conductors for Solid State Batteries Linda Nazar, Laidong Zhou, A. Assoud and K. Kaup; University of Waterloo, Canada

All solid-state batteries that employ highly ionically conductive solid electrolytes and a lithium metal anode represent a particularly promising next-generation Li-ion technology. Considering a range of inorganic Li-ion conductors that have been developed to date, sulfide solid electrolytes exhibit

conductivities that can even surpass that of conventional organic liquid electrolytes. Argyrodite-structured sulfide solid electrolytes are one of the most promising materials in this class and are currently the dominantly used solid electrolyte for all solid-state battery fabrication owing to their ultra-high Li-ion conductivity, solid electrolyte interphase formed with Li metal and their ability to be prepared via scalable solution-assisted synthesis approaches. This presentation reports on our recent development of several argyrodite superionic conductors (including several new phases) and a comprehensive understanding of the origin of the underlying high conductivity: namely sulfide/halide anion site-disorder and Li cation site disorder. A high degree of sulfide/halide anion site-disorder (changes in anion distribution) modifies the anionic charge that in turn strongly influences the lithium distribution. Lithium cation site-disorder generated by increasing Li carrier concentration through aliovalent substitution, creates high-energy interstitial sites which activate concerted ion migration and flatten the energy landscape for Li ion diffusion. These concepts promote rational new solid electrolyte design and fundamental understanding of the structure - ion transport relationships in inorganic ionic conductors. Collectively, this will lead to the bottom-up engineering of cathode/anode-solid electrolyte interfaces, which should accelerate the development of safe, high energy density all solid-state lithium batteries.

SESSION ES14: New Approaches and Theory
Friday Morning, July 22, 2022
Lobby Level, Avenue 34, Studio 2

11:00 AM *ES14.01

New Insights into Lithium Superionic Conductors and Their Interfaces from Accurate, Large Scale Simulations with Machine Learning Interatomic Potentials Shyue Ping Ong, Ji Qi, Manas Chandrappa, Yunxing Zuo, Swastika Banerjee, Hideyuki Komatsu and Chi Chen; University of California San Diego, United States

Lithium superionic conductors (LSCs) are of major importance as solid electrolytes for next-generation all-solid-state lithium-ion batteries. While simulations based on ab initio methods have been extensively applied to study these materials, they are inherently constrained to high temperatures, small cell sizes and short time scales due to the prohibitive computational cost and poor scaling. In this talk, I will discuss a transformative new tool in the study of such materials – machine learning interatomic potentials (ML-IAPs), which is an automatable approach to develop of highly accurate descriptions of the potential energy surface of complex material systems. By enabling large scale simulations with linear scaling, I will show how ML-IAPs can provide new insights into transitions in the mechanisms and dimensionality of diffusion in LSCs with temperature. Such transitions account for the often-large discrepancies between predicted and experimentally measured ionic conductivities at room temperature. I will further demonstrate that using state-of-the-art active learning techniques, ML-IAPs can even be fitted even for heterogenous interfaces, allowing us to probe reactivity and stability at the electrode/LSC interface. Finally, I will share some design insights into specific solid-state battery chemistries based on these studies.

11:20 AM *ES14.02

Understanding Materials Dynamics in Solid-State Batteries with High-Capacity Anodes Matthew McDowell; Georgia Institute of Technology, United States

Solid-state batteries offer the promise of improved energy density and safety compared to lithium-ion batteries, but electro-chemo-mechanical evolution and degradation of materials and interfaces can play an outsized role in limiting their performance due to the all-solid nature of these systems. Here, I will present my group's recent work using *in situ* and *operando* experiments to understand interfacial evolution and stress changes in solid-state batteries with lithium metal and alloy anodes. *Operando* X-ray tomography is used to reveal interfacial dynamics in solid-state batteries with Li metal anodes. Segmentation and detailed image analysis enable correlation of interfacial contact loss to electrochemical behavior of symmetric cells, and the loss of interfacial contact area at the Li metal interface is found to cause current constriction and cell failure. The effects of interphase formation on mechanical degradation, stress evolution, and contact area loss are also discussed. Short circuiting due to Li filament growth is shown to be a pervasive failure mechanism, even at currents far below the critical current density when cells are tested for sustained periods. As a final topic, stack pressure evolution during cycling of full solid-state batteries is measured *in situ* and correlated with fundamental processes within electrode materials and the properties of composite electrode structures. Cells with alloy-based anodes are found to exhibit large (megapascal-level) changes in stack pressure during cycling in a constant volume cell casing, with stable capacity and stress changes over long-term cycling. Together, these findings show the importance of controlling chemo-mechanics and interfaces in solid-state batteries.

11:40 AM ES14.03

Interpretable Tree-Based and Graph Neural Network Approaches for Novel Solid State Electrolyte Design Shreyas J. Honrao, Stephen R. Xie and John W. Lawson; NASA Ames Research Center, United States

All-solid-state batteries with Li metal anode can address the safety issues surrounding traditional Li-ion batteries as well as the demand for higher energy densities. However, the development of solid electrolytes simultaneously possessing high ionic conductivity and good chemical and electrochemical stabilities has proven to be a challenge. I will present our informatics approach to explore the Li compound space for promising solid electrolytes using high-throughput multi-property screening and interpretable machine learning. This is accomplished through the generation of a large database of battery-related materials properties of Li compounds. We use tree-based ensemble learning methods and graph neural network approaches to accurately learn relationships between crystal structures and corresponding thermodynamic and kinetic properties, with interpretability being a major focus. Our models give us the ability to enable rapid discovery and design of novel solid-state battery chemistries.

11:55 AM ES14.04

New Applications of the Finite Gaussian Processes Distribution of Relaxation Times Model Adeleke Maradcsa, Baptiste D. Py, Emanuele Quattrocchi and Francesco Ciucci; The Hong Kong University of Science and Technology School of Engineering, Hong Kong

Introduction

The electrochemical impedance spectroscopy (EIS) is a popular approach to study the properties of electrochemical systems [1]. To analyze EIS spectra, the distribution of relaxation times (DRT) appears as an accurate and straightforward technique. In this work, we demonstrate the applicability of a new model we recently developed [2] to handle challenging DRT data.

Methods

A Gaussian process (GP) can be defined as an infinite collection of random variables such that any finite subset of these random variables has a joint Gaussian distribution [3]. Our recently developed finite Gaussian processes distribution of relaxation times (fGP-DRT) was built using finite GP

approximation [2]. By taking \mathbf{x} and \mathbf{Z} to be the vectors of the DRT and impedance respectively and assuming that $\mathbf{x}|\mathbf{Z}$ is a truncated multinormal distribution bound by zero from below, we impose a nonnegativity constraint on the DRTs.

To sample \mathbf{x} from the truncated multinormal distribution, Hamiltonian Monte Carlo sampling can be used [4]. We generated 10,000 samples and discarded the first 1,000 as burn-in. The impedance can then be obtained from the sampled \mathbf{x} by matrix multiplication, i.e., $\mathbf{Z} = \mathbf{A}\mathbf{x}$ [2]

Results

The model was tested by analyzing artificial EIS data from Gerisher model [1] and validated on real experimental data from fuel cells. It consistently recovers the DRT, real and imaginary components of the impedance from noisy EIS spectra. The model also provides probabilistic estimates of the impedance at some unobserved frequencies. The recovered DRT matches the DRT of the conventional electrochemical model, and has positive values everywhere over the defined frequency ranges with the error bands for uncertainty quantification. These new applications extend the potential of our novel fGP-DRT model, opening a new research direction for the DRT analysis.

References

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12:10 PM ES14.05

Unification of Bulk Storage and Supercapacitive Storage Chuanlian Xiao, Robert Usiskin and Joachim Maier; Max-Planck-Institut für Festkörperforschung, Germany

In typical insertion electrodes for batteries, the capacity is determined by bulk storage within the electroactive particles, which is comparatively well investigated and understood. In contrast, supercapacitor electrodes are dominated by interfacial storage at interfaces, which is well addressed experimentally. However the charge carrier chemistry (defect chemistry) especially in the latter case is not taken seriously. Consequently a bridge between the two important fields is absent. Following and extending our quantitative concept of job-sharing storage, a generalized description that includes bulk and space charge storage (electrochemical and supercapacitive storage) is possible. In other words the treatment of defect chemistry as a function of the degree of storage as well as of position is key to a unification.

The experimental part of our research uses TiO₂ thin films. The precise measurement of the storage capacity of titania films as a function of thickness allows us to deconvolute bulk and interfacial contributions. We discuss the results in terms of bulk and space charge capacitance. The generalized treatment that comprises both contributions shows also how the ratio of both varies with the degree of storage. We expect this work to provide a better understanding of energy and power densities of storage devices which becomes particularly important for nanoionic systems.

12:25 PM ES14.06

In Situ Strain Measurements on LAGP Solid Electrolyte in Symmetrical Li/LAGP/Li Battery During Li Plating and Stripping Bertan Özdoğan and Ömer Ö. Çapraz; Oklahoma State Regents for Higher Education, United States

Solid electrolytes have potential to dramatically improve energy density of batteries for demanding applications such as electrical vehicles by allowing the utilization of high energy density-Li metal anodes. However, harvesting the benefits of the solid electrolytes for Li-metal batteries is limited to due to interfacial instabilities, dendrite formation and large impedance. Chemo-mechanical deformations in the electrode- solid electrolyte interface are still the bottleneck to improve performance of solid-state batteries. Investigation of the solid electrolyte - electrode interface during battery cycling is must to elucidate the governing forces behind the deformations and associated electrochemical performance loss in all-solid-state batteries. Various in situ characterization techniques such as Micro CT, XPS, and TEM have provided crucial information about the deformation mechanisms in the solid electrolyte¹.

In this study, we utilized digital image correlation (DIC) to monitor chemo-mechanical deformations in solid-state batteries during battery cycling. DIC computes strains with spatial and temporal resolution by tracking the changes in the speckle patterns in small neighborhoods called subsets during deformation². In situ strain measurements previously utilized to investigate the driving forces behind the structural and interfacial instabilities in alkali metal-ion battery electrodes^{3,4}.

A custom cell was designed to operate in operando strain measurements on solid electrolytes while cycling the all-solid-state battery. Shortly, symmetrical Li | LAGP | Li cells were fabricated, and stainless-steel disks were used as a current collector. Li_{1.5}Al_{0.5}Ge_{1.5}P₃O₁₂ (LAGP) powder was used to prepare LAGP solid electrolyte. In order to obtain a flat surface for the DIC measurements, the solid electrolyte was cut in half to obtain a semi-circle. Carbon black was used to decorate the flat side of the solid electrolyte as speckle pattern. In situ strain measurements demonstrated the impact of the early non-uniform deformations on the spatial distribution of Li plating and stripping on the solid electrolyte – electrode interface. The strain measurements provided quantitative analysis of the mechanical deformations and its coupling with the electrochemical behavior of the symmetrical battery cell. The measurements demonstrated the correlation between mechanical deformation in Li anode – LAGP interphase and the overpotential. Large amount of deformations in the center of the LAGP electrolyte was recorded at higher current densities and the fracture in the solid electrolyte was verified with ex-situ Micro-CT measurement. In this talk, we will present the spatial and temporal distribution of the strains in the LAGP solid electrolyte during battery cycling and we will discuss its coupling with the electrochemical performance.

Acknowledgement:

This work was supported by the NASA EPSCoR Research Initiation Grant. We are grateful for the valuable discussions with Dr. Behrad Koohbor and Dr. James Wu.

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Iono-Electronics

Iono-Electronics
July 18 - July 21, 2022

Symposium Organizers

Geoffrey Beach, Massachusetts Institute of Technology
Monica Burriel, CNRS - Grenoble INP
YiYang Li, University of Michigan

* Invited Paper

SESSION IE01: Electrochemical Redox Memory
Session Chairs: YiYang Li and Feng Xiong
Monday Morning, July 18, 2022
Lobby Level, Terrace

9:15 AM *IE01.01

ECRAM for Neuromorphic Computing [Alec Talin](#); Sandia National Laboratories California, United States

Tuning electronic conductance through solid state electrochemical ion insertion has emerged as a promising technology to enable next-generation, ultralow energy computing architectures¹⁻⁴. Unlike two-terminal non-volatile memory elements, the three-terminal redox transistor, also known as electrochemical random access memory (ECRAM), decouples the 'write' and 'read' operations using a 'gate' electrode to tune the conductance state through charge transfer reactions involving ion injection into the channel electrode through a solid-state electrolyte. The insertion of ions into the bulk of the channel acts to dope the material through a gradual composition modulation that leads up to thousands of finely spaced conductance levels (synaptic weights) with near-ideal analog behavior. These properties enable low-energy operation without compromising analog performance. However, the strong coupling of ionic and electronic processes sharply challenges our current understanding of solid-state electrochemical systems, particularly at decreasing dimensions and timescales relevant to computing technology. In my brief presentation I will summarize the rich portfolio of challenging, exciting fundamental science questions about ion tunable electronic materials systems and how we can harness these to realize a new paradigm for low power neuromorphic computing.

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9:35 AM *IE01.02

Exploring Novel Functions at Solid/Solid Electrolyte Interfaces for Application to Neuromorphic Computing [Takashi Tsuchiya](#) and Kazuya Terabe; Busshitsu Zairyo Kenkyu Kiko Kokusai Nanoarchitectonics Kenkyu Kyoten, Japan

Recently, breakthrough in artificial intelligence (AI) technology is becoming more and more important for handling the rapidly increasing amount of information. Ionic nanoarchitectonics, in which various functionalities are achieved by control of local ion transport/transfer in solid materials, have been applied to develop novel low power consumption and high performance AI devices/systems. Ionic nanoarchitectonics can be applied to ferromagnetic materials, in which dynamic behaviors of magnetization vector and spin wave play main roles in magnetic information storage devices and neuromorphic/reservoir computing. We reported magnetic property tuning behavior of our all-solid-state redox transistor consisted of magnetite (Fe₃O₄) and Li⁺ conducting oxide thin films^[1]. The device utilizes a topotactic Li⁺ insertion/desertion for high density electronic carrier control in the half-metallic magnetite thin film. Magnetization direction rotated clockwise as V_G increases and high density Li⁺ was inserted. Finally, the rotation of magnetization direction reached as high as 56° with $V_G = 2.0$ V application. Furthermore, the magnetic anisotropy was widely tuned in the range of 40% of the initial value. Ionic nanoarchitectonics at Li⁺ ion conducting solid electrolyte/hydrogenated (H-) diamond (100) interface was utilized to probe electric double layer (EDL) charges, which have been considered to play a key role in many energy and nanoelectronics applications^[2]. Whereas H-diamond-based transistor with a Li-Si-Zr-O (LSZO) Li⁺ solid electrolyte showed EDL-induced hole density modulation over a range of up to three orders of magnitude, a transistor with a Li-La-Ti-O (LLTO) Li⁺ solid electrolyte showed negligible enhancement, which indicates strong suppression of the EDL effect. Such suppression is attributed to charge neutralization in the LLTO, which is due to variation in the valence state of the Ti ions present. The method described is useful for quantitatively evaluating the EDL effect in various solid electrolytes. In the presentation, we will also report application of ionic nanoarchitectonics to neuromorphic computations.

References

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9:55 AM IE01.03

Electrochemical Artificial Synapses Based on Intercalation of Mg²⁺ Ions [Miranda Schwacke](#), Jesus del Alamo, Ju Li and Bilge Yildiz; Massachusetts Institute of Technology, United States

Deep learning based on neural networks has attracted much attention due to its success in a wide range of applications from computer vision to language processing. However, neural networks implemented on traditional computer systems based on CMOS circuits consume tremendous amounts of power and memory. Electrochemical artificial synapses (EAS) in cross-bar arrays have been suggested as an alternative device for analog deep neural networks. While EASs based on H⁺ shuffling have already been successfully demonstrated, larger ions such as Mg²⁺ may offer advantages like improved endurance and retention.

In this work, synthesis of candidate materials for the three layers of an EAS based on Mg²⁺ intercalation is explored. Preliminary devices successfully show modulation of WO₃ active layer conductance. Work is ongoing to improve devices and switch to CMOS-compatible, NASICON-type electrolyte which would allow these devices to be used as fast, enduring and energy-efficient computing elements.

10:10 AM IE01.04

Nanoporous Gadolinium-Doped Ceria-Based Protonic Solid-State Electrochemical Synapse for CMOS-Compatible Neuromorphic Computing [Seungchan Ryu](#), Han Gil Seo, Ju Li and Bilge Yildiz; Massachusetts Institute of Technology, United States

Artificial neural networks offer great opportunities in artificial intelligence (AI) application. However, the hardware structures must overcome the decreasing scaling effectiveness of transistors and the intrinsic inefficiency of employing transistors in von-Neumann computing architectures. Diverse physical neural networks have demonstrated promising implementation of machine learning algorithms. However, currently developed physical processors are suffer from poor device-to-device uniformity or high energy dissipation.

To address the issue, we focus on protonic electrochemical artificial synapse. The protonic electrochemical artificial synapse is modulating conductance states based on electrochemical proton intercalation. Thus, the protonic electrochemical memristors can provide low energy computation using shuffling of proton. Also, uniform switching properties can be obtained by controlling a fixed number of protons and electrons into active switching channel materials. However, currently demonstrated protonic electrochemical artificial synapses are incompatible with CMOS fabrication due to polymeric proton electrolytes. In this work, we developed nanoporous Gd-doped ceria as an inorganic solid proton electrolyte, which provides efficient proton diffusion *via* porosity and grain boundaries at room temperature. Controlling microstructures enables higher proton conductivities in the electrolytes and low energy electrochemical artificial synapse. This work provides a path to solution of CMOS-compatible energy efficient computing.

10:25 AM IE01.05

Nonvolatile Analogue Electrochemical Memory Using Tungsten Oxide [Diana Kim](#)¹, Alec Talin² and YiYang Li¹; ¹University of Michigan, United States; ²Sandia National Laboratories California, United States

The rapid increase in data quantity and processing necessitate novel approaches to computing. In-memory computing using analog resistive memory can substantially reduce the energy consumption of data-intensive processes like machine learning. Filament-type resistive memories suffer from high read and write currents as well as unreliable and stochastic switching behavior. On the other hand, nonfilamentary memory like the three-terminal electrochemical random-access memory (ECRAM)^{1,2} operate with low read and write currents (<10 nA), as well as highly reliable and predictable switching. However, previously developed ECRAM cells have poor retention times because the memory cell tends to revert back to a single equilibrium resistance state over time. Engineering an analog resistive memory cell with reliable switching, low currents, and long retention is a grand challenge for in-memory computing.

In this work, we develop a tungsten oxide (WO_{3-x}) based ECRAM with substantially improved state retention times, while maintaining the excellent analog switching properties of past ECRAM cells. WO_{3-x} ECRAM cells were fabricated by dc-sputtering and atomic layer deposition (ALD); the oxygen vacancy concentration X was controlled through the sputter gas content. Unlike in past works, this WO_{3-x} ECRAM cell contains multiple intrinsically nonvolatile analog states without needing a selector, with a projected retention time of several years at room temperature. These nonvolatile analog states arise from voltage hysteresis, and is likely a result of compositionally-driven phase separation. Our results are consistent across ECRAM cells containing different baseline oxygen vacancy concentrations. This work shows that it is possible to engineer an analog resistive memory cell that simultaneously has predictable switching, low currents, and nonvolatile state retention.

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10:40 AM BREAK

11:00 AM *IE01.06

High-Precision and Low-Power Electrochemical Two-Dimensional Dynamic Synapses for Neuromorphic Computing Mohammad T. Sharbati, John R. Erickson, Feng Xiong and [Qingzhou Wan](#); University of Pittsburgh, United States

While the Von Neumann based computing systems has enjoyed much success in the past decades, their limited bandwidth and large energy consumption make them inefficient in handling tasks such as pattern and speech recognition as well as real time analysis of large data sets. The brain, on the other hand, excels at these complicated tasks with much better energy efficiency because the storage and processing of information occurs at the same locations in massively parallel neural networks. Neuromorphic computing inspired by the brain have recently garnered significant research attention as a new computing paradigm. In particular, spiking neural networks (SNNs), with their event driven nature and inherently low power consumption and large bandwidth, offer an alternative approach to complement deep neural networks (DNNs). However, the challenge to implement temporal dynamics with CMOS devices has hindered the development of SNNs.

In this work, we present a high-precision, electrochemical-based dynamic synapses suitable for SNNs with programmable temporal dynamics and excellent energy efficiency. We employ molybdenum disulfide (MoS₂) as the channel material for our dynamic synapses because MoS₂'s two-dimensional (2D) nature makes it a good candidate for both ionic intercalation and electric-double-layer (EDL) gating. Leveraging the short-term and long-term doping effects from EDL gating and intercalation, we implement both short-term and long-term synaptic plasticity in our novel dual-gate synapse. When a programming pulse (+1 V, 100 ns) is sent to the inert Au gate, we observe an increase in synaptic weight (encoded in the channel conductance) due to induced charge carriers in MoS₂ via ionic gating. This response mimics the short-term plasticity in biological synapses since the induced carriers dissipates

after the programming gate voltage is removed. On the other hand, when we apply a similar programming pulse (+1 V, 100 ns) through the electrochemically reactive gate (LiFePO₃ or LFP), we can induce long-term change in the synaptic weight via electrochemical intercalation since charge transfer doping via intercalation is non-volatile.

We achieve potentiation and depression in 2D synapse by changing the polarity of the programming pulses. We can also modulate the change in synaptic response by varying the pulse amplitude and/or width. These short-term and long-term temporal dynamics are instrumental for implementing bio-realistic spike-based computations while the dual-gate structure allows us to elucidate the doping mechanisms from ionic gating and intercalation processes. We demonstrate basic neuronal functions such as paired pulse facilitation (PPF), spike-rating dependent plasticity (SRDP), and temporal filtering. Simulation results suggest that our synapses can lead to high accuracy in pattern recognition applications.

In summary, we develop a dual-gate MoS₂ synapse with tunable short-term and long-term temporal dynamics. The 2D synapse exhibits low energy consumption (<700 aJ/switching), good programming speed (>10 MHz), high precision level (>5000 states), as well as high linearity and symmetry. Capable of implementing basic neuronal functions, this dynamic synapse can lead to the hardware implementation of SNNs for event-based computations.

11:20 AM *IE01.07

Designing Polymeric Mixed Ionic/Electronic Conductors for Organic Electrochemical Transistors [Jonathan Rivnay](#); Northwestern University, United States

Organic electrochemical transistors (OECTs) have gained considerable interest for applications in bioelectronics, power electronics, circuits and neuromorphic computing. Their defining characteristic is the bulk-modulation of channel conductance owing to the facile penetration of ions into the (semi)conducting polymeric channel. For this reason, their device scaling relies on film thickness, and often relaxes the stringent demands of clean and controlled interfaces required in traditional FETs. Despite recent progress and a rapidly expanding library of new materials, the understanding of stability and transport/coupling of ionic and electronic carriers remain largely unexplored. We highlight recent synthetic and processing approaches used to tailor device properties and stability, as well as new device concepts enabled by such advances. Our understanding of critical processes in electrochemical devices further requires us to study these materials in device-relevant conditions, considering the effects of ions and solvent on microstructure and transport. To this end, we report on recent efforts using *ex situ* as well as *operando* scattering and spectroscopy to build a more device-relevant picture of structure-transport relations.

11:40 AM IE01.08

Imaging Nanoscale Phase Segregation in Li_xCoO₂ Particles and Predicting the Scalability of Electrochemical Random Access Memory [Elliot Fuller](#)¹, [David Ashby](#)¹, [Celia Polop](#)², [Enrique Vasco](#)³, [Joshua Sugar](#)¹ and [Alec Talin](#)¹; ¹Sandia National Laboratories California, United States; ²Universidad Autonoma de Madrid, Spain; ³Consejo Superior de Investigaciones Cientificas, Spain

Li_xCoO₂ (LCO) is a common battery cathode material that has recently emerged as a promising material for electrochemical random access memory (ECRAM)[1]. During charge-discharge cycling LCO exhibits phase transformations that are significantly complicated by electron correlation [2]. While the bulk phase diagram for an ensemble of battery particles has been studied extensively [3], it remains unclear how these phases scale to nanometer dimensions and the effects of strain and diffusional anisotropy at the single particle scale. Understanding these effects is critical to modeling battery performance and for predicting the scalability and performance of ECRAM. Here we investigate isolated, epitaxial LiCoO₂ islands grown by pulsed laser deposition. After electrochemical cycling of the islands, conductive atomic force microscopy (c-AFM) is used to image the spatial distribution of conductive and insulating phases and under strain conditions. Above island thicknesses of 20 nm, we observe a diffusion-limited phase boundary propagating perpendicular to the Li-planes. Thinner islands (14 nm) are found to exhibit a striping pattern which suggests surface energy can dominate below a critical dimension. Above a critical force threshold, the insulating regions of the islands are found to undergo an insulator-metal transition. The results suggest that strain and morphology become critical to battery or EC-RAM performance as particles approach nanometer dimensions.

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11:55 AM IE01.09

An Equivalent Circuit Model of Electrochemical Artificial Synapses for Neuromorphic Computing [Mantao Huang](#), [Murat Onen](#), [Jesus del Alamo](#), [Ju Li](#) and [Bilge Yildiz](#); Massachusetts Institute of Technology, United States

Employing brain-inspired principles, neuromorphic computing has the potential to achieve impressive computational power with superior energy efficiency. Electrochemical artificial synapses are of particular interest as building blocks for neuromorphic computing hardware, as they have shown features of neural systems such as long-term plasticity with energy efficiency on par with biological synapses[1,2]. The operations of electrochemical artificial synapses are based on shuffling of dopants across active device layers that control the conductance of a channel in a three terminal configuration. Understanding the physical processes and the behaviors of these devices are important for successfully applying them in brain-inspired computing systems. Here we present an equivalent circuit model that considers the charge transfer, ionic transport, and diffusion processes in the device layers and interfaces of electrochemical synapses, with the aim to predict the behavior of devices with different geometries and materials properties under various gate voltage/current waveforms. In addition to predicting the long term potentiation and depression, the model provides insights into complex behaviors such as the relaxations after potentiation/depression pulses and the nonlinear scaling of conductance change versus pulse duration. The model can potentially guide the design of material properties and the optimization of device performance for achieving lower operating voltage, faster operation speed and improved energy efficiency.

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12:10 PM IE01.10

Pushing Electrochemical Transformations and Enhancing Carrier Doping in Functional Oxides by Electrolyte Gating [Hua Zhou](#), [Wei Chen](#), [Hui Cao](#), [Dillon Fong](#) and [Changjiang Liu](#); Argonne National Laboratory, United States

The very high charge density induced by an electric double layer formed at the solid-liquid interface has recently been used to induced or “gate” exotic phase transitions, therefore electronic ground states of multifunctional oxides in the interfacial region, via the subtle interplay between electrostatic doping (electronic phenomena) and chemical redox effects (field-driven ionic motion) depending on field polarity and defect instability. It is highly expected that leveraging ionic electrolyte gating would be fertile ground for exploration in a broad range of functional oxides.

In this talk, I will present two developing frontiers of ionic electrolyte gating within two contrasting mechanistic frameworks by illustrating most recent in-situ and real-time X-ray studies to deliver fundamental understanding of structural and chemical basis and their inherent links during gating on representative functional oxide heterostructures. In one end, we drive forward the limits of electrochemically emergent transformations by manipulating ionic defects (e.g. vacancy formation and distribution) during gating. For example, a combination of electronic and ionic doping processes across the interface of perovskite nickelate heterostructure (e.g. NdNiO₃) by switching between positive and negative ionic gating voltages can be utilized in realizing electrochemical transistors. Moreover, ionic gating process can induce dynamically manipulating oxygen octahedra-controlled properties in the complex oxides (e.g. WO₃) for the design of highly responsive multifunctional materials (e.g. MIT and electrochromic behaviors). In the other end, we create a new paradigm of highly efficient ionic gating toward sub-voltage operation regime (e.g. enhancing carrier doping but without defect generation and perturbation across the interface) by designing redox actuatable poly-ionic-liquids.

12:25 PM IE01.11

CMOS-Compatible Protonic Programmable Resistor Based on Phosphosilicate Glass Electrolyte [Murat Onen](#), Nicolas Emond, Ju Li, Bilge Yildiz and Jesus del Alamo; Massachusetts Institute of Technology, United States

Programmable nonvolatile resistors are widely explored devices as building blocks for analog deep learning accelerators. Recently, devices that are programmed by ion intercalation were demonstrated to have superior modulation characteristics with respect to state-of-the-art phase change and filamentary resistive memories. Protonic devices are considered to be particularly promising since protons, the smallest cations, can be shuffled at higher speeds without causing mechanical deformation in the host materials. Previously, such protonic devices contained organic or polymer layers, which strictly limited the scalability, reproducibility, uniformity, yield, and CMOS-process integration of the technology. In this work, we show protonic programmable resistors consisting of a transition-metal-oxide channel (WO₃ or V₂O₅), P-doped SiO₂ electrolyte, and a Pd reservoir. We demonstrate reversible and nonvolatile conductance modulation by transferring protons between the channel and reservoir. We discuss material and device geometry optimization as well as the scaling trends in order to unlock the full potential of this new family of protonic resistive devices. This new device technology can satisfy the stringent requirements for analog crosspoint elements while using a fully CMOS-compatible and scalable fabrication flow.

SESSION IE02: Organic Iono-Electronics

Session Chairs: Simone Fabiano and Aristide Gumyusenge

Monday Afternoon, July 18, 2022

Lobby Level, Terrace

2:00 PM **IE02.01

Mixed Conduction in Polymeric Materials—Uses and Opportunities in Neuromorphic Computing [Alberto Salleo](#); Stanford University, United States

Organic semiconductors have been traditionally developed for making low-cost and flexible transistors, solar cells and light-emitting diodes. In the last few years, emerging applications in health care and bioelectronics have been proposed. A particularly interesting class of materials in this application area takes advantage of mixed ionic and electronic conduction in certain semiconducting polymers. Mixed conductivity opens up myriad new opportunities for these materials, from electrochromics to energy storage, biosensing, and iontronics (i.e. electronic devices that take advantage of ion transport). My presentation will first discuss the fundamental aspects of how mixed conduction works in polymeric materials and then describe some of these new opportunities. Finally, I will focus on one specific iontronic device: electrochemical RAMs (ECRAMs). Polymer-based ECRAMs are electrochemical devices suitable for neuromorphic operation (e.g. analog accelerators) that shows fast (<100 ns) switching, high (>10⁹) operations and the potential for parallel operation. Our organic neuromorphic device works by combining transport by two fundamental charges: protons and electrons. This concept is fairly general and can be applied to other materials families, such as MXenes. Finally, I will show how it can be integrated with living matter in a simple example of biohybrid synapse in addition to a few simple learning demonstrations.

2:30 PM *IE02.02

Organic Mixed Ionic-Electronic Conductors for Low-Power Electronics [Simone Fabiano](#); Linköping University, Sweden

Organic mixed ionic-electronic conductors (OMIECs) enable many (opto-)electronic and energy harvesting/storage applications. In OMIECs, the strong coupling between ions and electrons enables efficient charge storage and signal transduction. When implemented as the active channel materials in organic electrochemical transistors (OECTs), OMIECs endow these devices with record-high transconductance, low operational voltage, and high current density. These attributes make the OECTs a promising technology for chemical and biological sensing, medical diagnostics, large-scale printed electronic circuitries, and neuromorphic computing. Here, we will summarize our effort to develop OMIECs for OECTs. We will discuss the impact of polymer backbone rigidity on the OECT performance. We will show large-area printing/integration of these devices and demonstrate neurosynaptic circuits capable of Hebbian learning.

2:50 PM *IE02.04

Organic Neuromorphic Electronics and Biohybrid Systems [Yoeri van de Burgt](#); Technische Universiteit Eindhoven, Netherlands

Neuromorphic computing could address the inherent limitations of conventional silicon technology in dedicated machine learning applications. Recent work on large crossbar arrays of two-terminal memristive devices has led to the development of promising neuromorphic systems. However, delivering a compact and efficient parallel computing technology that is capable of embedding artificial neural networks in hardware remains a significant challenge.

Organic electronic materials have shown potential to overcome some of these limitations. This talk describes state-of-the-art organic neuromorphic devices and provides an overview of the current challenges in the field and attempts to address them. I demonstrate a concept based on novel organic mixed-ionic electronic materials and show how we can use these devices in trainable biosensors and smart autonomous robotics.

Next to that, organic electronic materials have the potential to operate at the interface with biology. This can pave the way for novel architectures with bio-inspired features, offering promising solutions for the manipulation and the processing of biological signals and potential applications ranging from brain-computer-interfaces and smart robotics to bioinformatics. I will highlight our recent efforts for such hybrid biological memory devices.

3:10 PM IE02.05

Ionic Communication for Implantable Bioelectronics [Zifang Zhao](#)¹, Jennifer Gelinas^{2,2} and Dion Khodagholy¹; ¹Columbia University, United States; ²Columbia University Irving Medical Center, United States

Implanted bioelectronic devices require data transmission through tissue, but ionic conductivity and inhomogeneity of this medium complicate conventional communication approaches. Here, we introduce ionic communication (IC) that leverages ions in biologic tissue to propagate MHz-range signals. We demonstrate that IC operates by generating and sensing stored electrical potential energy within polarizable media in a frequency-dependent manner. We determined the geometric properties that govern IC transmission depth and controlled transmission radius to permit multi-line parallel communication. We integrated IC with advanced neural interfaces to create a fully implantable device capable of acquisition and non-invasive transmission of neurophysiologic data from freely moving rats over a period of weeks. IC enabled a stable, efficient link with implanted components, and had communication efficiency (data rate/power consumption) several orders of magnitude above other approaches employed with implantable bioelectronics. We used IC for real-time transmission of multi-channel local field potential (LFP) and neural spiking data, with data quality sufficient for clustering of individual neuronal action potentials. IC creates a high-speed, low-power link between implanted and external electronics with the potential to enhance the safety and efficiency of a wide range of bioelectronic devices.

3:25 PM *IE02.06

Organic Neuromorphic Electronics—Bio-Inspired Functions and Sensorimotor Learning in Robotics [Paschalis Gkoupidenis](#); Max-Planck-Institut für Polymerforschung, Germany

Artificial intelligence applications have demonstrated their enormous potential for complex processing over the last decade. However, they are mainly based on digital operating principles while being part of an analogue world. Moreover, they still lack the efficiency and computing capacity of biological systems. Neuromorphic electronics emulate the analogue information processing of biological nervous systems. Neuromorphic electronics based on organic materials have the ability to emulate efficiently and with fidelity a wide range of bio-inspired functions including synaptic plasticity, homeostasis and spatiotemporal phenomena. In this work we present a path planning robot that uses a small-scale, locally-trained organic neuromorphic circuit to navigate through a maze. The neuromorphic circuit responds and adapts to environmental stimuli directly, as it is integrated with the robot's sensorimotor system. The on-chip integration of sensorimotor signals together with the unconventional form factors of organic neuromorphic electronics paves the way toward stand-alone, brain-inspired computing circuitry in autonomous and intelligent systems. Novel platforms for rapid prototyping and education, at the intersection of materials science and robotics, are also expected to emerge.

3:45 PM BREAK

4:00 PM *IE02.08

Translational Neuroelectronics [Dion Khodagholy](#); Columbia University, United States

As our understanding of the brain's physiology and pathology progresses, increasingly sophisticated technologies are required to advance discoveries in neuroscience and develop more effective approaches to treating neuropsychiatric disease. To facilitate clinical translation of advanced materials, devices, and technologies, all components of bioelectronic devices have to be considered. Organic electronics offer a unique approach to device design, due to their mixed ionic/electronic conduction, mechanical flexibility, enhanced biocompatibility, and capability for drug delivery. We design, develop, and characterize conformable organic electronic devices based on conducting polymer-based electrodes, particulate electronic composites, high-performance transistors, conformable integrated circuits, and ion-based data communication. These devices facilitate large-scale neurophysiology experiments and have led to discovery of a novel cortical oscillation involved in memory consolidation as well as elucidated patterns of neural network maturation in the developing brain. The biocompatibility of the devices also allowed intraoperative recording from patients undergoing epilepsy and deep brain stimulation surgeries, highlighting the translational capacity of this class of neural interface devices. In parallel, we are developing the high-speed conformable implantable integrated circuits and embedded acquisition and storage systems required to make high channel count, chronic neurophysiological recording from animals and human subjects possible. This multidisciplinary approach will enable the development of new devices based on organic electronics, with broad applicability to the understanding of physiologic and pathologic network activity, control of brain-machine interfaces, and therapeutic closed-loop devices.

4:20 PM *IE02.09

Design and Processing of Novel Organic Semiconductors for Electronics that Learn [Aristide Gumyusenge](#); Massachusetts Institute of Technology, United States

Even though memory devices and computing architectures have been extensively studied to mimic the functionality of biological synapses, the field of bioelectronics has yet to benefit from a material/device system that combines high performance neuromorphic computing and the required biocompatibility for potential body-computer integration. Such systems are key to realizing seamless body-machine integration in future electronics. Organic materials, though inferior to inorganic counterparts in electronic performance, are of special interest as they can marry their biocompatibility, solution processability, and tunable optoelectronic properties with high performance. My newly established research group (Laboratory of Organic Materials for Smart Electronics, OMSE Lab) aims to design and process organic semiconductors and demonstrate their synaptic functionalities in ionically gated transistor devices. In this talk, I will share my past research work on the design and processing of conjugated polymer composites, as well as 2D semiconducting thin films. I will also highlight how my lab will utilize such novel organic materials for generating programmable non-volatile currents to emulate biological synaptic behaviors. More specifically, I will highlight how we aim to balance ionic and electronic conduction in conjugated polymers, and the importance of such parity on the performance of electrolyte-gated devices. Through fundamental understanding of the structure-property-performance relationship, I will discuss key design principles that are needed for demonstrating all-polymer synthetic synapses and their use in smart bioelectronics.

4:40 PM IE02.10

Understanding the Device Physics of Ion-Gated Organic Electrochemical Transistors—A Study of the Channel Overlap Effect [Anastasios Polyravas](#) and [Dion Khodagholy](#); Columbia University, United States

Bioelectronic devices need to be conformable and biocompatible to interact with the neural tissue, while maintaining a fast and stable steady state to adequately record electrophysiological activity. A promising candidate that fulfills all these requirements and has been widely used in a variety of bioelectronics applications including bio-sensing, logic circuits and neural recordings, is the ion-gated organic electrochemical transistor (IGT). Although a lot of research has focused on the applicability of IGTs, optimisation of their design parameters has not been extensively investigated. Understanding how to tune such parameters can drastically improve the recording capabilities of IGTs and enhance their performance. In this study, we explore how the overlap between the organic semiconducting film and the contacts of the transistor impact the performance of our devices. Our experimental data suggests that a change in the contact overlap affects the frequency response of our transistors and leads to a decrease in the cut-off frequency. In addition, electrophysiology recordings of IGTs that reached steady state indicate that high quality contacts can be established with minimal overlap. This work

introduces new design rules that can be utilised to further improve the performance of IGTs and pave the way for more advanced, less invasive neural interface applications.

SESSION IE04: Resistive Switching I
Session Chairs: Monica Burriel and Stephan Menzel
Tuesday Morning, July 19, 2022
Lobby Level, Terrace

9:10 AM **IE04.01

Redox-Based Memristive Switching in Metal Oxides—Variants and Prospects in Neuromorphic Computing Rainer Waser^{1,2}, Regina Dittmann^{1,2} and Stephan Menzel^{1,2}; ¹Forschungszentrum Julich GmbH, Germany; ²RWTH Aachen University, Germany

Redox-Based Resistive Switching Memories (ReRAM), also called nanoionic memories or memristive elements, are widely considered to provide a potential improvement beyond the limits of current memory technology with respect to write speed, write energies, and scalability as well as an energy-efficient approach to neuromorphic computing concepts.

In this talk, fundamental aspects of the physics and chemistry (lattice disorder, ionic and electronic transport processes, and phase formation) of these elements will be presented. In particular, the polarity of the switching (eightwise or counter-eightwise) and the geometry (conducting filament vs. area dependent switching) will be discussed. Furthermore, the ultra-high non-linearity of the switching kinetics of redox-based resistive switching devices will be outlined with an emphasis on the so-called valence change mechanism (VCM) typically encountered as a bipolar switching in metal oxides, but also mentioning the electrochemical metallization (ECM) cells. The involved electrochemical and physical processes can be either electric field/voltage enhanced or accelerated by a local increase in temperature due to Joule heating

The two major strands of neuromorphic computing, namely the computational neuroscience for decoding the human brain and artificial neural networks for pattern recognition, will be worked out. And the different requirements on memristive elements to be applied in these two strands will be discussed.

9:40 AM *IE04.02

In Situ Transmission Electron Microscopy Studies on Switching Mechanisms in Memristor Devices Sabyasachi Ganguli¹, Krishnamurthy Mahalingam¹, Eunsung Shin², Rohan Dhall³ and Austin Shallcross²; ¹Air Force Research Laboratory, United States; ²University of Dayton, United States; ³E O Lawrence Berkeley National Laboratory, United States

The past decade has witnessed significant progress in the investigation of novel materials for memristor and neuromorphic computing applications. In particular, rapid advancements in characterization techniques offer capabilities for direct examination of resistive switching processes and their correlation with observed device properties. In this talk we review recent developments in transmission electron microscopy (TEM)-based techniques to examine resistive switching behavior and will present recent studies performed in our laboratory on a variety of materials based on phase-change and defect-migration phenomena. Specific examples of materials to be presented include device structures based on: (Ta(O)/Ta₂O₅ using electron energy loss spectroscopy (EELS), and SiO₂ and Ge₂Te₃ thin films using X-ray energy dispersive spectroscopy (X-EDS). Our studies indicate that significant information on the dielectric properties of the film may be gathered by examining low-loss region (10-30 eV) of EELS which, based on published DFT results, could be related to relative mixtures of TaO_x with different stoichiometry. Detailed examination of XEDS results upon electrical biasing clearly reveal a deleterious effect of Ti, characterized by in-diffusion of Ti that leads to significant degradation on morphology and composition at the dielectric/electrode interface in the SiO₂ devices. In the case of Ge₂Te₃ device, the Ti in-diffusion is accompanied by an out-diffusion of Ge, resulting in its enrichment at beneath the top Pt electrode. Further studies under systematic electrical biasing and heating conditions reveal that this diffusion process can be significant, leading to progressive degradation of the dielectric-electrode interface. Additional studies aimed at combating dielectric/electrode diffusion process will be presented.

10:00 AM IE04.03

Composition-Driven Phase Separation in Amorphous TaO_x for Valence-Change Memory Jingxian Li¹, Anirudh Appachar¹, Elisa Harrison², Sabrina Peczonczyk², Wenhao Sun¹ and YiYang Li¹; ¹University of Michigan, United States; ²Ford Motor Company, United States

Resistive memory or memristor is a highly potential memory and computing unit for next-generation information storage, in-memory computing, and neuromorphic computing. Valence change memory (VCM) is a promising memristor using transition metal oxides, and changes electronic resistance by moving oxygen vacancies under applied electric fields and joule heating. Amorphous TaO_x (0 < X < 2.5) has been widely used in the VCM due to its outstanding performance of fast switching, high endurance and long retention time. While phase information for crystalline TaO_x can be obtained from the phase diagram, the stable phases in the amorphous TaO_x is not known.

In this work, we combine experimental measurements and first-principles thermodynamic calculations to investigate phase separation in amorphous TaO_x. Experimentally, we use reactive sputtering to deposit TaO_x thin-film bilayers with different oxygen:metal ratios (X). We use Auger depth profiling to measure how the thickness and composition (X) of the two layers evolve after annealing at 300C. Our results show that, while the composition and thicknesses of each layer changed during annealing, the bilayer interface persists even after long annealing times. This suggests that amorphous TaO_x also phase separates like crystalline ones. We use TOF-SIMS to measure the oxygen tracer diffusivity and confirm that oxygen diffusion is sufficiently fast for these annealing times. We complement the experimental measurements with ab initio thermodynamic calculations of the amorphous free energies, and identify a spinodal in the free energy curve of amorphous TaO_x, indicating a thermodynamic driving force for phase separation. This phase separation is consistent with the stability of bilayer VCM during post-metallization anneal during fabrication. This combined approach provides new avenues for investigating the phase diagram of nanocrystalline materials.

10:15 AM IE04.04

Memristively Programmable Transistors for Neuromorphic Applications Sarah Beck, André Kosak, Raphael Ahlmann and Stefan Tappertzhofen; Technische Universität Dortmund, Germany

Non-volatile Flash memories are based on storing charge on a floating-gate. Progressive device scaling required to decrease the floating-gate charge down to hundreds of electrons or even below. To ensure long state retention for several years, the leakage current of the gate-dielectric needs to be in the order of 10e-26 A. This ultra-low leakage current requirement is opposed to a high tunneling rate required for device programming. Evidently, a tradeoff between state retention, programming speed, and endurance is necessary, which eventually limits the device performance for classical memory operation as well as application of Flash in neuromorphics. Here we demonstrate memristively programmable transistors (memTRs) as a novel concept to overcome these

limitations. A memTR is based on a memristive switch integrated in a field-effect transistor's gate-terminal. While the basic operation principle is similar to floating-gate transistors, the advantage is that information encoding relies on nanoionic processes instead of charge-storage. The larger mass of ions compared to the effective mass of electrons allows for a high flexibility in designing application-specific gate-dielectrics. We demonstrate the practicability of memTRs in an experimental and theoretical proof-of-concept study. Similar to conventional two-terminal memristive devices, memTRs show non-linear switching kinetics and analog behavior. This makes memristively programmable transistors ideal devices candidates for neuromorphic computing.

10:30 AM BREAK

11:00 AM **IE04.05

Point Defect Transport in Electroceramics and Implications for Electronic Conductivity Elizabeth Dickey; Carnegie Mellon University, United States

Lattice defects play an important role in the dielectric and conductivity properties of electroceramic materials, and thus great effort is expended on controlling point defect concentrations via doping, oxygen-activity and temperature control during processing. In device applications, because lattice defects are typically charged, applied electric fields provide a strong driving force for defect migration, and their spatio-temporal redistribution depends on numerous experimental variables including the interfacial boundary conditions. Ultimately the defect redistribution process leads to spatially varying conductivity profiles and often a concomitant macroscopic increase in leakage current in many dielectric materials. While this leakage current enhancement is detrimental in devices such as capacitors, the phenomenon can be utilized to form novel functional behaviors such as resistive switching in metal-oxides. This talk will review our current understanding and implications of point defect electromigration in important electroceramic materials. Recent efforts to effectively co-dope dielectric materials to improve their degradation resistance will be discussed.

11:30 AM *IE04.06

Effects of Materials Configuration and Capping Layer for Design Strategies in Memristive Devices Shaochuan Chen¹ and Iliia Valov^{2,1}; ¹Rheinisch-Westfälische Technische Hochschule Aachen, Germany; ²Forschungszentrum Julich GmbH, Germany

Redox-based memristive devices (ReRAM) are favored as fundamental units in the future brain-inspired hardware used as artificial neurons and/or synapses. Sharing same electrochemical fundamentals with their biological counterparts ECM and VCM memristors can generate and transmit electric signals, learn, forget, adapt, and sense. The selection of materials and materials combinations strongly influence the nanoscale processes, playing a crucial role in the device behavior and functionalities. Different memristive properties can be adjusted by material design and operation scheme.

Over the last decade, significant efforts were made toward understanding the electrochemical mechanism in ReRAM in order to enable easier performance optimization. For instance, in ECM cells cyclic voltammetry have been employed to study the half-cell redox reactions and ion migration. The filament formation and dissolution were revealed by *in situ* and *ex situ* transmission electron microscope. The impact of relative humidity level, active electrode material composition, catalytic activity of the counter electrode, as well as oxide materials on resistive switching behavior and device reliability have also been studied by above techniques. In VCM cells, significant progress has also been made regarding the understanding of oxygen vacancy defect formation, migration and cell switching stability. Multiple approaches such as selecting ohmic electrode material with proper defect formation energy, applying multilayer oxides, have been attempted to improve cell performance.

However, in most of the reported work, the conclusions were drawn based on studies containing only one type of variable, either the specie of active (ohmic) electrode material, or the counter (bottom) electrode material, overlooking the comprehensive analysis considering the configuration/combination of the electrode/electrolyte materials as a system. Besides, other important issues, for instance, the effect of active/ohmic electrode thickness in ECM/VCM cells, is rather scarce. Most important, to our knowledge, the impact of capping electrode material on electrochemical processes and switching behavior has not been considered.

In this work, we report on the influence of electrode and capping layer materials configuration in HfO₂ based ECM and VCM cells of the type TiN(Pt)/Cu(Ti)/HfO₂/TiN(Pt). HfO₂ is selected as switching film as it is CMOS compatible and widely used as insulating layer for ReRAM devices. The thickness dependence of active and ohmic electrode materials and HfO₂-film are also studied. For both memory systems, different configurations with TiN and Pt as bottom electrodes and/or capping materials have been tested, keeping constant the active/ohmic electrodes. Cyclic voltammetry and current-voltage (*I-V*) sweeps are employed to study the electrochemical redox processes and resistive switching behavior, respectively.

The results show the importance of selecting proper combination of oxide and active(ohmic) electrode materials and thicknesses. Particularly, the modulation of resistive switching characteristics by varying capping layer material in a combination with counter(bottom) electrode configurations are demonstrated.

11:50 AM *IE04.07

Complex Oxides as Building Blocks for Brain-Inspired Computers and Evolutionary Intelligence Shirram Ramanathan; Purdue University, United States

The ability to control the collective electronic behavior of complex oxides via dopants and external fields presents an opportunity to design circuit components of relevance to neuromorphic computing. In this presentation, I will discuss two case studies from our collaborative research. First, we will consider vanadium dioxide, wherein both structural and electronic contributions to the insulator-metal transition distinctly affect relaxation characteristics of oscillators. Carefully introducing point defects such as oxygen vacancies enables systematic control over the threshold voltage and spiking neuronal behavior. Then we will discuss hydrogen-driven insulator-metal transitions in perovskite nickel oxides. Hydrogen acts an electron donor and effectively controls the occupancy of Ni eg orbitals independent of typical constraints posed by epitaxial strain, temperature, substrate etc. The resulting interstitial proton can be shuffled via electric fields resulting in numerous electronic phases. We will examine the opportunities presented by such metastable phases in design of brain-inspired electronic hardware, mimicry of ancient sensory organs, and as testbeds to emulate foundations of learning noted by neuroscientists. We will highlight areas of further study urgently needed for high-resolution characterization of ion dynamics in emerging semiconductors that is essential for understanding microscopic physics and ground state perturbations.

12:10 PM IE04.08

Insight into the Switching Mechanisms of La₂NiO_{4+δ} Analog-Type Memristive Devices Suitable for Artificial Synapse Applications Khanh Khuu¹, Gauthier Lefèvre², Carmen Jimenez¹, Fabrice Wilhelm³, Serge Blonkowski⁴, Eric Jalaguier⁴, Ahmad Bsiesy² and Monica Burriel¹; ¹Univ. Grenoble Alpes, CNRS, Grenoble INP, LMGP, France; ²Univ. Grenoble Alpes, CNRS, CEA/LETI Minatec, LTM, France; ³ESRF, France; ⁴Univ. Grenoble Alpes, CEA, LETI, France

Resistive switching (RS) is the change in resistance of a Metal-Insulator (or Semiconductor)-Metal capacitor-like structure under an external electric field.

Due to their simple structure, high operation speed and low power consumption, RS has attracted researchers' attention for its application in Non-Volatile Memories (Redox-based Resistive Random Access Memories, or ReRAMs) and neuromorphic computing systems [1]. This work uses $\text{La}_2\text{NiO}_{4+\delta}$ (L2NO4), a mixed ionic electronic oxide, well known for its highly mobile oxygen interstitial ions, as a memristive layer. L2NO4 shows oxygen storage and oxygen transport capabilities thanks to the presence of oxygen interstitials as point defects in the structure, leading to interesting properties when used in interface-type valence change memories (VCM). It is widely accepted that in VCM redox reactions, activated by the application of an external voltage, lead to changes the interface properties of the oxide/metal junction, governing the RS of such devices. Recent studies reported remarkable results on nickelate memristive devices grown as epitaxial thin films [2,3]. It has also been reported that the oxygen content in L2NO4, which affects the devices' electrical response, can be tuned by thermal treatments in different gas atmospheres, leading to improved memristive properties for high oxygen content [2]. However, the epitaxial memristors still present shortcomings, such as the impossibility of building L2NO4-based devices in cross-bar array architectures and their integration into Complementary Metal Oxide Semiconductor (CMOS) technology.

Thus, in this study we focused on the use of Pt/TiO₂/SiO₂/Si, a CMOS-compatible substrate, to build TiN/L2NO4/Pt heterostructures as memristive devices in a vertical configuration. The L2NO4 films were grown using Pulsed Injection Metal-Organic Chemical Vapour Deposition (PI-MOCVD). The deposition conditions were carefully optimized to obtain highly dense, crystalline, continuous thin films on a stable Pt layer. The growth of polycrystalline L2NO4 films on Pt and the microfabrication of the TiN/L2NO4/Pt devices were characterized by combining structural, microstructural and chemical techniques, including Grazing Incidence X-ray Diffraction (GI-XRD), Electron Probe Analysis (EPMA), Scanning Transmission Electron Microscopy (STEM) equipped with Energy Dispersive X-ray Spectrometer (EDX). Migration of oxygen into the TiN top electrode during its deposition was observed, resulting in an oxidized interlayer, which plays a crucial role in the switching characteristics.

Here we demonstrate an analogue-type counter-eightwise bipolar RS behaviour with multiple resistance states for TiN/L2NO4/Pt devices for the first time using both continuous I-V sweeps and pulsed measurements. What is more, gradual changes in conductance by applying repetitive DC sweeps or pulses, which can be regarded as the evolution of the synaptic weight, were successfully obtained for these devices. Furthermore, the RS mechanism taking place was studied by X-ray absorption spectroscopy (XAS) using synchrotron radiation under *operando* conditions, and changes in the Ni-K edge could be reproducibly measured as the device was cycled in both polarities. These results open the door to the real implementation of L2NO4-based memristors as artificial synapses for neuromorphic computing.

[1] Z. B. Yan and J. M. Liu, "Resistance switching memory in perovskite oxides," *Ann. Phys. (N. Y.)*, vol. 358, pp. 206–224, 2015.

[2] K. Maas *et al.*, "Tuning Memristivity by Varying the Oxygen Content in a Mixed Ionic – Electronic Conductor," vol. 1909942, pp. 1–10, 2020.

[3] K. Maas *et al.*, "Using a mixed ionic electronic conductor to build an analog memristive device with neuromorphic programming capabilities," *J. Mater. Chem. C*, 2019.

12:25 PM IE04.09

Engineering of $\text{Pr}_x\text{Ca}_{1-x}\text{MnO}_3$ Based Interface Type Resistive Switching Devices for Neuromorphic Applications Alexander Gutsche, Sebastian Siegel, Sebastian Hamsch and Regina Dittmann; Forschungszentrum Julich GmbH, Germany

For the most common resistive switching memory systems which show filamentary switching, a high variability is caused by the stochastic filament formation process and a sharp SET process induced by the positive thermal feedback loop. In this work, we studied in detail heterostructures of the mixed-valence manganite $\text{Pr}_x\text{Ca}_{1-x}\text{MnO}_3$ (PCMO) and insulating interface tunnel barrier layers. These memory devices show area-dependent switching, a gradual SET and RESET due to the lack of Joule heating and suffer less from device variability. This provides the possibility of analog switching and to adapt the device current to a given circuit requirement.

We will present the impact of different interface layers and their processing conditions on the switching characteristics of polycrystalline PCMO thin films grown on Pt substrates, including variability measurements for I-V sweeps and pulse measurements. The impact of different heights and lengths of the applied voltage during pulse measurements will be shown. [1]

Additionally, we will present a two resistor model to describe the I-V-measurements mathematically. Starting with this mathematical approach, we assign the two resistors to the space charge region at the PCMO interface and to the tunnel oxide, respectively, and suggest physical models for the switching mechanism based on ion and electron transport across these two layers. [2]

Furthermore, we will demonstrate learning algorithms, such as Spike Timing Dependent Plasticity or Long Term Potentiation/Depression using the gradual switching behavior of the devices. We will use different sets of potentiation and depression measurements to find the best fitting combination for highest accuracy in pattern recognition for MNIST data set. [1]

[1] Gutsche A, Siegel S, Zhang J, Hamsch S and Dittmann R (2021) Exploring Area-Dependent $\text{Pr}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ -Based Memristive Devices as Synapses in Spiking and Artificial Neural Networks. *Front. Neurosci.* 15:661261. doi: 10.3389/fnins.2021.661261

[2] Gutsche et al. to be published.

SESSION IE05: Resistive Switching II
Session Chairs: Karsten Beckmann and Suhas Kumar
Tuesday Afternoon, July 19, 2022
Lobby Level, Terrace

2:00 PM **IE05.01

Ion-Based Volatile Memristors and Mem-Transistors for Neuromorphic Engineering Daniele Ielmini; Politecnico di Milano, Italy

Neuromorphic engineering, namely the development of electronic circuits that can mimic the human brain, has been a fascinating topic since many decades. A significant challenge for neuromorphic computing is the development of a scalable device technology that can describe the various neuromorphic functions, such as an integrate-and-fire neuron or a synapse with short-term memory. In the recent years, there has been a considerable effort in designing and testing new memory devices with improved neuromorphic performance, such as low current operation, short/long-term plasticity and scalability to enable a high neuron density and connectivity. In this regard, ion-based memories such as the resistive switching random access memory (RRAM) or memristor have shown compelling results which appears extremely promising for the technology of future neuromorphic engineering devices. This talk will present the status and outlook of ion-based volatile memristors and mem-transistors for applications in neuromorphic engineering. The volatile memristor structure and concept will be summarized and its physical mechanisms of switching and relaxation will be described. Its extension to the

3-terminal mem-transistor, adopting MoS₂ as the semiconductor channel material, and the multiterminal memristive nanowire network will be presented in detail. Various applications in neuromorphic computing will then be addressed, including short-term memory for spatio-temporal recognition and reservoir computing. The advantages and disadvantages of the volatile memristor/memtransistor technology in terms scaling, 3D integration and bio-plausibility of the typical time response will be finally discussed.

2:30 PM *IE05.02

On the Conduction Mechanism of Valence Change Memories Stephan Menzel; Forschungszentrum Julich GmbH, Germany

Redox-based resistive switching devices (ReRAM) based on the valence change mechanism (VCM) have attracted great attention due to their potential use in neuromorphic applications due to the possibility to program many different resistance levels in one device. The amount of achievable states depends on the type of conduction and the switching dynamics. In literature, VCM cells with linear I-V characteristic and exponential I-V characteristics are reported. In this talk, we discuss the origin of the linear I-V characteristics (called type I conduction) and the so-called type II conduction showing exponential I-V characteristics. It is revealed by density function theory calculations with non-equilibrium Green's function formalism that the oxygen vacancy defect level within the band gap defines the type of conduction [1]. For shallow defects, the transport by electron tunneling into the conduction band at the dominating metal/oxide interface. As this effect results in a triangular barrier, the I-V characteristics are highly nonlinear. For deep defect states, the electron transport occurs via electron injection into the trap levels around the Fermi energy. This can be approximated with a high trapezoidal Simmons tunneling barrier, which leads to a more linear I-V characteristic. In both cases, the tunneling distance is determined by the length of the space charge zone due to the positively charged defects close to the metal interface. Thus, in both cases the switching is related to the movement of the ionic defects. A depletion of oxygen vacancies close to the metal electrode leads to a high resistive state and an accumulation of defects to a low resistive state. Based on the two conduction types, two dynamic switching models are presented that allow us to simulate the device programming. The influence of the conduction type on the programming will be discussed. In addition, we compare the characteristics in relation to the needs of memristive devices as synaptic devices, i.e. symmetry of the programming, achievable resistance states, linearity.

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2:50 PM IE05.03

Retention Secured Non-Linear and Self-Rectifying Analog Charge Trap Memristor for Neuromorphic Application Geunyoung Kim, Hanchan Song, Jae Bum Jeon and Kyung Min Kim; Korea Advanced Institute of Science and Technology, Korea (the Republic of)

In memristive neuromorphic hardware, a self-rectifying memristor can allow the highest synapse density by eliminating a selecting component. Here we propose a Pt/Ta₂O₅/Nb₂O_{5-x}/Al₂O_{3-x}/Ti charge trap memristor (CTM), exhibiting desired characteristics for a neuromorphic synapse application. It showed high self-rectifying ($> 4 \times 10^4$) and non-linear characteristics at below 1 μ A of programming current, which can minimize sneak currents and power consumption in the crossbar array. Also, the device showed a continuous and uniform analog switching behaviors with respect to the amount of applied voltages. Moreover, its retention characteristic enhanced with blocking layer / charge trap layer / tunneling layer sandwich structure compared with 2-layer structured devices. We suggest a novel operation model supported by the thermal dependency and characteristic analysis. In addition, we fabricated 32 \times 32 size array device to evaluate the array scale operation, and demonstrate its high energy efficiency during neuromorphic computing in large-scale array.

3:05 PM IE05.04

Advanced Dynamic Physical Model of Valence Change Mechanism Memristors Juseong Park, Gwangmin Kim, Geunyoung Kim and Kyung Min Kim; Korea Advanced Institute of Science and Technology, Korea (the Republic of)

Valence change type resistance switching behaviors in oxide-based memristors can be understood by well-established physical models describing the change in oxygen vacancy distribution during switching. The models can also account for the origin of the device reliability problem and provide foundations for the appropriate material solutions. The previous resistance switching models were mostly developed for electroformed memristors, in which the possible oxygen vacancy concentration-dependent diffusivity was not considered. This study proposes an advanced physical model that considers the change in the oxygen vacancies' charged state depending on their concentrations and the resulting change in diffusivity during switching. The model suggests a formation of an hourglass-shaped filament due to the unconcentrated electric field at the thin oxide. Consequently, it can explain the origin of retention failure in the oxide-based memristor and suggests an optimized filament configuration for the reliable operation of the memristor. The suggested model is developed mainly for the electroforming-free memristor, but there is no reason why the same model can be applied to the memristors involving the electroforming step.

3:20 PM IE05.05

Lithium Intercalation as a Pathway to Diverse Biomimetic Functionality—Beyond Merely Changing Resistance W. A. Doolittle, Alex S. Weidenbach, Bill Zivasatienraj, Aheli Ghosh and Timothy M. McCrone; Georgia Institute of Technology, United States

While mammalian brains offer remarkable diversity in time response (short and long term, forgetting, and wide ranges of time constants), firing patterns, firing thresholds, pulse shape, and channel impedance, biomimetically inspired inorganic synapses often lack equivalent diversity. Many memristive synaptic analogues cannot change the timing dynamics of switching and opt instead for a digital approximation of timing dynamics. As newer architectures of neural networks such as recursive neural networks (RNN) emphasize the need for core elements with diverse analog temporal response, inorganic synapses are required that can be engineered with various advanced timing and behavioral functions envisioned by circuit architects. One family of ion intercalation devices built around Li-Niobium oxides and based on electrolyte free constructs shows remarkable diversity and can be engineered for various biomimetic functions using simple layout and fabrication paradigms all within the same material system[1]-[2]. Such engineering flexibility provides a "silicon-like" base material with device function modified by fabrication methods alone. Many of these diverse functions originate from the fundamental modification of the band structure during intercalation while others are derived from the device layout as defined lithographically[3]-[4]. Some of the experimentally demonstrated diversity includes: a) tunable temporal spans ranging from volatile time constants spanning microseconds to minutes, stable non-volatile memory, forgetting based learning and more; b) selectable analogue programing sensitivity from many volts to the order of ~100-150 millivolt scale¹ roughly equivalent to biology; c) up to 8900% $\Delta R/R$ analog dynamic range; d) selectable abrupt firing suitable for integrate and fire circuits or highly linear resistance changes suitable for linear regression; e) selectable resistance ranges from 100's ohms to megaohms via device length to wide ratio similar to CMOS scaling rules; f) true memristance flux linkage with memristance dependent on the entire history of voltage and time; g) retina analogues with directly photo-driven ion motion and corresponding changes in memristance; and h) ionic ensemble momentum capable of emulating the enormous inductances found in biology and resulting in negative differential resistance. The device operation of each diverse function will be related to ion kinetics, interfacial chemistry, band structure modifications, and device layout. Using a circuit model derived from actual device characteristics, several circuit level biorelevant examples of both subsystem responses such as habituation, integrate and fire, dynamic adaptation, and frequency modulation as well as higher level learning such as image recognition and experience-based learning will be demonstrated.

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Funding provided by AFOSR via the CEREBRAL MURI, PI W. Alan Doolittle

3:35 PM BREAK

4:00 PM **IE05.06

Detecting and Engineering Oxygen Vacancies in Tantalum Oxide Memristive Devices Regina Dittmann; Forschungszentrum Juelich, Germany

Ta₂O₅ is one of the most promising materials for non-volatile memories and neuromorphic computing. However, the details of the underlying switching processes is still under debate with respect to (i) the most active ionic species, namely oxygen vacancies vs Ta interstitial and (ii) to the driving mechanisms, namely thermodiffusion vs drift/diffusion. Gaining detailed information about the chemical and electronic properties of conductive filaments is therefore of key importance for a comprehensive understanding of the switching process as well as for a rational design of Ta₂O₅-based memristive devices. In this work, we use spectromicroscopy to probe the electronic structure of conductive filaments in Ta₂O₅-based memristive devices. We identified nanometer sized conductive filaments and could determine an oxygen vacancy concentration of $\approx 20\%$. The filament is not composed of a metallic Ta⁰ phase but of metastable substoichiometric phases. We can therefore exclude switching models for Ta₂O₅ based on the formation of a metallic Ta filament. The lateral distribution of the total Ta concentration across the filament is very homogeneous and rules out Ta movement as underlying process for filament formation and switching [1]. Using our experimental data as input for finite element simulations, we investigate the role of thermodiffusion for the formation process of conductive filaments in our Ta₂O₅ devices. We demonstrate thermodiffusion alone cannot explain the filament formation but might play a role in accelerating the forming process, as well as in the stabilisation of the filament.

We use the knowledge gained from spectromicroscopy to engineer the oxygen content in our devices. While reducing the oxygen in TaO_x thin films in the order of a few percent of oxygen vacancies results in a reduction of the forming voltage [2], the use of 20% oxygen vacancies as observed within the filaments results in too leaky devices to be switched. However, using a tunnel barrier of HfO₂ at the interface between the highly reduced TaOx and the Pt top electrode results in area-dependent [3], gradual switching that is in particular highly interesting for analog or neuromorphic computing.

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4:30 PM *IE05.07

Metal-Insulator Transition and Resistive Switching Effects in Metallic Perovskite Oxides Teresa Puig¹, Juan Carlos Gonzalez-Rosillo¹, Rafael Ortega¹, Anna Palau¹, Jordi Suné², Ivan Maggio-Aprile³, Regina Dittmann⁴ and Xavier Obradors¹; ¹Consejo Superior de Investigaciones Científicas, Spain; ²Universitat Autònoma de Barcelona, Spain; ³Universite de Geneve, Switzerland; ⁴Forschungszentrum Juelich, Germany

Strongly correlated perovskite oxides are a class of materials with fascinating intrinsic physical functionalities due to the interplay of charge, spin, orbital ordering, and lattice degrees of freedom. Among the exotic phenomena arising from such an interplay, metal-insulator transitions (MITs) are fundamentally not fully understood yet, but are of large interest for novel nanoelectronics applications, such as resistive switching-based memories and neuromorphic computing devices. In particular, rare-earth nickelates, lanthanum strontium manganites and even superconducting cuprates are archetypical examples of bandwidth-controlled MIT, in the first case, and band-filling controlled MIT, in the other two. In this work, I will present the bipolar Volume Resistive Switching (VRS) effects observed in these three types of materials, where small changes in carrier concentration induce huge resistance changes [1]. VRS characteristics have been evaluated by c-AFM and I(V) curves with metal electrodes. Large resistance ratios (10^2 - 10^4), over 100 cycles experiments, multilevel switching and switching dynamics have been evaluated. Local probes (STM and c-AFM) have been used to correlate the switching characteristics of the oxides at room temperature with their MIT properties, suggesting that an electric-field-induced MIT can be triggered in these strongly correlated systems upon generation of oxygen vacancies. We could establish that lower operational voltages and larger resistance ratios are obtained in those films where the MIT lies closer to room temperature [2]. A 3-terminal proof-of-principle non-volatile gate-controlled conductive bridge device based on Ag/CeO_{2-x}/LSMO has been studied, determining the rate limiting steps of oxygen exchange through oxygen partial pressure experiments, and demonstrating that a thin CeO₂ capping layer may act as an oxygen reservoir, making this device atmosphere resistant [3]. This work demonstrates the interest of further studying these strongly correlated systems for next generation nanoelectronics devices.

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4:50 PM *IE05.08

Material Strategies for Memristor-Based AI Hardware and Their Heterointegration Jeehwan Kim; Massachusetts Institute of Technology, United States

Conventional memristors typically utilize a defective amorphous solid as a switching medium for defect-mediated formation of conducting filaments. However, the imperfection of the switching medium also causes stochastic filament formation leading to spatial and temporal variation of the devices. In this talk, I will present our material strategy to precisely confine the conducting paths in memristors which allow us to operate 1R-based crossbar arrays with a great programmability. By embedding this crossbar array into the edge of heterogeneously integrated chip, we demonstrate a reconfigurable heterochips with stackability. The reconfigurable chip features (1) memristor crossbar arrays for non-von Neumann computing and (2) optical communication between chips enabled by heterointegrating LEDs and photodiodes. I will discuss about outlook of our recent reconfigurable heterogeneous integration schemes for future electronics

5:10 PM IE05.09

Demonstration of Neuromodulation-Inspired Stashing System for Energy-Efficient Spiking Neural Network Using a Self-Rectifying Memristor Array Woon Hyung Cheong, Jae Bum Jeon, Jae Hyun In, Geunyoung Kim, Hanchan Song, Juseong Park and Kyung Min Kim; Korea Advanced Institute of Science and Technology, Korea (the Republic of)

Neuromorphic engineering aims to mimic brain functions to achieve energy-efficient artificial intelligence. Since researchers have indicated that memristors can mimic synapses and neurons, various studies have demonstrated the operation of neural networks using memristive dot product engine (MDPE) hardware. However, although several feasible implementations of synapse and neuron behaviors have been reported, few studies have demonstrated the system-level energy-efficient operation on the hardware. This work proposes a novel system inspired by the neuromodulation of the

brain, referred to as a 'stashing system.' In the system, the trained synapses are stashed temporarily during the training of the spiking neural network and then merged for inferencing. The software simulation first confirmed the working principle of the stashing system. Then, a hardware demonstration was performed at an integrated 32×32 MDPE embodying a self-rectifying and electroforming-free memristor cell to validate the system. The results confirmed that energy consumption was reduced by 37% for the unsupervised learning of the MNIST dataset.

5:25 PM IE05.10

A Flexible and Self-Rectifying Synaptic 32×32 Crossbar Array for a Wearable Neuromorphic Application [Younghyun Lee](#), Geunyoung Kim and Kyung Min Kim; Korea Advanced Institute of Science and Technology, Korea (the Republic of)

Neuromorphic computing has spotlighted much attention for their high performance in a data processing, image recognition and classification.[1] Neural hardware for in-memory computing was proposed due to the Von Neumann bottleneck between the processor and memory because energy and speed limit problems occurred in conventional computing.[2] Neural hardware, like the brain, operates with energy efficiency by biologically reliable manipulation.[1] Artificial neurons and synapses are essential devices for performing such tasks in neurological hardware. However, comprehensive metal-oxide-semiconductor (CMOS)-based neural hardware demand a large chip area, and also significant energy consumption.[3] As the complexity of the neural network increases significantly, synaptic hardware must achieve energy-efficient operations in dense areas.[4] In this regard, memristor array is the appropriate candidate due to their high level of integration, high energy efficiency, and compatibility with CMOS technology.[5] Furthermore, because of problems at transmission delay and a disconnection of the cloud computing that may occur in the process of communication between IoT sensors and the cloud, an edge computing that processes artificial neural network directly at the edge devices is being studied extensively. Therefore, a memristor array is suitable candidate for edge computing by virtue of low power consumption, high level of density, and multi analog characteristics. However, despite of various efforts for developing the rigid memristor array,[6] a flexible memristor array for the wearable applications has been studied less. Herein, we fabricate a flexible thin oxide based memristor following charge trapping/detrapping mechanism (CTM) into a 32×32 size array on a flexible polyimide substrate. The CTM shows high self-rectifying ratio which is suitable for the array application without any transistors or selectors. The array was fabricated with 5 μm electrode line width exhibiting high density level. The CTM array shows multi analog-conductance states along 1000 s at high temperature (85°C) and maintains a low resistance state (LRS) and a high resistance state (HRS) along about 10 years. The CTM array also shows stable flexibility under the bended condition (5 mm bending radius) and preserves LRS and HRS along about 10 years. Furthermore, the potentiation and depression (P-DP) are performed by voltage pulses under the various bended conditions (flat, 10, 7.5, and 5 mm bending radii) and also performed after 2000 bending cycles at 5 mm bending radius. By using the P-DP analog states, a MNIST hand-written images recognition and an electrocardiogram (ECG) classification are conducted by artificial neural network for the neuromorphic computing application.

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SESSION IE06: Poster Session: Iono-Electronics
 Tuesday Afternoon, July 19, 2022
 6:00 PM - 8:00 PM
 Mezzanine Level, Second Floor, Stadler

IE06.01

Protonic Neuromorphic Memory with Perovskite Nickelates [Tae Joon Park](#) and Shiram Ramanathan; Purdue University, United States

Rare-earth perovskite nickelates (RNiO_3) are as a class of quantum materials that undergoes metal-to-insulator phase transition upon thermal cycling. Hydrogenation with catalytic metals (Pt or Pd) induce new insulating phase of this material with several orders of increase in the resistivity and independent of temperature. At triple phase boundary of hydrogen gas, catalytic electrodes, and nickelates, hydrogen split to proton and electron. Protons occupy interstitial sites of host lattice and electrons from hydrogen reconstruct the band structure of RNiO_3 opening up a large energy gap. At room temperature, hydrogen remains in the lattice locally near catalytic electrodes and can move by electrical fields due to its charge. In this presentation, we will discuss changes in the resistance of the hydrogen doped nickelate devices to nanosecond-time scale electrical pulses with varying both pulse magnitude and width. Multiple analog memory states can be programmed upon consecutive electrical pulses and are reversibly accessible. Furthermore, we demonstrated ultrametric tree structures in the nickelate device at room temperature controlled by electric fields, which has been previously found in spin glasses at low temperature ranging from 1 to 20 K and inspired the early neural network research nearly five decades ago. Such hierarchical features in hydrogen doped nickelates demonstrate a new design platform for neuromorphic learning and present a new direction for proton-based computation.

IE06.03

Synthesis, Structural and Vibrational Properties of Neodymium Substituted Nickel Tungstates and Molybdates [Asmaa El Khouri](#); Universite Cadi Ayyad Faculte des Sciences Semailia, Morocco

Materials derived from tungstates and molybdates have attracted much interest thanks to their potential applications in many fields of materials science, such as photoluminescence, photocatalysis, microwave applications, fiber optic scintillators. Several metal tungstates and molybdates $\text{M}(\text{W/Mo})\text{O}_4$ doped with Rare earth elements have already been studied for their interesting luminescent properties. However, tungstates and molybdates of nickel have been the subject of few studies. This work is devoted to the synthesis and characterization of new series of neodymium substituted nickel tungstates and molybdates powders prepared by solid state route. Multiple characterizations, specifically scanning electron microscopy (SEM), X-ray powder diffraction (XRD), Fourier transform infrared (FTIR), and Raman spectroscopy, were used to validate the structural feature. The crystallite size was estimated by Scherrer's formula, and the effect of doping on the band intensities of the FTIR and Raman spectra was investigated.

IE06.04

Physical Reservoir Computing Based on Solid-State Electric Double Layer Effect Daiki Nishioka^{1,2}, Takashi Tsuchiya¹, Wataru Namiki¹, Makoto Takayanagi^{1,2}, Tohru Higuchi² and Kazuya Terabe¹; ¹Busshitsu Zairyo Kenkyu Kiko Kokusai Nanoarchitectonics Kenkyu Kyoten, Japan; ²Tokyo Rika Daigaku, Japan

Reservoir computing (RC) is one of the machine learning methods derived from recurrent neural networks, and has attracted attention for its good computational performance and low computational cost in time series data analysis and speech recognition tasks etc. RC is composed of the following two parts. (1) the reservoir, which performs nonlinear transformation of the input data and transfer to high-dimensional space, and (2) the readout, which is a small network and linearly combines the data output from the reservoir. One of the main advantages of RC is that the recurrent connections in the reservoir are always fixed during training, and only the weights of the readout are trained to generate the desired output, which enables a significant reduction in computational cost. If the information processing with nonlinear transformations performed in the reservoir can be calculated directly in the physical process, further reduction of computational cost and application to edge AI devices can be achieved. Reservoirs are required to have high dimensionality, nonlinearity, and short-term memory. Various physical reservoirs have been reported as physical systems satisfying these requirements, such as soft robots, optics, spintronic devices, memristors, and cultured cells[1]. In this study, we have physically implemented a reservoir in a nano-ionic device (EDL-RC) that utilizes the unique electrical properties caused by the carrier modulation of semiconductors by the solid-state electric double layer (EDL) effect at the ionic conductor/semiconductor interface [2], and evaluated its computational performance through tasks such as image recognition and time series data analysis.

In the handwritten digit recognition task of the MNIST dataset, EDL-RC showed a recognition accuracy comparable to that of the 3-layer neural network, even though the readout network size of EDL-RC is one-twentieth of the neural network commonly used for this task. The prediction task of second-order nonlinear dynamic equations was performed as a time series data analysis task. In this task, which requires nonlinearity and short-term memory in the reservoir, EDL-RC showed good prediction performance and outperformed the memristor-based RC[3], even though the reservoir size was less than a tenth of the size of it. These good computational performance by the EDL-RC is attributed to the high reservoir output diversity of the EDL reservoir, which is driven by the dynamic behavior of electrons and ions at the interface. We will report on various tasks performed by the EDL-RC, including results from the NARMA10 task, which is commonly used as a benchmark task for reservoir computing, and discuss its characteristics as a reservoir and the details of its operation mechanism.

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IE06.05

Understanding Non-Volatile Programming in LiNbO₂ Memristors via Electrochemical Impedance Spectroscopy (EIS) Aheli Ghosh, Alex S. Weidenbach, Bill Zivasatienraj, Timothy M. McCrone and W. A. Doolittle; Georgia Institute of Technology, United States

The advancement of neuromorphic computing is contingent on the development of nanoscale analog electrical synapses¹ which are power efficient, scalable, and capable of implementing relevant learning rules to facilitate large scale neuromorphic functions. Among contemporary synaptic devices, drift-based intercalation memristors²⁻³ have the advantage of inherent analog operation in mimicking biological synapses and achieving adaptive learning. Lithium Niobate (LiNbO₂) based memristors have been demonstrated to exhibit conductance changes on the order of 8900% and non-binary operation with a dependence on flux-linkage⁴, enabling analog neuromorphic functions resembling synaptic weight updates in the neuron membrane. It has also been shown that intercalation based LiNbO₂ memristors are highly scalable with non-volatile operation at voltages as low as 100-150 mV⁴. LiNbO₂ based memristors are natively volatile, however, non-volatile resistance changes (programming) are implemented in these devices by using a lithium-absorbing/active contact electrode such as Ag or Al to de-lithiate the Li_xNbO₂ channel under applied bias⁵. The application of a negative bias on the Li-absorbing electrode moves Li ions under the active electrode and decreases device resistance by Li vacancy generation (programming) and a positive bias on the active electrode increases the device resistance by compensation of vacancies in the Li_xNbO₂ channel (deprogramming).

Electrochemical impedance spectroscopy (EIS) is a powerful characterization technique which can be used to decouple the internal dynamics of electrochemical systems and complex non-linear processes. In this work EIS is used to characterize the Li ion and hole conduction mechanisms in non-volatile LiNbO₂ memristors and their evolution with programming and de-programming in these devices. EIS spectra for LiNbO₂ memristors with one Li blocking Ti/Au electrode and another Li absorbing Ag/Ti/Au electrode were measured after programming and deprogramming. The impedance spectra were then fit to a circuit model whose components represent the ionic and electronic effects in the Li_xNbO₂ channel. This study helps gain insight into the electronic and ionic contribution to the non-volatile resistance modulation in LiNbO₂ memristors and design highly scalable multi-functional memristive systems for future applications in neuromorphic computing.

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IE06.06

All-Solid-State Redox Transistor for *In Situ* Manipulation of Perpendicular Magnetic Anisotropy in Half-Metallic NiCo₂O₄ Thin Film Tomoki Wada^{1,2}, Wataru Namiki¹, Takashi Tsuchiya^{1,2}, Daisuke Kan³, Yuichi Shimakawa³, Tohru Higuchi² and Kazuya Terabe¹; ¹Busshitsu Zairyo Kenkyu Kiko Kokusai Nanoarchitectonics Kenkyu Kyoten, Japan; ²Tokyo Rika Daigaku Rigakubu Daiichibu Daigakuin Rigaku Kenkyuka, Japan; ³Kyoto university, Japan

Spintronics based on half-metallic magnetic tunnel junctions (MTJ) have recently been attracting attention for their application to neuromorphic devices. Since magnetization dynamics play a key role in such applications, the *in situ* manipulation of magnetic anisotropy in ferromagnets can lead to breakthroughs in this area. The authors recently reported the magnetic anisotropy manipulation of half-metallic magnetite by topotactic ion insertion (redox) using a solid electrolyte.^[1] While the range of the said manipulation reached up to 40%, the resulting in-plane magnetic anisotropy was not sufficient for miniaturization. In this study, we focused on NiCo₂O₄ (NCO), a half-metallic material with high perpendicular magnetic anisotropy (PMA) at room temperature. An all-solid-state redox device was developed using a combination of an NCO electron/proton mixed conductor and a Nafion proton-conducting polymer electrolyte. The modulation of magnetic anisotropy was enabled by voltage-controlled proton transfer between Nafion and NCO, accompanied by high-density electron doping in NCO. This approach, using solid electrolytes, makes it possible to achieve a simple device structure with

low power operation.

In our all-solid-state redox device consisted of NCO and Nafion, the electronic carrier density of NCO is controlled *in situ* by employing the redox reaction; $\text{NCO} + x\text{H}^+ + xe^- \leftrightarrow \text{H}_x\text{NCO}$. Thus, it is shown that the magnetic anisotropy of NCO can be manipulated by gate voltage (V_G) application. Distribution of the magnetic anisotropy can be studied by measuring anomalous hall resistance while rotating the external magnetic field in NCO(010). The electrical resistivity of NCO was increased, by about 50 %, by tuning the V_G from -0.3 V (the open circuit potential of the gate electrode) to 0.7 V. This suggests that doped electrons had accommodated in the Ni octahedral sites and that the Ni valence state was reduced.^[2] Further, the anisotropic magnetic field was increased by about 5 %. The enhancement of PMA was as a result of changed orbit hybridization, which was due to electron doping and lattice distortion. While variation in electrical conductivity and PMA were significant with the application of V_G , magnetization rotation was not observed. Such behavior is in contrast to the case of magnetite-based devices, in which magnetization was seen to rotate by 56 degrees.^[1] We have succeeded in achieving the *in situ* manipulation of PMA in NCO thin film by proton insertion, at room temperature. Since this technique has distinct advantages in miniaturization, it follows that it can be applied to the development of novel artificial neural networks consisting of integrated MTJ devices.

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IE06.07

Enhancing Room Temperature Magneto-Ionic Motion in Cobalt Oxide by Electrolyte Engineering Sofia Martins, Zheng Ma, Eva Pellicer, Enric Menéndez and Jordi Sort; Universitat Autònoma de Barcelona, Spain

Magneto-ionics, that is the modification of a material's magnetic properties by voltage-driven ion migration, offers much promise in the pursuit of voltage control of magnetism for highly energy-efficient electronic devices. Room temperature voltage-controlled ON-OFF ferromagnetism (magnetic switch) via oxygen magneto-ionics has been shown in electrolyte-gated Co_3O_4 films [1,2], taking advantage of the formation of an electric double layer (EDL) at the interface between the films and the electrolyte, i.e., propylene carbonate (PC) with solvated Na^+ and OH^- species. While optimizing ionic transport via electrolyte engineering has inspired intensive work in the fields of battery and solid oxide fuel cells, few efforts have been devoted so far on enhancing magneto-ionic performance by such means. Herein, by dissolving various inorganic salts such as potassium iodide (KI), potassium chloride (KCl) and calcium tetrafluoroborate [$\text{Ca}(\text{BF}_4)_2$] in anhydrous PC, we aim to increase the electric field strength in the EDL and hence enhance voltage-driven oxygen ion motion in cobalt oxide thin films. Our results indicate that improved magneto-ionic motion is achieved when salts are added to PC. This is especially pronounced for the KI-containing electrolyte. For instance, applying -1.5 V to the films in 2.5×10^{-5} M KI electrolyte results in not only a much faster magnetization variation ($\Delta M/Dt$), but also the maximum M value upon biasing time of 1 hour is nearly twice that for PC alone, enhancing robustness of the magnetic switch. Moreover, the threshold voltage to induce magneto-ionic effects decreases with addition of KI, from about -10 V in pure PC to -1.5 V when KI is added in small concentrations. We have actually optimized the magneto-ionic properties of cobalt oxide films by tuning the concentration of KI. From the biasing time dependence of ΔM under a -1.5 V external voltage, the ΔM firstly increases as the concentration increases from 2.5×10^{-6} M to 2.5×10^{-4} M, and then it decreases with further addition of KI. Remarkably, after applying -1.5 V for 1 hour, the maximum ΔM for 2.5×10^{-4} M KI electrolyte (≈ 280 emu/cm³) is one order of magnitude larger than that for pure PC (≈ 25 emu/cm³). Room temperature hysteresis loops of actuated cobalt oxide films confirm the effects of different electrolytes and KI concentration on the ON-OFF ferromagnetic switching in this system. Our study suggests electrolyte engineering as a potential approach to achieving substantial improvements in voltage control of magnetism based on magneto-ionics.

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IE06.08

Hydrogenated VO₂ Switches for Neuromorphic Functions Sunbin Deng, Tae Joon Park, Qi Wang, Haoming Yu and Shriram Ramanathan; Purdue University, United States

Vanadium dioxide (VO₂) is a strongly correlated oxide that displays an electrically driven insulator-metal transition (IMT) near room temperature. Typically, VO₂-based electronic devices exhibit a threshold volatile resistive switching (VRS) behavior, and they are considered as a promising candidate for energy-efficient artificial neurons¹. Controlling the channel resistance towards realizing diverse neuron characteristics is of importance to design complex synthetic neural circuits.

VO₂ hydrogenation is a feasible method to effectively shrink the channel length. The H atoms diffusing into VO₂ are converted into protons by transferring one electron to the t_{2g} band via oxygen². Thus, VO₂ incorporated with low hydrogen concentrations (i.e., H_xVO₂) can maintain a metallic rutile-like phase even at room temperature. In this work, two-terminal planar VO₂ devices with a catalytic Pd electrode and an inert Au electrode were fabricated on (0001) sapphire substrates. Through catalytic spillover effects, the device showed a reduction of initial resistance to several thousands of Ohms. It reflects the gradual channel hydrogenation from Pd to Au, while a narrow pristine VO₂ region remains near Au. When the electric field in the shortened VO₂ region reached the critical intensity for IMT, the hydrogenated device showed neuron-like spiking functionalities. In addition, the VO₂ hydrogenation also provides freedom to tune each neuron's threshold voltage for IMT (i.e., V_{IMT}), and an inverse correlation between H doping level and V_{IMT} is observed. Fundamental understanding of diffusion physics and electric-field driven drift of the hydrogen ions is therefore essential. In this presentation, we will discuss electrical results from VO₂ devices of various channel lengths fabricated by lithography along with kinetics of doping processes in VO₂ thin films. The results demonstrate the potential of utilizing simultaneously ionic and electronic switching in correlated insulators such as vanadium dioxide for design of neuromorphic devices.

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IE06.09

Nonvolatile Electrochemical Random Access Memory for Analog In-Memory Computing Laszlo Cline; University of Michigan, United States

TBD

SESSION IE07: Sensors
 Session Chairs: Moran Balaish and Joon-Hyung Lee
 Wednesday Morning, July 20, 2022
 Lobby Level, Terrace

9:10 AM *IE07.01

Functional Organic Neuromorphics Biointerfaces [Francesca Santoro](#)^{1,2,3}; ¹Rheinisch-Westfälische Technische Hochschule Aachen, Germany; ²Forschungszentrum Jülich GmbH, Germany; ³Istituto Italiano di Tecnologia Center for Advanced Biomaterials for Healthcare, Italy

The interface between biological cells and non-biological materials has profound influences on cellular activities, chronic tissue responses, and ultimately the success of medical implants and bioelectronic devices. The optimal coupling between cells and materials is mainly based on surface interaction, electrical communication and sensing¹.

In the last years, many efforts have been devoted to engineer materials to recapitulate both the environment (i.e., dimensionality, curvature, dynamicity)² and the functionalities (i.e., long and short term synaptic plasticity)³ of the neuronal tissue to ensure a better integration of the bioelectronic platform and cells. In this scenario, resembling the operation and the composition of the neuronal membrane might be beneficial to reconstitute synaptic proteins' arrangement (i.e. synaptic receptors) and electronic functionalities to further optimize the communication between neuronal cells and in vitro bioelectronic platforms².

Here, we explore how organic neuromorphic devices and supported lipid bilayers (SLBs) can recapitulate short and long term plasticity in biohybrid synapses.

Through the neurotransmitters' oxidation (i.e. catecholamines) first, we were capable of modulating the synaptic potentiation and ultimately the coupling with biological cells to form a functional synapse.

and artificial membranes we were capable of tuning the response of a neuromorphic platform to modulate its conductance over time. Then, we functionalized the organic neuromorphic transistor with a supported lipid bilayer and investigated how the PEDOT:PSS – artificial membrane interface can affect the ion flow and thus the device's conductance over time and the short term plasticity of the biohybrid synapse.

In turn, this could represent a first step toward in vitro adaptive neurohybrid interfaces to engineering neuronal networks with biomimetic structural and functional connections at synaptic level.

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9:30 AM IE07.06

Interaction of Hydrogen with HfO₂ for Application as Memristive Gas-Sensitive Devices [Sarah Beck](#); Technische Universität Dortmund, Germany

TBD

9:45 AM IE07.04

Widening the Range of Trackable Environmental and Health Pollutants for Li-Garnet-Based Sensors [Moran Balaish](#)^{1,1} and Jennifer Rupp^{1,2,1}; ¹Technische Universität München, Germany; ²Massachusetts Institute of Technology, United States

Classic chemical sensors integrated into phones, vehicles, and industrial plants monitor the levels of humidity or carbonaceous/oxygen species to track environmental changes. According to current projections, the gas sensor market is estimated to grow at an annual rate of 7% between 2021-2026 (valued at USD 1.5 billion by 2026).[1] The projections indicate the strong need to increase the ability of sensors to sense a wider range of chemicals for future electronics not only to continue monitoring environmental changes but also to ensure the health and safety of humans. To achieve this goal, more chemical sensing principles and hardware must be developed. The critical factors that determine the sensing performance for rather corrosive toxins such as SO₂ are to develop suitable electrochemistry and sensor material selection stable in this environment and operating at low temperature (ideally below 300 °C) to assure a low energy footprint per sensing device volume. One of the best investigated SO₂ electrochemical (type III) sensors are those based on the solid-state Na⁺ conductor NASICON a known conductor vastly applied also as a battery solid-state electrolyte. Despite the promise, the limited Na⁺ conductivity at ambient around 10⁻⁷ S cm⁻¹ challenges intrinsically to establish fast sensor response time and lower operation temperatures (energy footprint); which is also typically accompanied by degradation of the sensor performance and poor reproducibility. We propose in this work as a promising alternative cubic Li-garnet Li₇La₃Zr₂O₁₂ (LLZO) as a solid-state electrolyte for new SO₂ sensors due to their three orders of magnitude increased ionic conductivity (~mS cm⁻¹) and higher electrochemical stability window, which allows a wider definition and choice for sensing material electrodes. The material class of Li-garnets is known for about a decade and has proven successful for solid-state batteries, however, it had only recently been introduced to serve as electrolyte for type III sensors tracking less corrosive gases such as CO₂ with fast sensing and recovery times.

Here, we provide a proof-of-principle for the specific electrochemistry, material selection, and design of a Li-garnet LLZO-based electrochemical sensor, targeting the highly corrosive environmental pollutant sulfur dioxide (SO₂). For that, we explore the following sensor electrochemistry and investigated the major aspects that affect the electromotive force response according to the Nernstian behavior and the response/recovery time of the sensor, explicitly the auxiliary sensing electrode composition and microstructure. Novel composite sensing electrode designs using LLZO based on the porous scaffold employed to define a high number of reaction sites, allowed to successfully track SO₂ at the dangerous levels of 0–10 ppm with close-to-theoretical SO₂ sensitivity. The introduction of the composite sensing electrode Li₂SO₄–CaSO₄–LLZO with the LLZO electrolyte conductor achieved close-to-theoretical sensitivity of 47.7 mV/dec at a remarkably low operating temperature of the sensor of 240 °C. We wish to highlight that this outperforms previously reported SO₂ type III electrochemical sensors operating on Zr⁴⁺ (400 °C) or Na⁺ (600 °C) ion-conducting solid electrolytes in terms of their operating temperature and has as a consequence impact on the sensor power consumption. The insights on the sensing electrochemistry, reactions involved, and control over the interface sensing electrode/Li⁺ electrolyte structures and phase stability provide first guidelines for future Li-garnet sensors to monitor with fast response a wider range of environmental pollutants and toxins.

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2021.

10:00 AM IE07.05

Mixed Potential Electrochemical Sensors—Ceramic Substrate and Electrolyte Effects on Sensor Response to Methane and Simulated Natural Gas Sleight Halley¹, Kannan Ramaiyan¹, Kamil Agi², Fernando Garzon¹ and Lok-kun Tsui¹; ¹University of New Mexico College of Arts and Sciences, United States; ²SensorComm Technologies, United States

EPA estimates emissions from US natural gas drilling and processing amounted to 197 million metric tons of CO equivalent in 2019.[1] This number could be much higher, as research by Marchese et al. suggests that CH₄ emissions could be up to three times higher.[2] Current natural gas detection methods consist mainly of active optical monitoring, typically with long path IR sensors.[3] These monitoring methods, while capable of ppb level accuracy are expensive and requiring accurately calibrated mirrors, the instruments themselves are quite fragile. Mixed potential electrochemical sensors (MPES) are robust, low-cost, and selective sensors, making them appropriate option for methane emission monitoring.[4] Previously we have reported on a four electrode MPES with 3 mol% YSZ electrolyte fabricated with direct write 3D printing[5], here we investigate substrate and electrode material effects on the sensor response.

The response of a four electrode La_{0.87}Sr_{0.13}CrO₃, Indium Tin Oxide (In₂O₃ 90 wt%, SnO₂ 10 wt%), Au, Pt mixed potential electrochemical sensor to methane and simulated natural gas at operating temperatures of 450 – 600 °C was studied. Sensors were fabricated on substrates of yttria stabilized zirconia, ceria stabilized zirconia, and magnesia stabilized zirconia manufactured by direct write extrusion 3D printing of aqueous pastes. Data is presented with a solid electrolyte of 3 mol % yttria stabilized zirconia, and various other solid ceramic electrolytes will be studied. The effect of sensor response with respect to the resistance of substrate material is studied.

Sensor response is automatically decoded by artificial neural networks (ANNs) to perform mixture identification and quantification. Identification ANNs are able to correctly classify simulated mixtures of wetlands, bovine, and two types of natural gas emissions with >99% test accuracy. Quantification ANNs were also able to quantify CH₄, C₂H₆, and NH₃ concentrations with error at the 2.5% ppm level.

The sensors are being integrated with an IoT-based mobile methane monitoring system (M3System™) to expand the sensor applicability. Data is transferred to the cloud, where additional analytics capabilities are being implemented to improve the performance. This M3System™ is part of an early warning system for methane leak detection that includes identification and quantification. Field testing will commence in summer 2022.

Acknowledgements

This project was supported by US Department of Energy Office of Fossil Energy through award DE-FE0031864.

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SESSION IE08: Transparent Conductors

Session Chair: Joon-Hyung Lee

Wednesday Morning, July 20, 2022

Lobby Level, Terrace

11:00 AM *IE08.02

Development of Sn-Rich Nano Fluorites in Indium Tin Oxide (ITO) Sintered Body Seong-Uk Oh¹, Dokyum Kim¹, Young-Woo Heo¹, Ji Hoon Lee¹, Tae Hoon Lee¹, Jeong-Joo Kim¹, Yong Hyuk Hur² and Joon-Hyung Lee¹; ¹Kyungpook National University, Korea (the Republic of); ²LT metal Co., Ltd., Korea (the Republic of)

Sn-doped indium oxide (ITO) is a typical material for transparent conducting oxides, and its films have been widely used as electrode layers in optoelectronic devices, such as LCDs, touch panels, OLED panels, solar cells, and others. However, we do not seem to understand ITO yet clearly. The solubility limit of Sn in In₂O₃ has been known around 5~6 at%, and the ITO10, in which 10 wt% SnO₂ (9.3 at% Sn) is added, is the most widely used in general purposes. The excess Sn over the solubility limit forms the second phase of In₄Sn₃O₁₂. However, we found another phase of nanoclusters (~ 100 nm in size) homogeneously distributed in the ITO grains. The nanoclusters have not been observed commonly in SEM and XRD due to their easy evaporation during thermal etching for microstructure observation and resemblance in the crystal structure with In₂O₃ bixbyite.

HRTEM studies revealed that there is no lattice mismatch between the nanoclusters and ITO matrix while their Sn concentrations have quite differed about 20~24 at% and 2~4 at%, respectively. Also, the nanoclusters were found to have the fluorite structure of which the oxygen vacancy sites of In₂O₃ bixbyite are filled. As the solubility decreases during the cooling process after sintering, more In₄Sn₃O₁₂ phases will be produced. In the meantime, it is believed that Sn-rich nanoclusters are generated as the concentration of Sn increases locally.

From the X-ray absorption fine structure (XAFS) analyses performed at In and Sn K-edges, it turns out that In serves as a charge compensation center for accommodating Sn and O atoms into the ITO structure. We have also performed DFT simulations to study possible local structures of atoms in the nanostructures and their energetic stabilities. The charge transfer among constituent atoms and the role of In are discussed in conjunction with experimental findings.

11:20 AM *IE08.05

Zn Anode-Based Electrochromic Devices Wu Zhang¹, Haizeng Li² and Abdulhakem Elezzabi¹; ¹University of Alberta, Canada; ²Shandong University, China

As an emerging energy conversion technology, electrochromism has attracted immense interest due to its various applications including variable optical filters, bistable displays and energy-efficient smart windows. Although the current electrochromic devices do not consume energy while maintaining their colored or colorless states, their bistable operation requires external electrical energy to be consumed during switching. As such, a novel design of Zn anode-based electrochromic devices was recently developed as a key strategy to partially retrieve the consumed electrical energy.^[1] Compared to conventional electrochromic devices, Zn anode-based electrochromic devices exhibit a rapid spontaneous switching behavior due to the high value of redox potential difference between a metal anode and an electrochromic cathode, thus providing the most energy-efficient consumption during operation.^[2] Moreover, Zn-based electrochromic devices enable independent operation of top and bottom electrochromic electrodes, thus providing additional configuration flexibility of the devices through the utilization of dual electrochromic layers under the same or different color states.^[4] As such, the color overlay effect can greatly broaden the color palettes via altering the coordinate of the 2D CIE color space.^[5] These key issues of Zn-based electrochromic devices make them very promising for the future development of electrochromic devices.

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11:40 AM IE08.03

The Role of Back Channel Controlling Layer for Suppressed Channel Length Dependency of Fully Integrated In-Ga-Zn-O Thin-Film

Transistors [Kyung Min Kim](#)^{1,2}, Sang-Hoon Jung², Joon-Young Yang², Soo Young Yoon² and Hyun Jae Kim¹; ¹Yonsei University, Korea (the Republic of); ²LG Display Co Ltd, Korea (the Republic of)

During the past few decades, multi-component oxide semiconductors such as InSnO, InZnO, and InGaZnO have been considered as attractive alternatives to replace conventional silicon materials due to their superior electrical properties, transparency, and large-area applicability. Although successful mass production has been made in display application with the above promising advantages, the remained gap between the emerging oxide semiconductors and conventional Si-based materials on the device characteristics still limits its widespread expansion of commercialized applications.

Particularly, to overcome the limit, short channel capability is highly demanded due to the increasing integration density, less circuit area, boosting driving current, and higher productivity. However, the irregular device behavior due to the channel length (L_{CH}) dependency makes it difficult to implicate the short channel device in applications. In this research, we engineered the interface of InGaZnO back channel using commercially favorable silicon oxide (SiOx) material, and investigated its effect on the electrical characteristics of fully integrated InGaZnO thin-film transistors (TFTs) by varying the L_{CH} from 20 to 4- μm . We found that the origin of poor device performance under the short L_{CH} is came from back channel defects, mainly affected by chemical wet agent of electrode patterning and subsequent plasma damages of depositing passivation due to the weak chemical resistance of InGaZnO semiconductor. Here, we proposed sequential formation of SiOx as a double layer upon the exposed back channel. By adopting the proposed method, we investigated the effect of double layered SiOx through various electrical, chemical, and physical analyses. The stoichiometry of InGaZnO at back channel and evolution of process-dependent atomic distribution profile revealed that the interfacial layer directly faced to the back channel plays multiple roles to alleviate the back channel damages. The proposed method promotes supply of oxygen inter-diffusion to the oxygen deficient back channel region as well as it suppresses extra hydrogen inflow by acting as diffusion filter and effectively extracts residual copper ion at the back channel due to the interface trap and reduced repulsive charges, respectively. As a result, we obtained excellent device uniformity and electrical characteristics with a field effect mobility of $\sim 14.0 \pm 1.0 \text{ cm}^2/\text{Vs}$, a threshold voltage (V_{th}) of $\sim 1.22 \pm 0.39 \text{ V}$, and a subthreshold gate swing of $\sim 0.46 \pm 0.09 \text{ V/dec}$ at $W/L = 4\text{-}\mu\text{m}/7\text{-}\mu\text{m}$. Furthermore, consistent V_{th} with boosted driving current was achieved at the L_{CH} down to 4- μm , originated from the controlled back channel properties providing longer effective L_{CH} by confining the current flow at the back channel. Finally, the variable range of V_{th} when L_{CH} decreases from 20 to 4- μm is dramatically suppressed from $> 11.39 \text{ V}$ at the pristine to 0.78V at the proposed. Through these results of reliable electrical characteristics in the short channel, it can widely spread to various applications beyond the TFT itself, such as sensors, memory devices, healthcare system and so on.

11:55 AM IE08.04

Designer Dopants for Improved Transparent Conducting Oxides [David O. Scanlon](#); University College London, United Kingdom

The combination of electrical conductivity and optical transparency in a single material gives transparent conducting oxides (TCOs) an important role in modern optoelectronic applications such as in solar cells, flat panel displays, and smart coatings. The most commercially successful TCO so far is tin doped indium oxide (Indium Tin Oxide – ITO), which has become the industrial standard TCO for many optoelectronics applications; the ITO market share was 93% in 2013. Its widespread use stems from the fact that lower resistivities have been achieved in ITO than in any other TCO; resistivities in ITO have reached as low as $7.2 \times 10^{-5} \Omega \cdot \text{cm}$, while retaining $> 90\%$ visible transparency. In recent years, the demand for ITO has increased considerably, mainly due to the continuing replacement of cathode ray tube technology with flat screen displays. However, indium is quite a rare metal, having an abundance in the Earth's crust of only 160 ppb by weight, compared with abundances for Zn and Sn of 79000 ppb and 2200 ppb respectively, and is often found in unstable geopolitical areas. The overwhelming demand for ITO has led to large fluctuations in the cost of indium over the past decade. There has thus been a drive in recent years to develop reduced-indium and indium-free materials which can replace ITO as the dominant industrial TCO. In this talk I will outline the strategies that we use in the Materials Theory Group to look beyond the current TCO materials, highlighting the interplay of theory and experiment, and showcase a number of designer dopants that have produced record conductivities and mobilities for SnO_2 , In_2O_3 and Ga_2O_3 . [1-5]

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SESSION IE09: Mechano-Ionics
 Session Chairs: Konstantin Klyukin and Jose Santiso
 Thursday Morning, July 21, 2022
 Lobby Level, Terrace

9:10 AM **IE09.01

Non-Classical Electrostriction in Ion Conductors—Current Understanding and Potential Applications Igor Lubomirsky; Weizmann Institute of Science Faculty of Chemistry, Israel

Electrostriction is a second order electromechanical response observable in all solid dielectrics. According to the scaling law presented more than two decades ago by Prof. R. Newnham (Penn State), the electrostriction polarization coefficient (Q) for a wide range of classical electrostrictors scales with the ratio of the elastic compliance to the material dielectric constant. This phenomenological theory successfully described many classes of materials from polymers, generating large strain and small stress, to relaxor ferroelectrics that generate small strain and large stress.

In 2012, Gd-doped ceria, one of the most technologically important, moderate temperature ion conductors, was reported to exhibit an unusually large electrostrictive response. This first report was followed by reports on non-classical electrostriction in other aliovalent-doped ceria, on (Nb,Y)-stabilized bismuth oxide and acceptor-doped, hydrated barium zirconate, suggesting that strong electrostriction may be an inherent property of superionics. At room temperature, these ceramics exhibit a longitudinal electrostriction strain coefficient ($|M_{33}| > 10^{-17} \text{ m}^2/\text{V}^2$). However, with elastic modulus $> 80 \text{ GPa}$ and dielectric constant < 100 , the experimental Q-coefficients of these materials are at least 100 times larger than values predicted by the classical scaling law. Of the three ceramics, aliovalent-doped ceria is the most studied. Below 1Hz, $|M_{33}|$ for 10mol% Sm- or Gd-doped ceria reaches relaxing to $< \text{above } 100 \text{ Hz}$, well below the technologically important range 100Hz-100 kHz. Aliovalent lanthanide dopants with smaller ionic radii than that of Gd, such as Lu or Yb, raise $|M_{33}|$ at 100Hz to \gg , making these compositions promising for practical applications. Nevertheless, aliovalent dopants with radii smaller than that of Lu do not continue the trend.

Acceptor-doped $\text{BaZr}_{1-x}\text{X}_x\text{O}_{3-x/2+\delta}\text{H}_{2\delta}$ proton-conducting ceramics, where X= Ga, Sc, In, Y or Eu, and $0.05 \leq x \leq 0.2$, exhibit non-classical electrostrictive strain for all dopants in both the dry and hydrated states: $|M_{33}| = (1-7) \times 10^{-16} \text{ m}^2/\text{V}^2$ below, and $\gg 10^{-18} - 10^{-17} \text{ m}^2/\text{V}^2$ above, the Debye-type relaxation frequency. The largest low frequency (a few Hz), longitudinal strain coefficient was found for Sc, the dopant with the smallest size mismatch with the host (Zr) cations. Hydration does not significantly affect M_{33} , but raises the relaxation frequency by a factor of 10 to 100, indicating that proton-based elastic dipoles can respond more quickly than those based on oxygen vacancies. Relaxation time is many-fold with increase in dopant ionic radius. Given that efficient proton trapping also depends on dopant size, one can suggest that in hydrated ceramics, electrostriction involves reorientation of OH-groups. According to our current understanding, non-classical electrostriction emerges from electric field-induced rearrangement of highly polarizable elastic dipoles induced by point defects: oxygen vacancies or proton interstitials. In this model, elastic and dielectric properties are largely defined by the host lattice, while electrostrictive strain is controlled by the strength of the elastic dipoles. There is also evidence that although rapid ion migration and electrostriction can occur in the same materials, these effects are not directly linked: in fact, high frequency electrostrictive response does not track ion conductivity; rather, opposes it. The currently available data on electrostriction in ion conducting ceramics imply that by systematically adjusting composition, the potential exists for development of a new class of Si-compatible non-toxic electrostrictors.

9:40 AM *IE09.02

Strain Effects in Vanadium Dioxide Films with Metal-Insulator Electronic Transition Jose Santiso¹, Felip Sandiumenge², Laura Rodríguez¹, Carlos Frontera² and Gustau Catalán¹; ¹Institut Català de Nanociència i Nanotecnologia, Spain; ²Institut de Ciència de Materials de Barcelona, Spain

Vanadium dioxide (VO_2) is an archetypical material showing a metal-insulator (M-I) Mott transition at about $T=68^\circ\text{C}$ with several orders of magnitude change in the resistivity between the semiconducting low-T M1 phase and the high-T metallic rutile R phase. It has been proposed as a good candidate directly for Resistive-Random Access Memory (RRAM) devices or as complementary selector in combination of a bipolar RRAM device because of its high on/off ratio, fast switching speed and high current density. Although in bulk form the transition is above room temperature either chemical doping or mechanical strain have been demonstrated to bring the transition closer or even below room temperature making it very attractive in different devices. This work studies the structure features across transition of high quality strained VO_2 films deposited on isostructural rutile $\text{TiO}_2(001)$ single crystals. Since M-I transition in VO_2 is accompanied by a structural change between monoclinic M1 phase and tetragonal R phase, with substantial variation in cell parameters, the nucleation of the high-T R phase embedded in the low-T M1 phase upon transition, is expected to generate local interfacial regions with a large strain. Thorough characterization of the structural features of the films by means of synchrotron X-ray Diffraction upon thermal cycles revealed the formation of local strain effects during the phase transition in competition with the epitaxial strain induced by the growth on the mismatched TiO_2 substrates. Such interphase regions between M1 and R crystal domains are submitted to a uniaxial strain (overlapped to the biaxial in-plane epitaxial strain) that stabilizes other polytypic VO_2 insulating phases (monoclinic M2, and triclinic transitional M3 or T phase).[1] Concomitant to the subtle structural distortions a slight rotation of the monoclinic crystal domains occurs to accommodate the elastic energy constraints. The persistence of the coexistence of those polytypic phases even at room temperature turns VO_2 into a complex heterogeneous material. Nonetheless, at conditions where XRD of the films seems to indicate a pure rutile R phase, HRTEM analysis revealed certain degree of heterogeneity at the nanoscale forming an intricate tweed pattern of other polytypes with different arrangement of V-V dimers along the c-axis direction [2], still displaying a metallic character. Altogether these observations evidence that VO_2 micro and nanostructure, and therefore its electrical response, depends on a subtle balance of unconventional strain relaxation mechanisms.

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10:00 AM *IE09.03

Symmetry-Breaking Yields Emergent Phenomena at Oxide Interfaces Haiwu Zhang¹, Daesung Park², Dennis Valbjørn Christensen¹, Dragan Damjanovic², Vincenzo Esposito¹ and Nini Pryds¹; ¹Danmarks Tekniske Universitet, Denmark; ²Swiss Federal Institute of Technology-EPFL, Switzerland

Heterostructure materials result in symmetry breaking, electronic and/or atomic reconstruction(s) as well as strain gradients from which a wealth of new intriguing properties can emerge. Such richness arises from a strong interaction between the charge, orbital, spin, and lattice degrees of freedom. Here, I will discuss how symmetry-breaking phenomena at interfaces or surfaces can open the possibility to engineer and manipulate electrostriction that could extend to a broad family of dielectric materials. In another example, I will show a way to break the lattice symmetry and induce large and sustainable piezoelectric effect in centrosymmetric materials as a result of ionic migration induced by electric field. These and other emergent interfacial phenomena that I will present can be employed as a promising direction for future study.

SESSION IE10: Metal-Insulator transition
 Session Chairs: Konstantin Klyukin and Jose Santiso
 Thursday Morning, July 21, 2022
 Lobby Level, Terrace

11:00 AM *IE10.01

CMOS based Neuromorphic Test Platform Enabled Advances in Resistive Memory and Selector Device Karsten Beckmann; SUNY Polytechnic, United States

TBD

11:20 AM *IE10.02

Novel Thermal Material Properties for Post-CMOS Neuromorphic Computing Suhas Kumar; Sandia National Laboratories California, United States

The world of electronics is urgently looking for post-CMOS solutions due to the end of Moore's law saturating our present computing capacities. Such a post-CMOS paradigm would have to incorporate novel features at all levels from materials and devices to architectures and algorithms. The most promising candidate among several paradigms in research is classical neuromorphic computing, which mimics biological brains to solve classification and optimization problems in general. Here we will talk about how thermal properties of novel materials, such as phase change materials (e.g., Mott insulators such as VO₂ and NbO₂), offer unique functional behaviors at the device level, which we call thermally engineered memory elements ('thermems'). Specifically, we show how thermem can be designed to express dynamics of higher-order complexity (e.g., chaos). Such complex behavior, originating from a single thermem, would require hundreds of transistor circuits to simulate. We will further show how such higher-order dynamics mimic biological behaviors such as neuron-like periodic burst spiking and chaos. Finally, we will show with examples as to how such unique higher-order dynamics can enable unique algorithmic functions that offer improved efficiencies previously not possible in digital CMOS computers.

11:40 AM IE10.04

Hydrogen Intercalation Voltages in V₂O₅, Ta₂O₅, MoO₃, WO₃ from First Principles Pjotr Zguns and Bilge Yildiz; Massachusetts Institute of Technology, United States

Transition metal oxides are used as a working material for electrochemical synapse in neuromorphic computing hardware: reversible intercalation of H into oxide tunes its electronic conductivity and, in this way, H₂MO₃ represents a synaptic weight [1, 2]. Efficient operation of these devices, among many things, requires the ease of reversible H (de)intercalation (*i.e.* low-voltage, low-power). In this work, we perform a computational study of H intercalation into V₂O₅, Ta₂O₅, MoO₃, WO₃. We find that the hydrogen charge state is protonic and accompanying electrons localize as small polarons (in the low doping limit). We calculate H intercalation voltages vs. H₂ gas and PdH_x source, and vs. H₂O (oxidation in the air). Eventually, WO₃ is the best for reversible H intercalation from the PdH_x source, while V₂O₅ is the most stable against unwanted oxidation in air.

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11:55 AM IE10.05

Second-order Flexible Mott Neuron Gwangmin Kim, Jae Hyun In, Younghyun Lee and Kyung Min Kim; Korea Advanced Institute of Science and Technology, Korea (the Republic of)

Neuromorphic computing models have received much attention due to its high performances on classification, data processing, and robotics et cetera. After energy and speed limitation issues in conventional computing arise, by the Von Neumann bottleneck between the processor and the memory, neuromorphic hardware for in-memory computing has been proposed. The neuromorphic hardware operates in energy efficiency by a bio-plausible operation like in the brain. The artificial neurons and synapses are essential elements that perform such operations in neuromorphic hardware. However, Complementary Metal-Oxide-Semiconductor (CMOS) based neuromorphic hardware required large chip area as well as significant energy consumption. As the complexity of neural network is highly increasing, the neuromorphic hardware should achieve energy efficient computing possessing in a small area. In this regard, a memristor is an appropriate candidate owing to its high degree of integration, high energy efficiency, and compatibility with CMOS technology. There are many studies developing neuromorphic hardware utilizing non-volatile memristors as the artificial synapses, but fewer efforts to develop memristive artificial neurons have been made. The Negative Differential Resistance (NDR) endowed devices are promising candidates for the artificial neurons as they can generate spiking oscillations under a constant voltage when a series resistor is with. A Mott memristor is one of the NDR inherent devices where the NDR is originated from Mott transition, or the positive feedback in conductance and temperature. As both the NDR mechanisms are thermally activated, the conductance of the Mott memristor depends on the heat environment in which heats are transferred inwards and outwards the Mott memristor. However, a few studies noted the heat influences on the Mott memristor, and there has been no attempt to develop spiking artificial neurons based on the heat exchanging system. Rather, they relied only on electronics consequently requiring a couple of devices connected in a complicated way by resistors, or capacitors to perform complex neuronal dynamics. Here, we propose a flexible Mott neuron based on a NbO_x-based Mott memristor. The Mott memristor could temporally change its electrical property by bidirectional heat exchange with the substrate, which was not achievable on a thermally conducting substrate. Based on the novel heat exchange system, the proposed Mott neuron could achieve 14 various neuronal behaviors in a single NbO_x-based Mott memristor and resistor. We developed a heat exchange model, and the neuronal behaviors are well emulated by numerical simulation regarding the heat exchange model. Furthermore, the Mott neuron could modulate its sensitivity to external stimuli upon the amount of heat energy stored in the substrate. Also, the Mott neurons could be thermally linked, and communicate via heat transfer even when they are electrically isolated. Thus we suggest the flexible Mott neuron as an ideal device for neuromorphic hardware mimicking various bio-neuronal signals.

12:10 PM IE10.06

Self-Clocking, Fast and Variation Tolerant True Random Number Generator Based on a Stochastic Mott Memristor Jae Hyun In, Gwangmin Kim and Kyung Min Kim; Korea Advanced Institute of Science and Technology, Korea (the Republic of)

In future electronics, as the internet of things (IoT) expands the reach of technologies, chip authentication for secure communication will be increasingly important. Accordingly, developing a hardware-based true random number generator (TRNG) is crucial, since it is intrinsically non-decryptable, unlike the software-based TRNG. For better security, researchers have proposed novel methods for realizing a TRNG, utilizing the stochastic switching devices such as spin transfer-torque, magnetic memory, and resistive memory. The early TRNGs utilized the stochastic characteristics in the switching voltages or the programmed states of the non-volatile memristors. Although the proposed methods were viable, they commonly relied on stochastic variation in relation to reference values, which can be vulnerable if the reference value changes over time or over cycling.

To overcome the problem, H. Jiang et al. proposed a volatile memristor-based TRNG. They observed the stochasticity in the switching delay in the Ag:SiO₂-based diffusive memristor and designed a novel circuit which converted the stochasticity to randomness by introducing a clock and counter. The device counted the number of clocks after the stochastic turn-on switching and digitalized it. This method suggested a way to generate dimensionless values that required no reference value to define the randomness. Afterward, K. S. Woo et al. introduced a nonlinear feedback shift register (NFSG) with a HfO₂-based volatile memristor to further increase the TRNG rate. The NFSG can increase the bit size proportional to the number (n) attached to the device, making the rate n times faster. However, in both methods, the switching delay time was intrinsically long, several hundreds of ms, preventing fast TRNG operation. Also, they required an exterior clocking circuit, which can be difficult to integrate.

A NbO_x-based mott memristor shows a stochastic (or chaotic in specific condition) threshold switching behavior. Various applications have been proposed to exploit it such as the Hopfield network or fundamental oscillatory computing. Considering such high usefulness of the NbO₂ mott memristor for various applications, its application to the TRNG should be reasonable, but no studies have demonstrated it yet.

In this study, we propose a self-clocking TRNG device utilizing the oscillating behavior of a mott memristor. We identified the origin of the randomness to be thermal fluctuations during oscillation, using a numerical simulation and a thermodynamic simulation. The oscillation speed is fast, allowing the fastest random bit generation rate of 40 kb s⁻¹ at least. Also, it has an inherent self-clocking capability, so that no external clocking circuit is needed. From the integrated device, we collected 130 millions random bits and they passed all of the NIST random number tests successfully. Furthermore, we confirmed that the device worked well under a wide range of ambient temperatures, ranging from 300 K to 390 K, and in different characteristic devices, suggesting the high tolerance of the TRNG system.

SESSION IE11: Magnetoionics and Ferroelectrics
Session Chairs: Geoffrey Beach and Sean Bishop
Thursday Afternoon, July 21, 2022
Lobby Level, Terrace

2:00 PM **IE11.01

Electrolyte Gating of Perovskites and Pyrites for Magneto-Ionics [Chris Leighton](#); University of Minnesota Twin Cities, United States

Magneto-ionics offers potential routes to low-power voltage-based control of magnetic elements, which is highly attractive for various next-generation data processing and storage paradigms. Electrolyte gating is a powerful approach to magneto-ionics, where electrolytes such as ionic liquids and gels (essentially solid-state ionic liquid/polymer composites) are employed in transistor-type devices for wide-range voltage-control of magnetic order and properties [1]. In this talk I will review recent advances in this area from my group and collaborators, focused on voltage control of magnetism in perovskite oxides (particularly cobaltites [2-6]) and pyrite-structure transition metal disulfides (FeS₂ [7] and NiS₂ [8]).

In perovskite cobaltites I will review our work on reversible electrochemical toggling between ferromagnetic metallic perovskite and antiferromagnetic insulating brownmillerite phases *via* ion gel gating [5,6]. This has now been achieved across almost the entire La_{1-x}Sr_xCoO_{3-δ} phase diagram, studied *via* operando synchrotron X-ray diffraction, transport, magnetometry, and optical spectroscopy, including detailed gate voltage hysteresis loops [5,6]. We have thus understood doping- and strain-dependent threshold voltages, the relative importance of thermodynamic and kinetic factors, and many features of the perovskite ↔ brownmillerite phase transition [5,6]. The latter include the first-order nature of the transition, the associated phase coexistence, and the asymmetry of the voltage-driven transition [5,6]. Such advances enable voltage-based control over electronic, magnetic, optical, and thermal properties over extraordinary ranges, with substantial application potential.

In pyrite-structure transition metal disulfides we have explored ionic liquid gating of both diamagnetic semiconducting FeS₂ and antiferromagnetic Mott-insulating NiS₂ [7,8]. Gating of FeS₂ occurs *via* a highly volatile and reversible electrostatic mechanism, leading to the first demonstration of voltage-induced ferromagnetism in an initially diamagnetic material [7]. Gating of NiS₂, on the other hand, occurs *via* a highly non-volatile and irreversible electrochemical mechanism, leading to a Mott-insulator-to-metal transition [8]. The origin of the stark differences in gating mechanisms between these closely related materials lies in vastly different diffusion rates for S vacancies, generating important insight into electrolyte gating mechanisms [9].

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2:30 PM *IE11.02

Magneto-Ionic Control of Heterostructures and Interfaces [Kai Liu](#); Georgetown University, United States

Magneto-ionics has shown promise for energy-efficient nanoelectronics, where ionic migration can be used to achieve atomic scale control of interfaces in magnetic nanostructures, and in turn modulate a wide variety of functionalities. Recently, we have discovered that chemisorbed oxygen and hydrogen on the surface of ferromagnetic films can induce significant Dzyaloshinskii–Moriya interaction (DMI) [1], a handle to introduce topology into nanoscale

magnets. This has enabled direct tailoring of skyrmions winding number as well as wall type at room temperature via oxygen chemisorption. We have also demonstrated a sensitive and reversible chirality switching of magnetic domain walls [2] and writing/deleting of skyrmions [3] via hydrogen chemisorption/desorption. These chemisorption induced magnetic effects on controlled ferromagnet surfaces offer an ideal platform to gain quantitative understanding of magneto-ionics at buried interfaces, where the ionic motion can be further controlled by an electric field [4]. These effects are relevant for 3-dimensional information storage as a potentially contactless way to address spin textures, such as in interconnected nanowire networks [5]. Interestingly, nanoporous metal foams made of random assemblies of nanowires have found applications in deep-submicron particulate filtration, relevant to combatting COVID-19 and air pollution. Such foams are efficient, breathable, light-weight, robust, and can be reused and recycled [6]. Our mask design based on such foams has been selected by BARDA-NIOSH as a Phase 1 Winner of the Mask Innovation Challenge [7].

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2:50 PM *IE11.03

Effect of Hydrogen Intercalation on Electronic and Magnetic Properties of Functional Materials—Insights from First Principles [Konstantin Klyukin](#); Auburn University, United States

Ionic control of materials properties has gained much attention in recent years due to the sizable effects that can be induced by the electrically controlled motion of small ions such as hydrogen. Hydrogen intercalation can alter the electronic, magnetic and optical properties of functional materials in a reversible and controllable manner. This approach promises to revolutionize spintronics, information storage, neuromorphic computing, and other fields of nanoelectronics. Despite extensive experimental investigations, very little is known about the phenomena on the atomistic scale, and systematic studies are needed to provide fundamental insights on the physical origin of phenomena.

In this talk, we provide an overview of our recent first principles-based investigations aimed to unveil the effect of hydrogen gating on electronic conductivity [1], magnetic anisotropy [2-3], and magnetic order [4] in representative materials. These results clarify the underlying mechanisms of functional properties switching and help to optimize material combinations for nanoelectronics based on hydrogen intercalation.

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3:10 PM IE11.04

DC Lifetime and Thermally Stimulated Depolarization Current (TSDC) of Bi(Zn,Ti)O₃-BaTiO₃ (BZT-BT) [Sean Bishop](#), Mia Blea-Kirby, Amanda Peretti, Luis Jauregui, William Bachman and Jon Bock; Sandia National Laboratories, United States

Bi(Zn,Ti)O₃-BaTiO₃ (BZT-BT) is a relaxor ferroelectric with high energy density and high resistivity at elevated temperatures. Little is known of the long-term stability under high electric fields and elevated temperature of operation for BZT-BT. In this presentation DC lifetime results for BZT-BT with acceptor and donor doping are discussed. The DC lifetime results are correlated with thermally stimulated depolarization (TSDC), impedance spectroscopy, capacitance, and phase and microstructure. Relationships between electrical properties and electronic and ionic defects will be discussed.

Sandia National Laboratories is a multimission laboratory managed and operated by National Technology & Engineering Solutions of Sandia, LLC, a wholly owned subsidiary of Honeywell International Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525.

3:25 PM IE11.05

Improvement of Hydrogen-Based Magneto-Ionic Effect in Ni Films by Changing the Electrolyte Composition Maksim Kutuzau^{1,2}, Stefan Topolovec³, [Markus Göbeler](#)^{3,1}, Roland Würschum³, Sandra Schiemenz² and Karin Leistner^{1,2}; ¹Technische Universität Chemnitz, Germany; ²Leibniz-Institut für Festkörper- und Werkstofforschung Dresden eV, Germany; ³Technische Universität Graz, Austria

Hydrogen is one of the most promising ions for the implementation of voltage-control of magnetism in nanomaterials through ionic migration and electrochemical reactions (so-called magneto-ionic control) (1). So far, hydrogen-based magneto-ionic control was mainly applied to ultrathin films and nanoporous materials (1,2). In this work, we implement hydrogen-based magneto-ionic control in Ni films beyond the thin film limit and study the impact of electrolyte composition to increase the magneto-ionic efficiency.

To analyze the magneto-ionic effect in electrodeposited nanocrystalline nickel films polarized in alkaline electrolyte, we carried out *in situ* SQUID and *in situ* Anomalous Hall effect (AHE) measurements. To determine the influence of the electrolyte composition on the magneto-ionic effect we investigated the magneto-ionic response for different electrolytes, i.e. solutions with different concentrations (0.5, 2 and 5 M KOH) and with and without thiourea as an additive.

The *in situ* AHE measurements reveal a voltage-induced change in the AHE resistance in saturated state (large magnetic field), which is indicative for a change in the saturation magnetization. The magnitude of this magneto-ionic effect significantly increases for higher KOH concentration. These results can be explained by the formation of a unique H₃O⁺ intermediate layer causing an anomalous acid-like activity towards the hydrogen ion reduction reaction, an effect known from nanostructured electrocatalysts in concentrated alkaline electrolytes (3).

Comparative *in situ* SQUID measurements reveal that the addition of a small amount of thiourea additive to KOH electrolyte leads to a voltage-induced magnetic moment change of 3.99%. This is at least 15 times more than the change observed in pure KOH electrolyte. Moreover, in this case, for the

implementation of the magneto-ionic switching a smaller reduction overpotential is required. This contributes to an increase in the magnetoelectric coefficient, which is an important parameter for determining the efficiency of magneto-ionic systems (4). The positive effect of thiourea is ascribed to the formation of a nickel hydroxide layer on the surface as a result of chemical reactions triggered by thiourea. Ni(OH)₂ not only shows significant catalytic effect on hydrogen ion reduction in an alkaline medium (5), but also serves as hydrogen reservoir, which improves key steps of hydrogen-based magneto-ionic control: hydrogen ad- and absorption (6).

The obtained results allow to optimize magneto-ionic systems operating in an alkaline medium by choosing the optimal composition and concentration of electrolyte and should make them more suitable for practical applications.

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3:40 PM BREAK

4:00 PM *IE11.06

Low Voltage-Tunable Magnetism in Thin Films and Nanostructures by Magneto-Ionic Approaches [Karin Leistner](#)^{1,2}; ¹Technische Universität Chemnitz, Germany; ²Leibniz-Institut für Festkörper- und Werkstofforschung Dresden eV, Germany

Magneto-ionic control is an emerging approach for the development of ultra-low power magnetic devices for data storage/processing and actuation. [1] It presents a promising route to tackle the global issue of a growing energy demand when larger data storage capabilities are required. In magneto-ionic materials, voltage-triggered electrochemical reactions such as interfacial oxidation/reduction or electrochemical hydrogenation are utilized to set different magnetic states. A small electric current is only required to set the magnetic state. This circumvents the significant energy loss encountered in conventional magnetic devices, which are controlled by micro-electromagnets or by high spin-polarized currents causing Joule heating. Magneto-ionic control can be efficiently applied to simple and abundant magnetic oxides and metals with high magnetization and can operate at room temperature and low voltage. [2]

In the presentation, I will shortly review current advances in magneto-ionic systems and present recent examples from our group. The focus lies on the electrolytic gating of FeO_x/Fe thin films and 3D nanostructures. Here, we achieve electrically tunable magnetization, coercivity and magnetoresistance via reversible oxidation/reduction reactions triggered by a low voltage (around 1 V). [3,4] The underlying mechanisms are revealed by the combination of electrochemical analysis, in situ Raman spectroscopy and advanced in-situ magnetic techniques such as in situ magneto-transport measurements and in situ Kerr microscopy. For example, during the voltage-triggered reduction of the iron oxide layer in FeO_x/Fe thin films, in situ Kerr microscopy reveals inverse changes of coercivity and anisotropy, and a coarsening of the magnetic microstructure. These results confirm a magneto-ionic de-blocking mechanism, which relies on changes of the Néel wall interactions, and of the microstructural domain wall-pinning sites. An estimation of the switching energy confirms the potential for low-power devices here. I will show that we can extend the magneto-ionic functionality by combining the tunable ferromagnetic layer with an antiferromagnetic layer. This way, we demonstrate reversible voltage-control of in-plane and perpendicular exchange bias [5,6] The results open a path towards voltage-reprogrammable magnets for spintronics, actuation and sensor applications.

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4:20 PM *IE11.07

Atomically-Precise Synthesis of “Stubborn” Metal Oxides [Bharat Jalan](#); University of Minnesota Twin Cities, United States

A fascinating consequence of electron-electron correlation and spin-orbit coupling is the emergence of a wide range of quantum phases in complex oxides such as iridates and ruthenates. However, it has been notoriously difficult to grow these materials in an atomically precise manner using molecular beam epitaxy (MBE) due to ultra-low vapor pressures and difficulty of oxidation for Ru and Ir. In this talk, we will present our group's effort to address these challenges using a novel solid-source metal-organic MBE approach. We show, for the first time, controlled synthesis of metal and metal oxides of these “stubborn” elements with the *same ease and control* as afforded by III-V MBE. We will present detailed growth study with the focus to understand and control electronic and magnetic ground states in defect-managed complex oxide films.

4:40 PM *IE11.08

Magneto-Ionics Using Nitrogen Ion Transport—Towards Emulation of New Neuromorphic Functionalities Zhengwei Tan¹, Julius de Rojas¹, Jose Luis Costa-Kramer², Alberto Quintana³, Eric Menéndez¹ and [Jordi Sort](#)¹; ¹Universitat Autònoma de Barcelona Facultat de Ciències, Spain; ²Consejo Superior de Investigaciones Científicas, Spain; ³Georgetown University, United States

Magneto-ionics, understood as voltage-driven ion transport in magnetic materials, usually relies on controlled migration of oxygen ions. Here, I will show that voltage-driven transport of nitrogen ions (*i.e.*, nitrogen magneto-ionics) can be triggered at room temperature in transition metal nitride (CoN, FeN)

films via liquid electrolyte gating [1,2]. Nitrogen magneto-ionics can induce reversible ON-OFF transitions of ferromagnetic states at faster rates and lower threshold voltages than oxygen magneto-ionics. This is due to the lower activation energy for ion diffusion and the lower electronegativity of nitrogen compared to oxygen. Remarkably, and in contrast to oxygen magneto-ionics, nitrogen transport occurs uniformly through a plane-wave-like migration front, without the assistance of diffusion channels, particularly interesting for the implementation of multi-stack memory devices. Furthermore, I will show that nitrogen magneto-ionics can be used to emulate some important neuromorphic functionalities. By cumulative effects of DC and pulsed voltage actuation (at frequencies in the range 1 – 100 Hz), learning, memory retention, forgetting and self-learning by maturity (with zero energy consumption) can be mimicked by proper tuning of the CoN film thickness and the pulse frequency. Sub-1s nitrogen magneto-ionics can be achieved by decreasing the CoN film thickness down to 25 nm. The interplay between the high ion speeds in thin CoN films and the pulse frequency results in a trade-off between generation (voltage ON) and partial depletion or recovery (voltage OFF) of ferromagnetism, giving rise to a controllable ion accumulation effect at the interface between the films and the electrolyte [3]. From a hardware viewpoint, this effect can serve as a logical function for the device to decide between self-learning or forgetting emulation, at will, without any additional electric voltage input (*i.e.*, with no power consumption). This constitutes a novel approach to emulate some specific neural functionalities (*e.g.*, learning under deep sleep), that are challenging to achieve using other classes materials currently employed for neuromorphic computing applications.

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5:00 PM IE11.09

Tuning Magnetization of Nanoporous Pd(Co) via Pseudo-Capacitive Reactions Markus Göbller^{1,2}, Stefan Topolovec², Alexander Steiner², Karin Leistner^{1,3}, Heinz Krenn⁴ and Roland Würschum²; ¹Technische Universität Chemnitz, Germany; ²Technische Universität Graz, Austria; ³Leibniz-Institut für Festkörper- und Werkstoffforschung Dresden eV, Germany; ⁴Karl-Franzens-Universität Graz, Austria

Palladium, as the paramagnetic metal closest to ferromagnetism, has always been a promising element for studies on the electrical tuning of magnetic properties. As a natural consequence, palladium has also found its place in the young field of magneto-ionics, where magnetic properties are controlled via electrochemical reactions.

Previously, we could demonstrate a reversible ON- and OFF-switching of magnetization in a nanoporous Pd(Co) system, triggered by electrochemical hydrogen-intercalation [1]. In this study, we expand our experiment to electrochemical charging of nanoporous Pd(Co) electrodes in pseudo-capacitive charging regimes. In particular, we investigate pseudo-capacitive reactions for the tuning of magnetization in both aqueous and Li-ion-based electrolytes. We thereby revisit the original idea of tunable magnetism in Pd, based on the filling of electronic bands. Optimized high-surface-area Pd(Co) electrodes close to the ferromagnetic threshold were selected as a promising electrode material, while pseudo-capacitive reactions could potentially provide the electrons for such a band filling mechanism.

Nanoporous Pd(Co) electrodes were prepared experimentally via electrochemical dealloying synthesis from a Co-rich alloy. For a systematic study of the effects of pore size and Co distribution on the magnetic switching performance, nanoporous samples were post-treated using a thermal annealing procedure. For a direct correlation of the electrochemical processes with magnetic properties we used an in situ electrochemical cell designed for the use in a SQUID magnetometer [3].

Our results show a systematic variation of magnetization in the order of a few percent as a result of pseudo-capacitive charging in both Li-ion based and aqueous electrolytes. Based on our data we assess that a magnetic tuning based on a true band filling mechanism is difficult to achieve in Pd. Instead, we discuss the magnetic tuning for annealed nanoporous Pd(Co) in terms of superficial Co, which is oxidized upon pseudo-capacitive charging and magneto-elastic contributions.

Financial support by the Austrian Science Fund FWF (P30070-N36) and by the German Science Foundation (DFG) under project 400178764 is acknowledged. This work was performed in the framework of the inter-university cooperation of TU Graz and Uni Graz on natural sciences (NAWI Graz).

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5:15 PM IE11.10

Ionic Control Over Polarization Switching in 2D Layered van der Waals Materials Sabine M. Neumayer¹, Mengwei Si², Junkang Li², Pai-Ying Liao², Lei Tao³, Andrew O'Hara³, Sokrates Pantelides³, Peide Ye², Petro Maksymovych¹ and Nina Balke⁴; ¹Oak Ridge National Laboratory, United States; ²Purdue University, United States; ³Vanderbilt University, United States; ⁴NC State University, United States

The interplay of ionic properties and electric polarization in ferroelectric van der Waals layered CuInP₂S₆ leads to novel functional phenomena.

Ferroelectric materials are characterized by a spontaneous electric polarization that can be reoriented (or “switched”) by applying an electric field.

Typically, ionic conductivity in ferroelectrics is associated with defect migration, screening, and leakage conductivity. However, in CuInP₂S₆, cooperative ionic-polar coupling can be observed. In this material, the polarization orientation and magnitude are underpinned by the position of Cu ions in the crystal lattice [1]. These Cu ions are also highly mobile, which leads to a coupling of ionic and polar properties that can manifest as polarization switching against an electric field based on ionic displacement across van der Waals gaps – a process that is fundamentally distinct from ferroelectric polarization switching due to dipole rotation [2]. In addition, ferroelectric polarization switching can be controlled by ionic currents. Here we demonstrate how ionic currents that are activated through tailored direct voltage pulses to a CuInP₂S₆ capacitor affect the polarization switching behavior in subsequent fast triangular voltage sweeps. Ionic currents can even result in a complete deactivation of hysteretic behavior. Notably, hysteretic polarization switching can be fully restored by activating ionic migration in the opposite direction. Coupled polar-ionic effects can be utilized as tuning knobs for ferroelectric polarization and provide exciting opportunities for ferroelectric information storage beyond binary limitations, applications in solid-state synapses and for tailoring the electromechanical performance of sensors and actuators.

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5:30 PM IE11.11

ON-OFF Ferromagnetism in Co₃O₄ by Voltage-Driven Oxygen Ion Transport Enric Menéndez¹, Sofia Martins¹, Julius de Rojas¹, Alberto Quintana² and Jordi Sort^{1,3}; ¹Universitat Autònoma de Barcelona, Spain; ²Georgetown University, United States; ³Institució Catalana de Recerca i Estudis Avançats (ICREA), Spain

Using voltage-driven ion transport to modulate magnetism (magneto-ionics) could represent a significant breakthrough in the search for routes to enhance energy efficiency in magnetically-actuated devices. In particular, voltage-driven oxygen ion motion in Co₃O₄ allows for voltage-controlled ON-OFF ferromagnetism, since Co₃O₄ (paramagnetic: OFF) can be partially reduced to Co (ferromagnetic: ON) by voltage actuation and, subsequently, reversed by applying a voltage of opposite polarity [1]. The way an electric field is applied (voltage actuation) can have a strong impact on the room temperature magneto-ionic motion. Specifically, in electrolyte-gated 100 nm-thick paramagnetic Co₃O₄ films, the oxygen magneto-ionic motion can be increased by one order of magnitude (from 1000 to 100 s) by applying the electric field through an electrochemical capacitor configuration (*i.e.*, using, as a working electrode, an underlying conducting buffer layer beneath the Co₃O₄ film) rather than using an electric-double-layer transistor-like configuration (*i.e.*, placing the electric contact at one side of the Co₃O₄ film as a working electrode). This is due to the greater uniformity and strength of the electric field in the capacitor design [1,2]. However, ion motion at room temperature is still too slow for applications. By reducing the Co₃O₄ film thickness down to 15 nm, sub-10 s ON-OFF ferromagnetism can be achieved in electrolyte-gated films [3]. Remarkably, cumulative magneto-ionic effects can be generated by applying voltage pulses at frequencies as high as 100 Hz, which is the frequency at which dynamic effects of biological synapses occur. Magneto-ionics in Co₃O₄ can then be used to emulate synapse functionalities, including potentiation (magnetization increase), depression (*i.e.*, depletion of magnetization), voltage-controlled threshold activation of ferromagnetism, and spike time-dependent plasticity (learning and forgetting capabilities) of the generated magnetization upon pulsed voltage actuation. These features show Co₃O₄ magneto-ionics could be useful for the design of neuromorphic-like systems [3].

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5:45 PM IE11.12

Ferroelectric Ordering and Energy Storage Density in Mixed Doped Lead Zirconate Titanate Ceramics by La³⁺ and Sc³⁺ Cations Mohan K. Bhattarai, Karuna Mishra and Ram Katiyar; Universidad de Puerto Rico Recinto de Rio Piedras, Puerto Rico

Mixed doped La³⁺ & Sc³⁺ on lead zirconate titanate electro-ceramics with the stoichiometric formula 0.90(PbZr_{0.53}Ti_{0.47})_{0.10}(La_xSc_{1-x})_{0.10}O₃ (PLZTS10x) for $x = 0.2, 0.4, 0.6$ & 0.8 were prepared by using a conventional solid-state reaction method, & investigated their structural, microstructural, dielectric, and ferroelectric properties. Rietveld analyses on X-ray diffraction data indicate tetragonal phase (Sp. Gr. *P4mm*) of these compounds with decreasing tetragonal anisotropy (c/a ratio). Temperature-dependent phonon spectra investigation elucidated tetragonal-to-cubic structural phase transition in these compounds in the temperature window of 80-580 K. Dielectric spectroscopic studies were carried out on Ag/PLZTS10x/Ag metal-ferroelectric-metal capacitors covering the frequency range from 10²-10⁶ Hz in the temperature range 100-600 K, exhibited high dielectric constants and low losses. Modified Curie-Weiss law analyses on the dielectric data for $x = 0.8$ indicates diffuse phase transition with diffusivity parameter $\gamma \sim 1.94$. High breakdown field and spontaneous polarization were obtained from electrical hysteresis loop measurement. The remanent polarization is found to progressively decrease upon increasing x and became slimmer hysteresis loop for $x = 0.8$ corroborating the dielectric diffusivity. A significant amount of recoverable energy density (U_{rc}) of ~ 1162 J/cm³ with an efficiency (η) of $\sim 79\%$ was estimated. These results may provide insights into the PLZTS10x ferroelectric capacitor for its potential memory and power device applications.

Electrochemical Interfaces

Electrochemical Interfaces

July 18 - July 22, 2022

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* Invited Paper

SESSION EI01: Surface Chemistry
Session Chairs: Simone Mascotto and Liliana Moggi

Monday Morning, July 18, 2022
 Mezzanine Level, Second Floor, Berkeley/Clarendon

9:10 AM *EI01.01

What is the Active Site of the Oxygen Reduction Reaction on Solid Oxide Fuel Cell Cathodes? Theoretical Investigation of Oxygen Reduction on the Reconstructed LSM25(001) Surface Emmanuelle Hagopian and [Franziska Hess](#); Technische Universität Berlin, Germany

One of the most important and best-studied perovskite materials for energy conversion applications is $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ (LSM). It is a promising material for Solid Oxide Fuel Cell (SOFC) electrodes that exhibits superior electronic conductivity, oxygen reduction kinetics and thermal stability. As the oxygen exchange at the surface is typically rate-limiting, tuning of the electrode surface is a key aspect in the development and optimization of materials for energy conversion applications. Sr-doped perovskite materials form passivating Sr-rich layers and particles on the surface due to segregation of the dopant strontium ions. This surface layer inhibits the oxygen exchange at the surface, thus increasing polarization resistance and reducing the energy efficiency of the SOFC.

Although the basic features of the LSM defect chemistry have been well-understood for at least 20 years based on experiments, substantial progress on understanding the influence of cation vacancies, A/B ratio, temperature, and oxygen partial pressure on Sr segregation has only recently been accomplished by a combination of computational methods, such as Density Functional Theory (DFT), ab-initio thermodynamics, and ab-initio defect chemistry. Based on ab-initio thermodynamics calculations of the LSM25(001) surface, a new model for the termination of the (001) surface has been developed, which exposes both Mn and Sr cations. In contrast to previously proposed surface terminations, this partially SrO/MnO₂-terminated surface is not polar, which explains its high thermodynamic stability. So far, it is unknown whether this surface termination is active in the oxygen reduction reaction (ORR) or not.

To assess the ability of the partial SrO/MnO₂ termination to activate O₂ and whether it represents an active or a degraded state of the LSM25 surface, we examine the mechanism and energetics of the oxygen reduction reaction including subsurface oxygen vacancy migration using DFT calculations on the GGA+U level.

Because partial LaO/MnO₂ and SrO/MnO₂ terminations are not highly polar, we find that they are able to stabilize both negatively (adsorbed oxygen) and positively (oxygen vacancies) charged defects, both of which are required to complete a full ORR cycle. This property sets them apart from the perfect LaO, SrO, and MnO₂ terminations, which are either positively or negatively charged and thus only stabilize one kind of intermediate: adsorbed oxygen in the case of the LaO/SrO terminations and oxygen vacancies in the case of the MnO₂ termination. Depletion of one kind of intermediate is a severe kinetic bottleneck, because both oxygen vacancies and adsorbed oxygen must be present on the surface to enable efficient steady-state ORR.

We find that the partial SrO/MnO₂ surface can stabilize a variety of oxygen vacancies. The presence of Sr edge atoms plays a crucial role in stabilizing and dissociating O₂ molecules by providing undercoordinated sites where O₂ is able to bind. On this termination, the Sr cations assist in the dissociation of O₂, which suggests that this termination could be active in the oxygen reduction reaction. To assess the role of this surface termination in electrode degradation, we compare the ORR mechanism and energetics with the partial LaO/MnO₂ termination, which is less thermodynamically stable and is thus not expected to occur in the equilibrated system.

These results enable a deeper understanding on the ORR can take place at the (001) facet of LSM25, and how catalytic activity is affected by the accumulation of Sr at the surface.

9:30 AM *EI01.02

Oxygen Vacancy Dynamics and Oxygen Exchange: Fluxionality on Reducible Oxide Surfaces [Peter A. Crozier](#); Arizona State University, United States

Electroceramic oxides such as fluorites and perovskites are often employed in solid oxide devices due to their ability to support cation dopants, changes in cation oxidation state and varying oxygen vacancy concentrations. In these materials systems, oxygen exchange and transport involves creation/annihilation of oxygen vacancies. For example, in solid oxide fuel cells (SOFC), molecular oxygen exchange takes place on perovskite cathodes at temperatures in excess of 600°C and activation energies of around 1.5 eV. On the other hand, in catalytic oxidation of CO, oxygen exchange takes place at a much lower temperatures via a Mars van Krevelen process near the three-phase boundary with a metal nanoparticle and activation energies on 0.7 eV or lower. The detailed atomic configuration of the surfaces such as anion/cation point defects, surface facets and steps, and strain fields may all be associated with changes in surface exchange activity.

When oxygen transport/exchange occurs via oxygen vacancy creation/annihilation it gives rise to local distortions in the cation sublattice. The cations may shift by up to 20 pm and such displacements can now be observed and quantified with *in situ* aberration corrected transmission electron microscopy (TEM). We have used this approach to investigate the dynamic behavior of oxygen vacancies on or near the surfaces and metal/ceramic interfaces for CeO₂ [1]. This activity also results in structural fluxionality in the cation sublattice with the local degree of fluxionality related to the oxygen vacancy creation/annihilation rate and it may also drive cation diffusion. Even at room temperature, oxygen vacancies are created/annihilated at very different rates at different sites on the surface. A large and rapidly varying tensile/compressive strain which varies between adjacent surface cations is also present and likely to impact oxygen exchange activity between adjacent atomic sites.

The fluxionality occurring near Pt/CeO₂ interfaces during CO oxidation was correlated with catalytic activity [2]. We showed that the catalytic turnover frequency correlates with fluxional behavior that (a) destabilizes metal-ceramic interfaces, (b) marks an enhanced rate of oxygen vacancy creation and annihilation, and (c) leads to increased strain and reduction in the CeO₂ support surface. Overall, the results implicate dynamics at the interfacial Pt-O-Ce bonds anchoring the Pt to the support as being involved also in the catalytically-driven oxygen transfer process, and they suggest that oxygen reduction takes place on the highly reduced CeO₂ surface before migrating to the interfacial perimeter for reaction with CO.

Probing atomic-level structural evolution with temporal resolutions approaching 1ms results in TEM images that are plagued by high levels of shot noise requiring the development of machine learning approaches for information extraction from noisy data streams [3]. Moreover, in many systems subject to thermo-chemical or electrochemical stimuli, the complexity of the structural dynamics is not easy to describe. The structures of the metastable states and the triggers that lead to instabilities are not well understood and remain an important problem in the characterization of atomic level dynamics in functional materials.

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9:50 AM *EI01.03

Interaction of O₂, H₂O, CO₂ with AO Terminated Perovskite and Ruddlesden Popper Oxides. The Effect of the Surface A-Site—Sr, La, Pr. [Aleksandar Staykov](#); Kyushu Daigaku, Japan

First-principal calculations were performed to elucidate the origin of catalytic activity of the pristine AO-terminated surface of SrTiO₃, SrTi_{1-x}Fe_xO₃ and two Ruddlesden Popper phase oxides of industrial interest. Our study reveals that while O₂ dissociation is not favored on the SrO-terminated perovskite surface, oxygen vacancies can act as active sites and catalyze the O-O bond cleavage. Electron transfer from lattice oxygen atoms to the O₂ molecule, mediated by the subsurface transition metal cations, plays an important role in the resulting formation of surface superoxo species. Electron density plots and electron density distribution through the entire slab models were investigated in order to understand the origin of surface electrons that can participate in oxygen reduction reaction. Among various perovskite-structured oxides, certain members of the Ruddlesden-Popper series, e.g. La₂NiO₄, have been identified as significantly active for surface oxygen interactions. However, the challenge remains to be the identification of the structure and composition of active surfaces, as well as the influence of these factors on the mechanisms of surface exchange reactions. Recent experimental and theoretical studies on some members of these materials, e.g. La₂NiO₄, revealed that the La-O terminated surfaces are catalytically active under operational conditions. These findings suggested that the conventional understanding of such oxides being fully ionized, and composed of catalytically inert La³⁺ ions needs to be revised. The presence of the available d-orbital electron on La and associated partial covalency were postulated as being responsible for the catalytic behavior observed in experiments. The direct comparison of molecular oxygen interaction with La₂NiO₄ and Pr₂NiO₄ allowed us to evaluate the electronic effect on the oxygen reduction reaction energetics. We have further addressed the surface catalytic activity as a function of interstitial oxygen occupancy in the rock salt layer and provided a possible explanation for the limits of the interstitial oxygen concentration. The oxide ion transport in the rock salt layer was compared for La₂NiO_{4,125} and Pr₂NiO_{4,125}. The diffusion difference was attributed to the electronic structure of the valence shells of Pr and La. The different polarizability of those elements would lead to opposite effect on the transition states stability. In depth understanding of the La₂NiO₄ and Pr₂NiO₄ (including La₂NiO_{4,125} and Pr₂NiO_{4,125}) electronic properties allowed us to refer electronic and hole conductivities to the computed band gaps and the electronic structure of the valence bands. Our study shows that while La₂NiO₄ and Pr₂NiO₄ share similar crystallographic structure, the most important properties, such as surface catalytic activity, ionic diffusivity, and electron transport, are direct consequence of the valence shell structure of the A site cations: La and Pr.

10:10 AM EI01.04

The Effect of Humid Operating Environments on Surface Composition Evolution of Perovskite-Type MIEC Electrodes [Zijie Sha](#), Zonghao Shen, Eleonora Cali, John A. Kilner and Stephen J. Skinner; Imperial College London, United Kingdom

The ability of mixed ionic and electronic conducting (MIEC) perovskite oxides (ABO₃) to support both electronic and ionic conductivity, as well as their favourable catalytic properties and chemical and redox stability, make them promising electrode materials in electrochemical energy conversion devices, such as solid oxide fuel/electrolysis cells (SOFC/SOEC) and oxygen transport membranes (OTM). In these applications, the exchange of oxygen across the gas phase and an electrode often determines the overall device performance, and the surface exchange kinetics have been found strongly related to the surface composition of electrodes. Currently, the nature of these electrode surfaces, particularly under gas atmospheres closer to those experienced in operation, still remains unexplored. In this work, the effect of humid environments on the surface chemistry of MIEC perovskite oxides was investigated, as water vapour is a fundamental molecule in the input gas stream of the solid-state electrochemical systems, present as impurities beside molecular oxygen in ambient air and acting as an electrolysis source for hydrogen production.

Taking (La_{0.8}Sr_{0.2})_{0.95}Cr_{0.5}Fe_{0.5}O_{3-δ} (LSCrF8255) as a model MIEC perovskite oxide, the surface chemistry evolution was studied in water vapour (pO₂ < 1 mbar, pH₂O = 30 mbar) and wet oxygen (pO₂ = 200 mbar, pH₂O = 30 mbar) atmospheres comprehensively through X-ray photoelectron spectroscopy (XPS), angle-resolved XPS (ARXPS), low energy ion scattering (LEIS), scanning electron microscopy (SEM), and scanning transmission electron microscopy (STEM). The results were also compared to those measured under dry oxygen (pO₂ = 200 mbar) conditions. The Sr surface segregation phenomenon has been observed on the surface of all samples annealed in wet oxygen, water vapour, and dry oxygen. The segregation level increased with annealing temperature and was found particularly high at 900 °C. For the samples annealed at 900 °C in different atmospheres with the same 27-hour annealing time, the surface of the sample annealed in water vapour displayed the highest atomic fraction of Sr in surface species compared to Sr in the perovskite structure, however, the surface of the sample annealed in dry oxygen showed the highest total Sr content. Meanwhile, on the sample annealed in wet oxygen, Sr surface enrichment was likely suppressed. In addition, the Sr segregation phenomenon observed on LSCrF8255 can be correlated to other mass transport phenomena such as Cr evaporation and redeposition and Si deposition. Further, the Sr segregation behaviour on LSCrF8255 can also be related to annealing duration, crystal orientation, and defects such as grain boundaries and dislocations. Apart from the A-site cation segregation, phase separation was consistently observed on all samples annealed in the three conditions. The secondary phase was B-site cation enriched (relatively Cr enriched, significantly Fe enriched) and A-site cation (La and Sr) deficient. Our scientific findings are expected to provide an advancement in understanding and guidelines for material design, performance, and durability of MIEC perovskite oxides in energy conversion applications.

10:25 AM EI01.05

Atomic-Scale Surface Overcoat to Suppress Agglomeration and Dopant Segregation of Perovskite Cathodes Haoyu Li, Orbel Barkhordarian, Hung-Sen Kang and [Min Hwan Lee](#); University of California Merced, United States

Long-term durability of solid oxide fuel cell (SOFC) cathodes has been mainly hampered by morphological agglomeration and surface segregation of A-site dopant in the ABO₃ perovskite-based cathodes. First, while a high-surface-area morphology is preferred for maximized electrode kinetics, a high-surface-area structure tends to agglomerate during high temperature operation to minimize its surface energy, which leads to a decrease of catalytically active surface area. The cathode degradation is also caused by the accumulation of A-site dopants in the close vicinity of surface and their formation of the dopant-based inert phase on the surface.

In this talk, we present an atomically thin oxide overcoat on the perovskite is highly effective in addressing these two processes of cathode degradation (i.e., agglomeration and A-site dopant segregation) simultaneously, killing two birds with one stone. For the oxide overcoat, we applied atomic layer deposition (ALD) technique. Additionally, we present a mechanistic interpretation of the observed behavior.

A. Suppression of morphological agglomeration

Infiltration of catalytically active species enhances the electrode surface area significantly, but the tiny infiltrated nanoparticles (NPs) naturally carry a high surface energy, making them susceptible to severe agglomeration. We demonstrate how an angstrom-level ALD oxide overcoat affects the performance and durability of a ceria NP-infiltrated LaNi_{0.6}Fe_{0.4}O_{3-δ} (LNF) cathode. Since LNF does not have A-site Sr, it does not suffer from Sr segregation, a major degradation mechanism, simplifying the analysis of degradation in this study. We use angstrom-level oxide overcoat is highly effective not only in enhancing the thermal stability of underlying infiltrated ceria nanoparticles but also in facilitating electrode kinetics. By employing Sr-free electrodes and Cr-free gas environment, we focus on the thermal agglomeration as the major degradation pathway and reveal the close correlation between thermal agglomeration rate of infiltrated nanoparticles and degradation rate of electrode performance in a quantitative manner.

B. Suppression of Sr segregation

We applied a few angstroms of oxide overcoat (ZrO₂, Y₂O₃, CeO₂ and TiO₂) by atomic layer deposition (ALD) on a La_{0.8}Sr_{0.2}MnO₃ (LSM) electrode and observed the resulting change in Sr segregation behavior and oxygen reduction activity for ~250 h of heat exposure at 750 degree C. The number of ALD cycles for each overcoat oxides were chosen to make the nominal coating thickness to be all ~2 Å.

X-ray photoelectron spectroscopy (XPS) analysis revealed that ALD-treated samples, compared to the bare sample, show weaker Sr surface segregation. Particularly, those coated with CeO₂ and TiO₂ were found the most effective in suppressing Sr surface segregation or even desegregating Sr species. On the other hand, the sample with CeO₂ and TiO₂ overcoat exhibited the best performance for the first ~200 h at 750 degree C and concurrently show the lowest surface segregation. These data show the electrode activity is highly dependent upon the amount of segregation and proves the effectiveness of atomic-scale coverage of a proper oxide in controlling dopant segregation behavior. We present a conjectured framework based upon electrostatic-force and chemical potential-driven segregation to understand the observed data.

ACKNOWLEDGEMENTS

The authors acknowledge the support from and U.S. NSF (DMR 1753383) and NASA MIRO program (NNX15AQ01A).

10:40 AM BREAK

SESSION EI02: Oxygen Exchange Kinetics
Session Chairs: Franziska Hess and Alexander Opitz
Monday Morning, July 18, 2022
Mezzanine Level, Second Floor, Berkeley/Clarendon

11:00 AM **EI02.01

Mixed Conducting Oxide Thin Films—Model Systems for Kinetic Studies or a Nightmare? Juergen Fleig; Technische Universitat Wien, Austria

Mixed conducting oxides play an important or even vital role in some of the most important applications in solid state ionics: They are common as cathodes/anodes in SOFCs/SOECs and they are employed as intercalation electrodes in lithium-based batteries. In real life, applications of such devices mostly employ porous electrodes. However, a detailed understanding of electrochemical parameters in the corresponding materials and of kinetic processes at interfaces is strongly hampered by the complicated geometry and the surface inhomogeneity of such porous electrodes. Moreover, easy and direct access to the decisive interfaces by analytical tools is often impeded.

Not surprisingly, geometrically and structurally simple, mixed conducting thin films, prepared by pulsed laser deposition or sputtering, have become very popular for investigating kinetic processes in such materials and at their interfaces. Thin films are thus often used as model systems for gaining a better understanding of the “real” electrochemical devices, i.e. of SOFCs/SOECs and (somewhat less frequently) of batteries. What is often neglected in this context is the empirical fact that properties of thin films do not necessarily correspond to those measured on bulk materials or macroscopic porous electrodes. Accordingly, thin films can be phantastic tools for obtaining a detailed knowledge on materials properties and atomistic processes, but can also be a bit misleading when emphasizing effects with little relevance in bulk materials. And they can even develop into a kind of “nightmare” by displaying completely unexpected properties that may remain unexplained for many years.

In this talk, examples are presented for all three kinds of thin film studies in solid state ionics, from impressive to somewhat misleading to really worrying. Several examples are taken from the SOFC/SOEC field and refer to (La,Sr)(Co,Fe)O_{3-x} (LSCF). It is shown that the oxygen exchange rate constant on such thin films can vary by many orders of magnitude and that very much care is required to truly measure properties of pristine surfaces or to obtain relevant mechanistic information. On the other hand, defects in such films can often be tuned very precisely by an applied voltage, which strongly helps in identifying the role of individual defects during interfacial oxygen exchange. Moreover, determining the chemical capacitance as well as the ionic or electronic conductivity and interfacial reaction rates is often more straightforward than in porous electrodes, also because of the availability of physically accurate equivalent circuit models. This is not only true for SOFC-relevant high temperature materials, but also for thin film cathode materials used in lithium-based batteries, e.g. sputter-deposited LiMn₂O₄ and LiCoO₂ layers investigated by in- and across-plane measurements in different charge states. As an oxide thin film with very unusual properties, SrTiO₃ is discussed. Here, ultralow conductivities are almost ubiquitously found in PLD deposited films, irrespective of dopant (Fe, Ni, Al) and doping level (0.0 to 10 %). It is shown that a model based on cation non-stoichiometry and a complex electronic buffer system can turn this seemingly incomprehensible nightmare into a highly interesting example illustrating the power of defect chemical considerations in solid state ionics.

11:30 AM EI02.02

2D Optical Transmission Relaxation Measurements of Inhomogeneous Oxygen Surface Exchange Kinetics in SrTi_{0.65}Fe_{0.35}O_{3-d} Emily J. Skiba and Nicola H. Perry; University of Illinois at Urbana-Champaign, United States

Triple phase boundaries (TPBs) between a metal, mixed ionic and electronic conducting (MIEC) oxide, and gas phase may exert significant control over the efficiency of solid-state ionic devices. Due to the relatively poor electrode performance of these metals in isolation, when compared to mixed conductors such as SrTi_{0.65}Fe_{0.35}O_{3-d} (STF35), it is commonly assumed that metal current collectors have an insubstantial effect on MIEC performance. However, recent work instead suggests that these metals may exhibit a pronounced synergistic effect, improving the oxygen surface exchange kinetics of STF35 thin films by orders of magnitude. [1,2] Such studies have evaluated macroscopic behavior of MIECs coated with metals, whereas spatially resolved kinetic measurements, coupled with local chemical analysis, would help to investigate the possibility of synergistic metal-MIEC activity.

This presentation will describe continuous 2D optical transmission relaxation measurements of the locally inhomogeneous oxygen transport kinetics of STF35 thin films grown by pulsed laser deposition with partial covering by metals. The entire uncovered (native) area of two STF35 films (with porous painted Au or reactively sputtered Pt applied to half of the 0.9 x 0.4 cm² film area) was simultaneously monitored in response to step changes in oxygen partial pressure over the temperature range ~500-600 °C. Combined with COMSOL Multiphysics simulations and X-ray photoelectron spectroscopy measurements, the spatially resolved oxygen exchange kinetics reveal not only a profound catalytic influence of the metal current collector, but also notable surface diffusion of the metal onto the adjacent film region at distances up to ~1 mm. As a result of the rapid oxygen exchange at the metal/MIEC interface and sluggish surface exchange kinetics of the native MIEC surface, the role of bulk diffusion is explored, despite the film thickness being significantly below the critical length. Simulations demonstrate that the spatially inhomogeneous 2D optical transmission data can best be described through a model with rapid oxygen surface incorporation/evolution at the metal/MIEC/gas interface followed by in-plane lateral oxygen diffusion to/from more distant regions with slow oxygen surface incorporation/evolution kinetics. It is hypothesized that the metal current collectors improve the rate of surface oxygen exchange by modifying the reaction pathway away from the film surface/gas interface (double phase boundary) toward the film-metal-gas TPBs, which locally overcome Sr-segregation related surface deactivation. These results highlight the need for a more critical approach when applying current collectors for the measurement of oxygen surface exchange kinetics, with greater consideration of the potential role of metal/MIEC/gas TPBs on the macroscopic kinetics.

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11:45 AM EI02.03

Investigating Oxygen Reduction Pathways on Pristine SOFC Cathode Surfaces by *In Situ* PLD Impedance Spectroscopy [Christoph Riedl](#), Matthäus Siebenhofer, Alexander Schmid, Andreas Limbeck, Alexander K. Opitz, Juergen Fleig and Markus Kubicek; Technische Universität Wien, Austria

Understanding and improving the oxygen exchange kinetics (OER) on promising SOFC cathode materials is a major goal of current research activities. However, the detailed mechanism of the OER, is surprisingly complex and the single reaction steps are still not completely understood. A comprehensive understanding of the underlying mechanics of these reactions (particularly of the rate limiting steps) is thus highly desirable in order to optimize devices for energy-related applications and to develop materials with extraordinary activity and stability.

In this contribution, the oxygen exchange reaction rates on truly pristine surfaces of the different SOFC cathode materials La_{0.6}Sr_{0.4}CoO_{3-δ} (LSC), La_{0.6}Sr_{0.4}FeO_{3-δ} (LSF) (La_{0.6}Sr_{0.4})_{0.98}Pt_{0.02}FeO_{3-δ} (Pt doped LSF), SrTi_{0.3}Fe_{0.7}O_{3-δ} (STF) and Pr_{0.1}Ce_{0.9}O_{2-δ} (PCO) were investigated via *in-situ* impedance spectroscopy during pulsed laser deposition (*i*-PLD) over a wide temperature and pO₂ range. Our *i*-PLD measurements guarantee pristine electrodes without any contaminations of the surface and thus high stability of the polarization resistance. Besides demonstrating the astonishing catalytic capabilities of these materials in their pristine state, it is possible to discuss the oxygen exchange reaction mechanism based on experiments on clean surfaces unaltered by environmental degradation factors.

All investigated materials exhibit polarization resistances with very similar T-dependences and very characteristic pO₂ dependences with changing power laws. In combination with non-equilibrium measurements under bias voltage and defect chemical modeling, these results clarify several aspects of the oxygen exchange reaction mechanism and refine the understanding of the role the different defects in the materials play in the OER. In a novel approach, electrode polarization was used to control defect concentrations and to extract concentration amended activation energies, which prove to be drastically different for oxygen incorporation and evolution (0.26 vs. 2.05 eV for LSF). We show that a large part of the effective activation energy of the OER, which is observed during equilibrium measurements, has its origin in thermally activated charge carrier concentrations.

12:00 PM **EI02.04

Impact of Operating Environment on the Key Electrochemical Processes in Solid Oxide Cells [Stephen J. Skinner](#), Zijie Sha, Mudasir Yattoo, Zheng Xie and Chen-Yu Tsai; Imperial College London, United Kingdom

Understanding the phenomena that occur at the interfaces in solid oxide cells is critical to the effective development of both electrodes and electrolytes for next generation technologies. Of increasing importance, with the advent of the hydrogen economy, is the performance of ceramic ion conductors under steam electrolysis conditions. At the air electrode, in both electrolysis cell and fuel cell mode, typical fundamental measurements are conducted under ideal conditions, with oxygen diffusion measurements occurring under a dry equilibrated high purity oxygen environment which does not reflect the operating conditions of the devices, and hence the surface chemistry extracted does not accurately reflect the processes occurring, particularly at the gas:solid interface. Furthermore, the electrodes developed for fuel cell operation are not necessarily most appropriate for electrolysis mode. In this presentation our efforts to develop alternative electrode systems will be discussed, along with our approach to measuring exchange kinetics of these oxides under humid atmospheres.

The use of a combination of techniques to provide detailed analysis of exchange and segregation processes in a model perovskite will be presented, including X-ray photoelectron spectroscopy, Secondary Ion Mass Spectrometry and Transmission Electron Microscopy. This will be complemented with our efforts to develop new composite Sr free electrodes with low polarisation resistance, including our development of effective interlayers that significantly reduce polarisation resistance. Using impedance spectroscopy we identify the key processes governing the exchange processes in these electrodes, and through consideration of the two systems provide direction for future electrode development.

12:30 PM EI02.05

Investigation of the Oxygen Exchange Kinetics on Erbium-Stabilized Bi₂O₃ at Intermediate Temperature [Seung Jin Jeong](#)¹, Ruiyun Huang², Richard Kim³, Sossina Haile⁴ and WooChul Jung¹; ¹Korea Advanced Institute of Science and Engineering (KAIST), Korea (the Republic of); ²Applied Materials Inc, United States; ³Georgia Institute of Technology, United States; ⁴Northwestern University, United States

Recent issues in solid oxide fuel cells (SOFCs) are brought up under operation at high temperature, such as higher system costs, and operating complexities (e.g., thermal cycling). Thus, it is heavily aimed to lower the operation temperature of SOFC and following two major polarization loss should be surely achieved in order to reach the goal: (1) ohmic loss across the electrolyte, (2) activity loss in electrodes reaction kinetics. In this perspective, stabilized Bi₂O₃ can be a powerful candidate as a composite cathode due to its exceptionally high oxygen ion conductivity and comparatively high surface exchange rate. Indeed, it has been reported to show very high cell performance at reduced temperature when it utilized with La_{0.8}Sr_{0.2}MnO_{3-d} (LSM), and also, its surface exchange kinetic parameter reaches almost the state-of-the-art perovskite cathode materials. However, since the morphological complexity in realistic porous system, it has been rarely reported about its intrinsic electrocatalytic role in a mechanistic point of view.

In this study, we embarked on a more quantitative approach to enable identification of reaction pathway and facilitate measurement of the site-specific electro-catalytic activity. The dense oxide thin film and metal microelectrodes are fabricated by PLD and photolithography process, hence the surface and interface of metal/oxide system is precisely controlled. Briefly, we observed that exceptionally high site-specific electro-catalytic activity of stabilized Bi₂O₃ compare to Y-stabilized ZrO₂ (YSZ) case. Furthermore, its active feature was resulted independent on a choice of metals (Au, Pt), which suggests the significant role of bismuth oxide phase for oxygen electro-catalysis.

SESSION EI03: Grain Boundaries and Heterostructures
Session Chairs: Peter Crozier and Aleksandar Staykov
Monday Afternoon, July 18, 2022
Mezzanine Level, Second Floor, Berkeley/Clarendon

2:00 PM **EI03.01

Grain Boundaries in MIECs—A Help or a Hindrance? [John A. Kilner](#)^{1,2}; ¹Imperial College London, United Kingdom; ²Kyushu Daigaku Carbon Neutral Energy Kokusai Kenkyujo, Japan

Mixed Ionic Electronic Conductors (MEICs) have been investigated for over 30 years since the early work of Teraoka and co-workers [1]. Applications have included dense polycrystalline gas separation membranes and porous polycrystalline air electrodes in solid oxide cells. The lattice transport of oxygen has been analysed by many authors and is fairly well understood (e.g. [2]) however a fuller understanding grain boundary transport in these polycrystalline materials is necessary to gain a more complete picture. In the applications mentioned above it is necessary to consider the oxygen ion transport in grain boundaries both perpendicular, where ion blocking effects can occur, and parallel to the direction of the net oxygen flow. For the case of parallel transport, this can become faster than bulk transport when temperatures are lowered. Indeed, interest in using fast grain boundary transport as a method of improving the performance of MEICs at lower temperatures has grown since the publication of papers [3-5] showing that fast grain boundary can provide significant enhancement of oxygen diffusion and surface exchange coefficients, however most of the materials so far investigated are rather poor mixed conductors (e.g. $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_{3-d}$ LSM20) compared to materials such as some of the highly substituted cobalt based perovskite materials such as $\text{Sm}_{1-x}\text{Sr}_x\text{CoO}_3$ -d (SSC) [6].

A common material for both research and application is the doubly substituted perovskite $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-d}$ (LSCF6428). This material is a good mixed conductor at high temperatures but at low temperatures the oxygen transport is very much reduced because of a rather high activation energy for oxygen transport (~1.8 eV) and grain boundary diffusion was noted to be significant for LSCF ceramics at temperatures below ~500°C [7].

In this contribution the level of grain boundary oxygen diffusivity in various materials obtained by tracer diffusion experiments will be compared to that found for ceramic and thin film LSCF6248. It was clear from this comparison that boundary diffusion in LSCF6248 can be up to 6 orders of magnitude higher than that found for LSM20 at temperatures below 500°C. Analysis of the samples by multiple techniques will be discussed to elucidate the origin of this enhanced oxygen transport.

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2:30 PM *EI03.02

Dynamics of Oxygen Ions in SrCoO_{3-δ} Heterostructures Dillon Fong¹, Guoxiang Hu², Vitalii Starchenko³, Gang Wan¹, Eric Dufresne⁴, Yongqi Dong¹, Huaqun Liu⁵, Hua Zhou⁴, Hyoungjeen Jeon³, Kayahan Saritas³, Jaron Krogel³, Fernando Reboredo³, Ho Nyung Lee³, Alec Sandy⁴, Irene C. Almazan¹ and Panchapakesan Ganesh³; ¹Argonne National Laboratory, United States; ²Rutgers University New Brunswick, United States; ³Oak Ridge National Laboratory, United States; ⁴Argonne National Laboratory Advanced Photon Source, United States; ⁵Agency for Science Technology and Research, Singapore

Strontium cobaltite or SrCoO_{3-δ} is an end member of La_{1-x}Sr_xCoO_{3-δ}, a fuel cell material and oxide catalyst [1]. In reducing conditions, oxygen exits from the surface, δ approaches 0.5, and SrCoO_{3-δ} forms the brownmillerite phase, creating a superlattice peak from oxygen vacancy ordering. As oxygen is re-incorporated into SrCoO_{3-δ} via a surface redox reaction, the superlattice peak disappears as the perovskite phase is re-formed. The speed at which δ is varied depends on the sample temperature and the surrounding oxygen partial pressure (pO₂). While the redox behavior of such oxides has been the subject of recent interest [2-6], much concerning the kinetics and dynamics of these materials remain unknown.

Utilizing *in situ* coherent X-ray scattering at the Advanced Photon Source, we monitored speckle from epitaxial SrCoO_{3-δ} thin films grown on both SrTiO₃(001) and (LaAlO₃)_{0.3}(Sr₂TaAlO₆)_{0.7}(001) as oxygen was incorporated and evolved (switching the environment from O₂ to N₂) to gain insight into the dynamics of oxygen-induced phase evolution in complex oxide materials. We found that the kinetics of the brownmillerite to the perovskite phase transition could be varied from tens of minutes to several hours over a small temperature range (300°C to 350°C), observing pronounced differences between the oxidation and reduction behaviors, the latter involving substantial incubation times to re-nucleate the brownmillerite phase. From X-ray photon correlation spectroscopy performed at the brownmillerite superlattice reflection, we find that the two-time correlation function differs greatly between the two different substrates. We will discuss the kinetics and dynamics of the oxygen ion / vacancy-ordering phase transition and the methods used to distinguish the different atomic and electronic mechanisms taking place.

2:50 PM EI03.03

Reactions of Oxygen and Hydrogen at the Aluminum Oxide/Aluminum Interface Using *Ab Initio* Grand Canonical Monte Carlo Vrinda Somji and Bilge Yildiz; Massachusetts Institute of Technology, United States

The Al₂O₃/Al interface is important in a wide range of technological applications, such as corrosion barriers and micro-/nano-electronic devices. Hydrogen is a common impurity that can have profound effects on this system, such as causing blistering in Al₂O₃-based passivation coatings, increasing the leakage current in Al/Al₂O₃/Al electronic devices, and causing decoherence in Al₂O₃/Al-based superconducting qubits. Thus, identifying the Al₂O₃/Al interfacial structure is important to improve the performance of these different applications. However, the structure of the interface (clean and with hydrogen defects) has not been resolved at the atomic scale. Moreover, the stages of oxide growth into the metal are also unknown. Experimental studies claim that the interface is sharp, coherent and indicate the presence of undercoordinated aluminum atoms, but provide no information on the atomic arrangement at the interface. Computational studies have primarily only looked into the stability of different terminations of the oxide on the metal, computed the work of adhesion, electronic structure, etc. Given that the interface presents an environment vastly different from either the bulk oxide or metal, it is likely that it has different structural features and properties.

In this study, we utilize *ab initio* Grand Canonical Monte Carlo, a physically motivated, bias-free method, to accurately search the interface configuration space and identify the structure and evolution of the interface in the presence of oxygen and hydrogen. We show that 12.5% aluminum vacancies are present at the interface at the oxide/metal equilibrium. As the oxygen chemical potential is gradually increased, the interface propagation occurs in a layer-

by-layer fashion, with an Al-rich interfacial plane. We also identify the local events that lead to interfacial propagation and Al_2O_3 formation at the interface, and discuss the trends in electronic structures of these interfacial configurations, including Schottky barrier heights and interface core level shifts. Finally, we observe that hydrogen prefers to segregate to the interface, forming multicenter bonds. The results of this study provide deeper insight into experimental observations made for the $\text{Al}_2\text{O}_3/\text{Al}$ interface, and have important implications for interfacial defect transport, charge trapping and adhesion of $\text{Al}_2\text{O}_3/\text{Al}$ -based corrosion barriers and electronic devices.

3:05 PM EI03.04

Self-Assembly $\text{SrCo}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}/\text{Fe}_3\text{O}_4$ Heterostructure Proton Membrane for Advanced Semiconductor Ionic Fuel Cell [Nabeela Akbar](#); China University of Geosciences, China

Proton conducting perovskite oxides are emerging demand for advanced electrochemical energy systems. Herein we develop semiconductor $\text{SrCo}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ (SCF) with significant proton conductivity by constructing a heterostructure using a guest component Fe_3O_4 from the bulk on the surface. This process may be called a self-assembled SCF and Fe_3O_4 exsolution heterostructure (SCF- Fe_3O_4) used as a new functional proton electrolyte for semiconductor ionic fuel cell (SIFC). The optimum composition of SCF- Fe_3O_4 SIFC has reached a power density of 583 mW cm^{-2} and OCV of 1.01 V at 550°C . exhibiting the extraordinary ionic conductivity of 0.2 S cm^{-1} . An energy band alignment mechanism based on a p-n heterojunction may explain the suppression of electronic conductivity and promotion of ionic conductivity in the heterostructure due to the built-in electric field effect. Our findings reveal that semiconductor SCF can be developed as promising protonic electrolytes by self-assembly SCF- Fe_3O_4 heterostructure approach.

3:20 PM EI03.05

Nano-Scale Imaging and Spectroscopy of Interfaces in (Co,Cu,Mg,Ni,Zn)O High Entropy Oxides [Hasti Vahidi](#)¹, Alexander Davis Dupuy¹, Justin Cortez¹, Julie M Schoenung¹ and William Bowman^{1,2}; ¹University of California Irvine, United States; ²University of California Irvine Materials Research Institute, United States

In recent years, the entropy-driven formation of single-phase structures with equimolar amounts of five or more cations has extended from metals to ceramics and particularly, oxides research communities. Since high entropy oxides (HEOs) greatly expand the available compositional space and possess promising functional and mechanical properties, they are strong candidates for solid electrolytes in batteries, fuel cells/electrolyzers, solid-state electrochemical devices, etc. [1-4]. However, research on CCMs is still in its early stages, with fundamental and exploratory studies required to understand their uniqueness and similarity compared to conventional oxide ceramics. Previously, it was shown that the rocksalt structured (Co,Cu,Mg,Ni,Zn)O high entropy oxide (HEO) compound, undergoes a phase transformation when heat treated, forming a multi-phase material consisting of the rocksalt phase alongside copper-rich tenorite and cobalt-rich spinel secondary phases [5]. The interfaces created in the multi-phase HEO take many forms, including grain boundaries and inter-phase boundaries within grains. It is known that microstructural defects, such as grain boundaries in polycrystals and heterointerfaces between phases in multi-phase ceramics, play a significant role in their properties [6]. Therefore, not only the presence of the transformed phases but also the various types of interfaces present in the multi-phase state, are expected to influence properties, such as ionic conductivity and mechanical behavior [7]. However, little is known about the interfaces and atomic-level phase transformation mechanisms in these complex concentrated materials. Additionally, there are challenges in characterizing such interfaces at the nano and atomic scales. Therefore, learning about interfaces in CCM ceramics can expand our knowledge about their intrinsic properties and their differences with interfaces in conventional ceramics and shed light on the mechanisms of the phase transformation, leading to improved CCM synthesis and microstructural design.

This study presents observations of the local atomic structure, composition, and electronic structure of grain boundaries and heterointerfaces in single- and multi-phase (Co,Cu,Mg,Ni,Zn)O CCMs. A 300-kV double spherical aberration-corrected scanning transmission electron microscope (AC-STEM) equipped with dual large-angle energy-dispersive X-ray spectroscopy (EDXS) detectors, Gatan GIF Quantum, and K_2 direct electron detector (JEOL Grand ARM) were used to record spatially resolved electron energy-loss spectroscopy (EELS) and EDXS data. Core-loss EELS edges and near-edge fine structures were used to analyze the local concentration of cations, oxygen vacancies, and oxidation states of cations (i.e., Co^{3+} , Cu^{3+}). This information elucidates the nature of interfaces in these complex systems, which can be correlated to potentially promising macroscopic functional properties such as electrical conductivity in bulk and thin-film forms [8].

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3:35 PM BREAK

SESSION EI04: Interfaces and Space Charge
Session Chairs: Dillon Fong and Jeong Woo Han
Monday Afternoon, July 18, 2022
Mezzanine Level, Second Floor, Berkeley/Clarendon

4:00 PM EI04.01

Discrete Modeling of Ionic Space Charge Zones in Solids [Chuanlian Xiao](#), Chia-Chin Chen and Joachim Maier; Max-Planck-Institut für Festkörperforschung, Germany

When considering interfaces in charge carrier containing systems, space charge effects play a significant role due to redistribution of individual charge carriers, which can explain various interfacial transport and storage phenomena. A continuum picture based on classic Gouy-Chapman (or Mott-Schottky) models is usually applied to describe space charge zones. However, this continuum approach becomes questionable or even inapplicable if interfacial effects are very pronounced; this is due to high virtual fields as well as to the appearance of non-idealities that are neglected in the Poisson-Boltzmann equation (elastic effects, saturation effects, changes in dielectric constant). Rather than formally correcting the already overstretched continuum solutions, we prefer a discrete modeling. It does not only allow for a much more realistic treatment, it also gives surprising insight in the concept of double layer

capacitance. Such 1D discretization or a combination of 1D discrete modeling with continuum approach also enables a straightforward incorporation of deviations from the dilute carrier assumption used in the conventional approach. Various relevant examples for functional ceramics and batteries are discussed.

4:15 PM **EI04.02

The Consequences of Space-Charge Zones for Short-Circuit Diffusion along Extended Defects [Roger A. De Souza](#); Rheinisch-Westfälische Technische Hochschule Aachen, Germany

In contrast with the bulk phase, an extended defect (dislocation, grain boundary, surface, domain wall) in an ionic solid is not constrained in equilibrium to remain locally electroneutral. Because of re-distribution of point defects between the extended defect and the bulk phase, the extended defect will in general become electrostatically charged, with the adjacent bulk phase concomitantly developing diffuse, enveloping space-charge zones [1]. The altered concentrations of point defects in these space-charge zones have long been understood to affect, for instance, the transport of charge across grain boundaries in polycrystalline systems [1,2]. In this presentation, I will draw attention to one particular aspect that has received far less attention: that space-charge zones can provide the dominant contribution to short-circuit diffusion along grain boundaries [3] and dislocations [4]. I will also show that space-charge zones can affect the excess Gibbs free energy of a grain boundary [1,5]. Throughout the presentation, I will emphasise the need to consider space-charge zones from a thermodynamic perspective; and that concentrated solid solutions cannot be treated with the standard Poisson–Boltzmann approach [2,6].

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4:45 PM EI04.03

Interfacial Zirconate Formation Influenced by the Porosity of Sm-Doped Ceria Barrier Layers [Yoosuf Picard](#)^{1,2}, [Bo Guan](#)^{3,2} and [Harry Abernathy](#)³; ¹National Energy Technology Laboratory, United States; ²NETL Support Contractor, United States; ³National Energy Technology Laboratory Morgantown, United States

In this study, Sm-doped ceria (SDC) barrier layers are synthesized by two different techniques, resulting in variations in the SDC layer porosity. These SDC layers are deposited onto yttria-stabilized zirconia (YSZ) substrates and sintered at different temperatures (1350°C and 1400°C). Additionally, $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3$ (LSCF) cathode layers are deposited and sintered on top of the SDC/YSZ samples at different sintering temperatures (1050°C and 1100°C). Electrochemical testing suggests higher Ohmic and polarization resistances with higher sintering temperatures. Composition profiles obtained by energy dispersive spectroscopy (EDS) inside a scanning electron microscope (SEM) show significant Sr migration from LSCF through porous SDC layers to the YSZ electrolyte, forming SrZrO_3 at the SDC/YSZ interface. Meanwhile, dense SDC layers prevent Sr migration but facilitate Zr transport from the YSZ electrolyte to the LSCF, resulting in SrZrO_3 formation at the LSCF/SDC interface. Coordinated SEM-based backscattered electron imaging and scanning transmission electron microscopy (STEM)-based EDS mapping further confirm SrZrO_3 formation as a function of the SDC layer porosity. Both Sr and Zr transport is greater with higher sintering temperature and appears negligible during electrochemical testing.

5:00 PM EI04.04

Opto-Ionic Materials—The Role of Above Band-Gap Radiation on Ionic Transport Across Grain-Boundaries and Surfaces in Gd-Substituted Ceria Using Surface Exchange and Tracer Diffusion Studies [George Harrington](#) and [Roger A. De Souza](#); Rheinisch-Westfälische Technische Hochschule Aachen, Germany

Until very recently, the use of light radiation has not been considered to impact the concentration or mobilities of defects in crystalline materials. From conventional wisdom, the photon momentum is too low to directly create ionic defects or cause ionic migration, and therefore it is assumed that any changes in observable properties under light radiation should be absent. Several studies, published in recent years, have challenged this assumption. In the hybrid perovskite methylammonium lead iodide (MAPI), above-bandgap radiation enhanced the ionic conductivity by more than two orders of magnitude.[1] This was explained by photo-generated electron-hole pairs modifying the iodine valence state, leading to an increase in anti-Frenkel disorder.[2] UV radiation has also been reported to induce battery-type voltages in zirconia-based electrochemical cells with SrTiO_3 as the working electrode,[3] and explained by non-stoichiometry changes induced by above-bandgap radiation.[4] In the latest study on this topic, Defferriere and Klotz et al. demonstrated an enhancement in the specific grain-boundary conductivity of $\text{Gd}_{0.03}\text{Ce}_{0.97}\text{O}_{2-\delta}$ which was attributed to a decrease in blocking space-charge effect at the grain boundaries.[5] The evidence for light-modified behavior of ionic defect is becoming considerable, but a fundamental understanding of these effects is still lacking.

Typical methods of measuring ionic transport in oxides, such as electrical measurements, present a challenge when including photo-effects. The conductivity may be dominated by photo-induced electronic carriers, the electrodes may have to be transparent, and Schottky contacts between the electrodes and oxide may be modified by electron-hole pairs. Further, when working on bulk ceramics or single-crystals, intensity gradients of illumination will be present due to the absorption of the material, making interpretation of results more challenging. In this work, we have employed a combination of isotopic tracer surface exchange and diffusion experiments on thin film samples to avoid these complications.

We have carried out in-plane ^{18}O tracer diffusion on thin films of $\text{Gd}_{0.05}\text{Ce}_{0.95}\text{O}_{2-\delta}$ using a modified 2-step procedure under a 375nm UV source, corresponding to above bandgap radiation for Gd-substituted ceria. By fabricated films by pulsed laser deposition (PLD) on MgO with a double buffer layer of BaZrO_3 and SrTiO_3 , Al_2O_3 single crystals, and quartz substrates we can modify the film growth from fully epitaxial, a subset of well-defined grain boundaries, and polycrystalline with a random distribution of grain boundaries. The effect of UV light on the diffusion of oxygen across grain boundaries of different character can be unambiguously assessed. Further, we present ^{18}O profiles from the surface of epitaxial CGO films grown on SrTiO_3 , allowing for a spatially resolved “image” of the space-charge zone under above-bandgap radiation. From these analyses the UV modified diffusion coefficient, D^* , surface exchange coefficient, k^* , and space charge potential, ϕ_0 , can be extracted. Finally, we will discuss the prospects for light-enhanced ionic transport at interfaces for other ionic and mixed-conducting materials.

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5:15 PM EI04.05

An Electrochemical Model of the LSM/YSZ Interface Jose Bohorquez^{1,2} and David S. Mebane^{1,2}; ¹West Virginia University, United States; ²National Energy Technology Laboratory Morgantown, United States

Solid oxide fuel cells (SOFCs) constitute one of the pillars in the future strategy to build a sustainable low carbon energy technology. The SOFC specific power has reached acceptable values, but degradation remains an open issue. The enhancement of the cathodic performance requires a detailed knowledge of chemical and electrochemical phenomena. To study the electrochemical phenomena that takes place at the LSM/YSZ interface a data driven computer model has been developed. The model is derived from Poisson-Cahn theory which allows for the incorporation of defect interactions and the gradient effects to model interfaces in solid solutions of high concentrations. The Poisson-Cahn methodology allows the model to conform to physically reasonable parameter spaces and to incorporate potentially complex concentration-dependences. Paired with a Bayesian data-driven model building method, the parameters of the model are calibrated to experimental data.

5:30 PM EI04.06

Electrochemical Control of Resistance States in Pr_xCe_{1-x}O₂/La_{2-x}Ce_xCuO₄ Bilayer Stack for Rational Design of Large Area Switching Devices Thomas Defferriere¹, Jennifer Rupp^{2,1} and Harry Tuller¹; ¹Massachusetts Institute of Technology, United States; ²Technische Universitat Munchen, Germany

Recent advances in electrochemical control of nanoionic devices have led to the development of a variety of new reprogrammable microelectronic devices. These include electronic/magnetic/optical/thermal switches for various memory and functional applications or three-terminal ion gated transistors that emulate neuron behavior potentially leading to more efficient neuromorphic computational hardware. The advantages in using ionic species to modulate and program the functional properties of active layers (electronic/magnetic/optical/thermal) originate from the lower power consumption required to induce changes in materials properties. The operational concept of such devices relies on the shuttling of ionic species from an ionic conducting oxide towards either an active interface or active oxide layer where a chemical reaction or exchange of ionic species occurs, changing the functional properties of that layer. While this concept of electrochemically gated microelectronic devices has been demonstrated in many materials systems, many open questions still remain about how to best optimize their device performance. While ionic mobility within and interfacial ion transfer between the two solid layers are key device parameters, little reliable information exists regarding these key parameters given their predominantly electronic character near room temperature. Such knowledge is vital for mastering overall device performance such as speed, retention, and predictability. To address these challenges, we have begun to investigate the reversible exchange of ions between two adjacent solid oxide layers, thereby overcoming complications associated with sluggish oxygen exchange kinetics with the gaseous environment often encountered in published studies^[1]. Specifically, we have investigated the reversible ionic transport and interfacial transfer kinetics in a thin film bilayer oxide system based on a Pr_xCe_{1-x}O₂/Ce_xLa_{2-x}CuO₄ stack that utilize model materials for which the defect chemical and transport properties have previously been carefully characterized, that offer high ionic mobilities and can accommodate large levels of non-stoichiometry^[2,3,4]. By studying the characteristics of our devices with a combination of electrochemical impedance spectroscopy and potentiostatic measurements, we demonstrate the ability to reversibly modulate the bilayer device resistance near room temperature and isolate the resistance contributions of both layers as a function of the total device resistive state. Furthermore, dynamic current-voltage studies enable us to separate the rate-limiting kinetics related to the defect mobilities and the interfacial exchange kinetics of the system. The findings in this work can be expected to aid in developing material selection and design criteria for similar bilayer systems, and be used to achieve faster resistance switching speeds, larger resistance switching ranges, and longer device retentions.

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SESSION EI05: Poster Session
Session Chairs: WooChul Jung and Jonathan Polfus
Monday Afternoon, July 18, 2022
6:00 PM - 8:00 PM
Mezzanine Level, Second Floor, Stadler

EI05.01

The Influence of the Oxygen Partial Pressure on the Exsolution in Ba_{0.5}La_{0.5}Co_{1-x}Fe_xO₃ Daria D. Balcerzak, Sebastian Wachowski, Iga Szpunar and Maria Gazda; Politechnika Gdanska, Poland

The cobaltite and ferrite perovskites are mixed ionic-electronic conductors (MIEC) and have already been studied for their structural, electrical, and magnetic properties. They exhibit high electronic conductivity, and the ability to incorporate water and conduct protons; hence, they find novel promising applications as cathodes in protonic ceramic fuel cells (PCFCs) [1,2]. The catalytic activity of electrodes can be increased as a result of the modification of the surface with nanoparticles. This can be done either via exsolution or infiltration or other methods. Exsolution, has great superiority over other deposition methods, because it anchors nanoparticles into the matrix, ensuring their durability and preventing agglomeration. The characteristics of nanoparticles vary, depending on external factors, such as the atmosphere or temperature of the process. This could allow controlling exsolved nanoparticles in the material by changing e.g. the oxygen partial pressure. Finally, the characteristics of the nanoparticles can be adjusted, depending on the material applications.

In this research, we present study of exsolution in Ba_{0.5}La_{0.5}Co_{1-x}Fe_xO_{3-δ} (x = 0, 0.5, 1). The compounds were synthesized using the solid-state reaction method. The influence of the oxygen partial pressure was examined by using oxygen, synthetic air, and nitrogen atmosphere, each in dry and wet conditions. The structure was investigated with the X-ray diffraction method (XRD), and phase composition was determined using Rietveld refinement. To observe the microstructure, and the characteristics of the nanoparticles, scanning electron microscopy (SEM) was used. The chemical composition of exsolved oxide nanoparticles was examined by the use of energy-dispersive spectroscopy (EDS).

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Structure and water uptake in BaLnCo₂O_{6-δ} (Ln = La, Pr, Nd, Sm, Gd, Tb and Dy). *Acta Mater.* **2020**, *199*, 297–310, doi:10.1016/j.actamat.2020.08.018.
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Acknowledgements

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EI05.02

Oxygen Exchange Kinetics of BaGd_{0.3}La_{0.7}Co₂O_{6-δ} Steam Electrodes for Proton Ceramic Electrochemical Cells Jonina B. Gudmundsdottir¹, Einar Vøllestad², Jonathan Polfus¹ and Vincent Thorét¹; ¹Universitetet i Oslo Det Matematisk-naturvitenskapelige Fakultet, Norway; ²SINTEF, Norway

Proton ceramic electrochemical cells show great promise as a for cost-efficient stationary energy storage, power generation, and fuel production technology, with good electrical efficiency. A mechanistic understanding of the reaction steps at the electrodes is, however, required to further develop high-performance electrodes and cell architectures.

Gas-phase isotope exchange methods such as Pulsed Isotope Exchange (PIE) is used to analyse the surface exchange rate and chemical diffusion coefficient of the electrode material. The *in situ* surface exchange of oxygen is measured as a function of oxygen partial pressure and temperature. Further studies will include the influence of steam on the oxygen exchange kinetics, as well as water exchange using D₂O isotopes.

A further look into the reaction mechanism and rate determining steps will be done with electrochemical impedance spectroscopy (EIS) and DC voltammetry. These methods will be used to extract pre-exponentials, activation energies, *p*O₂-dependency, and *p*H₂O-dependency of the different electrode responses.

Ba_{1-x}Gd_{0.8-y}La_{0.2+x+y}Co₂O_{6-δ} (BGLCs) are double perovskite type materials that have been shown to be an efficient steam- and oxygen-electrode for protonic ceramic electrochemical cells [1], as well as an oxygen evolution reaction catalyst at room temperature [2]. Furthermore, BGLC materials have been shown to be triple conducting (protons/oxide ions/electrons) oxides [3]. From the different BGLC compositions, BaGd_{0.3}La_{0.7}Co₂O_{6-δ} (BGLC37) has shown good proton incorporation. BGLC37 was therefore chosen as an electrode material for investigation of the kinetics and mechanistics using the aforementioned methods

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EI05.03

Surface Composition Control on (La_{0.6}Sr_{0.4})_{0.95}Co_{0.2}Fe_{0.8}O_{3-δ} to Eliminate Sr Segregation and Cr and S Poisoning Sophie C. Coppieters[†] Wallant, Filip Grajkowski, Bill Liu and Bilge Yildiz; Massachusetts Institute of Technology, United States

In order to improve the oxygen exchange kinetics and durability of state-of-the-art perovskite oxygen electrode (La_{0.6}Sr_{0.4})_{0.95}Co_{0.2}Fe_{0.8}O_{3-δ} (LSCF) in solid oxide electrolysis cells (SOECs), we address known degradation mechanisms through control of surface composition. The degradation pathway of interest is the segregation of aliovalent dopant cations (Sr) to the surface of the oxygen electrode which passivates the surface and interface of the oxygen electrode. Furthermore, segregated SrO at the electrode surface can react with key impurity poisons, Cr and S, to form inactive surface phases. Our approach involves the infiltration of more oxidizable cations at the surface compared to the bulk, which reduces the electrostatic driver of Sr segregation by decreasing the net positive charge (oxygen vacancies) at the surface. Suppression of Sr segregation through this approach not only addresses the passivating effects of SrO precipitate but also prevents the reaction of SrO with Cr and S and the resulting deposition of poisoning species (SrCrO₄ and SrSO₄). The potential gain in oxygen exchange rates is on the order of 10 to 100 fold. Our surface composition approach provides a simple method to improve the durability and exchange kinetics of perovskite oxygen electrodes through suppression of cation segregation and resulting poisoning reactions.

EI05.05

Revealing the True Capabilities of SOFC Cathode Materials and Fundamental Degradation Processes by *In Situ* PLD Impedance Spectroscopy Matthäus Siebenhofer^{1,2}, Christoph Riedl¹, Andreas Nennung¹, Juergen Fleig¹ and Markus Kubicek¹; ¹Technische Universität Wien, Austria; ²Center for Electrochemistry and Surface Technology CEST, Austria

The oxygen exchange reaction (OER) is the essential reaction for a variety of applications in energy- and environment-related technologies and its kinetics is commonly regarded as the bottleneck for the performance of low and intermediate temperature solid oxide cells. The development of new materials is therefore focused on the optimal combination of high intrinsic catalytic activity and high stability against a variety of degradation sources. Amongst these degradation sources, two phenomena have been discussed in particular, namely Sr segregation for perovskite cathode materials like La_{0.6}Sr_{0.4}Co_{0.2}O_{3-δ} (LSC) and SrTi_{0.3}Fe_{0.7}O_{3-δ} (STF) as well as poisoning effects due to different elements in the environment like S, Si or Cr.

In this contribution, we report the examination of truly pristine surfaces of various SOFC cathode materials *via* in-situ impedance spectroscopy during pulsed laser deposition (i-PLD). These measurements revealed an astounding performance of all materials, with area specific resistances being up to 2 orders of magnitude lower than observed in conventional ex-situ setups. Supported by ambient pressure XPS measurements, it was possible to identify trace amounts of sulphur (< 0.5 ppm) present in all measurement gases as the main reason behind the sudden performance decrease of SOFC cathode materials after fabrication.

Consequently, we contemplate that Sr segregation *per se* might not at all have a deteriorating effect on the oxygen exchange kinetics of Sr-based SOFC cathode materials. On the contrary, we find that in-situ surface decoration with SrO accelerates the surface exchange coefficient of various materials (including LSC). Only in combination with e.g. sulphur, Sr segregation becomes detrimental due to SrSO₄ formation. From a mechanistic point of view, it was possible to fully explain the observed effects with a model based on the acidity/basicity of the investigated surface which can either be advantageous or detrimental for the kinetics of the oxygen exchange reaction.

EI05.06

Unveiling the Interaction of CH₄ with Ni-Doped Sr(Ti,Fe)O₃ (STFN) Electrodes Decorated with Exsolved Fe-Ni Nanoparticles—An Operando AP-XPS Study on STFN Model Cells [Mauricio D. Arce](#)^{1,2}, Catalina Jimenez¹, Mariano Santaya², Lucia Toscani², Nadia S. Gamba², Ignacio J. Villar-García³, Virginia Pérez-Dieste³, Liliana V. Mogni² and Marcus Bär¹; ¹Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, Germany; ²Instituto de Nanociencia y Nanotecnología, Argentina; ³ALBA Synchrotron, Spain

Electrodes based on metallic nanoparticle (NP) exsolution are gaining increased attention due to its enhanced catalytic activity and remarkable stability in aggressive environments^[1]. These materials are appealing for Reversible Solid Oxide Cell (RSOC) technologies, which have low environmental impact, operate at high temperature and can use carbon sources to efficiently generate electricity or fuels in the Solid Oxide Fuel Cell (SOFC) and Electrolyzer Cell (SOEC) modes, respectively. Ni-based electrodes are typically employed for this purpose, as they are inexpensive good hydrocarbon cracking catalysts, but coking is a major issue since it deactivates the electrode leading to degraded cell performance^[2]. Recently, electrocatalysts based on Ni-Fe NP exsolution from Ni-doped Sr(Ti_{0.3}Fe_{0.7})O_{3-δ} perovskites (STFN) have been proposed as RSOCs electrodes due to its excellent stability, enhanced electrocatalytic activity and high C-tolerance^[3,4]. NP exsolution and reabsorption can be triggered by a combination of atmosphere and electrode polarization. Comprehensive understanding of the conditions where these processes take place, and to what extent regeneration is feasible is critical for optimized operation. The high tolerance towards C-containing gas feeds on this type of electrodes makes them suitable for RSOC, by oxidizing CH₄ to generate electricity in SOFC mode and co-electrolysis of CO₂ and H₂O for power-to-gas conversion in SOEC mode. Nonetheless, it is still unclear if NPs promote the redox reactions in regenerative operation, *i.e.* during cycling between SOFC/SOEC modes.

Carbon gas feeds can interact with electrodes in many ways, such as C adsorption, migration, dissolution, and C-metal compound formation. Although widely studied on Ni-based catalysts, the complex nature of CH₄ oxidation makes elucidation of reaction mechanisms and degradation processes very challenging. Temperature, atmosphere, and electrode polarization play a crucial role in the C-metal interaction, NP stability, degradation processes, and hence these parameters need to be adjusted for optimizing RSOC operation. Furthermore, this knowledge can help for designing smart regeneration strategies to recover the electrode, prolonging its lifetime. Surface-sensitive operando characterization by ambient pressure X-ray photoelectron spectroscopy (AP-XPS) is ideal for studying the metal-carbon interface in combination with electrochemical techniques, allowing us to get a close-to-real picture of STFN electrodes under operation in C-containing atmospheres.

In this study, we will present a complete characterization of the surface chemistry of exsolved Ni-Fe NP from STFN under dry/wet CH₄ atmospheres, focusing on the C-metallic NP interaction. Element depth distribution and surface segregation are studied by AP-XPS using different photon energies. Furthermore, we acknowledge the effect of temperature and polarization on model cells for CH₄ oxidation under operating conditions by combining electrochemical techniques such as chronoamperometry and electrochemical impedance spectroscopy with AP-XPS, to understand the correlation between surface and electrochemical performance. These studies allowed us to gain atomistic information about electrode reaction mechanisms and degradation processes, with particular attention to coking and its effect on the electrocatalytic activity of the STFN electrode, and NP stability under working conditions. We could establish that between 500 and 700 °C (relevant to RSOC application) C-deposition is prevented in highly aggressive dry CH₄, whereas coking occurs below this temperature and is enhanced at 400 °C. Despite this, C-deposition at 400 °C can be reversed upon oxidation above 500 °C in wet CH₄ conditions.

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EI05.07

Chemical Stability of Proton Conducting BaZr_{1-x}Ce_xO₃-Based Electrolytes in Pressurized CO₂ -Containing Atmospheres [Belma Talic](#)¹, Einar Vøllestad¹, Elena Stefan¹, Martin F. Sunding¹ and Jonathan Polfus^{1,2}; ¹SINTEF, Norway; ²Universitetet i Oslo, Norway

Acceptor doped barium cerates and zirconates are attractive electrolyte materials for use in various proton ceramic electrochemical devices such as fuel cells and hydrogen pumps. However, the long-term durability of these materials may be challenged by poor chemical stability in CO₂-containing atmospheres. In this work, the chemical stability of the electrolyte material BaZr_{0.8}Ce_{0.1}Y_{0.1}O₃ (BZCY81) is studied in CO₂ and CO₂-H₂. Dense pellets prepared by sintering with NiO as a sintering aid were exposed to up to 10 bar CO₂(-H₂) for up to 150 h at elevated temperatures (400-800°C). After exposure, the pellet surface was analyzed by grazing incidence X-ray diffraction (XRD), scanning electron microscopy (SEM), and X-ray photoelectron spectroscopy (XPS) to search for BaCO₃ formation. Overall, the electrolyte material displayed excellent stability towards CO₂. A small increase in apparent BaCO₃ concentration on the pellet surface was only detected by XPS for samples aged in CO₂ and CO₂-H₂ at 800 °C. However, BaCO₃ was not visible by XRD and SEM-EDS, indicating that the reactivity is limited to a nm-thick region of the electrolyte surface. The impact of processing conditions such as sintering temperature and use of NiO sintering aid on the electrolyte stability will be discussed.

EI05.08

Understanding the Chemical and Structural Changes in SrFeO₃ During Electrochemical Oxidation and Oxygen Evolution (OER) [Jan M. Bosse](#) and Andrew R. Akbashev; Paul Scherrer Institut, Switzerland

Perovskite oxides (ABO₃) have emerged as a promising class of materials for oxygen electrocatalysis (OER/ORR) due to their easily tunable electronic structure. However, the structure and chemical composition of transition-metal perovskites often change under electrochemical non-equilibrium conditions, exhibiting (1) oxygen (de)intercalation, (2) A-site cation leaching, and (3) B-site oxidation, the relationship between which is poorly understood.

In this talk, I will show how these fundamental processes are linked to the electrochemical response in the pre-OER and OER potential region of a representative perovskite SrFeO₃. Using epitaxial thin films of SrFeO_{3-x} as a model system, I will discuss how a significant **Sr leaching** from the near surface region, which occurs long before the OER onset potential, affects the **equilibration processes** at the solid-liquid interface. Strontium ferrite experiences a brownmillerite-to-perovskite transition during oxygen intercalation (SrFeO_{2.5} into SrFeO₃), which manifests itself in significant changes of the conductive properties during electrochemical experiments and further complicates the behavior of the perovskite near the OER region. Our results demonstrate the complexity of the electrochemical and structural behavior of Fe-based perovskites and the importance of in-depth analysis of oxide systems using model single-crystalline materials.

EI05.09

Flexible Synthesis of Mixed-Anion Compounds by Electrochemical Reactors [Takuya Katsumata](#)¹, Hajime Yamamoto¹, Ryotaro Aso², Yuta Kimura¹, Koji Amezawa¹ and Takashi Nakamura^{1,3}; ¹Tohoku Daigaku, Japan; ²Kyushu Daigaku, Japan; ³PRESTO,JST, Japan

Introduction

Mixed-anion compounds are promising functional materials for variety of applications such as energy storage, energy conversion, catalysts, electronic and

magnetic devices. However, difficulties of their syntheses hinder the development of mixed-anion compounds. To solve this problem, some effective synthesis techniques such as atmosphere-controlled sintering, high-pressure synthesis and low temperature topochemical treatment have been developed so far [1]. To expand controllable synthesis conditions beyond the above-mentioned techniques, we developed an electrochemical reactor composed of anion-conducting electrolytes. The electrochemical reactor used for the anion doping is composed of a target material, an anion conductive electrolyte and an anion source (reversible electrode). In principle, by using this reactor, the driving force of the anion doping can be controlled by voltage application according to the Nernst equation, and the total amount of doped anionic species can be determined by the amount of charge passed through the reactor. Because of these advantages, the electrochemical reactor developed in this study could pave the way to flexible synthesis of mixed-anion compounds. In this presentation, the fluorination of the perovskite oxide $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_{3-\delta}$ (LSC55) is reported as a demonstration of the synthesis of mixed-anion compounds by the electrochemical reactor.

Experimental

LSC55 was synthesized by Pechini method. The electrochemical reactor was composed of LSC55 and ball-milled BaF_2 composite, ball-milled BaF_2 (solid electrolyte) and PbF_2 - Pb composite (fluorine source). 20 mol% fluorine was electrochemically doped into LSC55 under the constant current 0.3 mA/g at 250°C. For comparison, an only heat-treated LSC55 (LSC55-heat) was prepared in the same environment in the reactor. After their respective electrochemical fluorination and heat treatment, LSC55- BaF_2 composites were collected from the reactor and washed by purified water to remove water soluble BaF_2 . The obtained LSC55s were characterized by X-ray diffractometry (XRD), X-ray photoelectron spectroscopy (XPS) and Transmission electron microscope (TEM).

Results and discussion

An F1s peak was clearly observed from the electrochemically fluorinated LSC55 (LSC55-F) by XPS, while negligible F1s signal was observed for the pristine and LSC55-heat, suggesting the success of electrochemical fluorination by the electrochemical reactor. By XRD, no peaks of impurity phases were observed in all samples, the pristine, LSC55-heat and LSC55-F. The splitting of the diffraction peaks in LSC55-F suggests F doping into LSC55 may induce the phase transition from Rhombohedral to Monoclinic. The microstructure near the particle surface was observed by TEM. It was revealed that polycrystalline nano-domains were formed at the outermost surface of the LSC55-F particles, while such nano-domain regions were not observed in the pristine and LSC55-heat particles. Moreover, stronger F signal was observed in the nano-domain surface region compared with the bulk part of the particle. These mean that the electrochemical fluorination modified both the surface and bulk regions, the F-rich nano-domain surface and the monoclinic perovskite structure in the bulk.

Summary

To advance synthesis techniques for mixed-anion compounds, we developed an electrochemical reactor composed of anion-conducting electrolytes and demonstrated an electrochemical fluorination of perovskite-type LSC55. According to characterizations, it was confirmed that the electrochemical fluorination of the perovskite type LSC55 has been successful using the reactor developed in this work.

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Acknowledgement

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EI05.11

Cation Aggregation on Extended Defects, Grain Boundaries and Phase Boundaries in LSM/YSZ Composite Cathodes [Yoosuf Picard](#)^{1,2}, Jonathan Poplawsky³ and Harry W. Abernathy⁴; ¹National Energy Technology Laboratory, United States; ²NETL Support Contract, United States; ³Oak Ridge National Laboratory Center for Nanophase Materials Sciences, United States; ⁴National Energy Technology Laboratory Morgantown, United States

While performance degradation for solid oxide fuel cells (SOFCs) comes in many forms, one important contributor is cation transport during long-term operation. This transport alters the chemical composition at electrode/electrolyte interfaces. These interfaces are carefully engineered to provide the critical reaction sites for oxidation and reduction reactions that regulate SOFC electrical production. Therefore, fundamental understanding of the chemical evolution of these interfaces is critical. This work coordinates scanning transmission electron microscopy (STEM) with atom probe tomography (APT) in order to probe atomic-scale composition across cathode/electrolyte interfaces for anode-supported commercial SOFCs. These SOFCs contain a porous composite cathode layer, consisting of sintered $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ cathode particles and yttria-stabilized zirconia (YSZ) electrolyte particles. SOFCs are operated up to 500 hours in duration at 0.75 A/cm² current density (or at open circuit) and 800°C. Measured cell voltage increases over the first 100 hours of operation, followed by a steady and linear drop in cell voltage that translates to 5.35% performance loss per 1000 hours. STEM-based energy dispersive spectroscopy (EDS) indicates nanoscale Mn-oxide formation near triple-phase boundaries (TPBs) during operation. Compositional profiles acquired by APT across LSM/YSZ particle interfaces indicate as-sintered interfaces are chemically well-defined, but La and Mn penetrate up to 5 nm into YSZ particles over the course of 500 hours. These results suggest that initial cell voltage increase within 100 hours corresponds to Mn-rich LSM surfaces transferring Mn to YSZ, enriching the YSZ particle surfaces with Mn^{2+} which can enhance oxygen incorporation into the electrolyte. Mn-oxide formation and growth over time will lead to triple-phase boundary length loss that contributes to the steady cell voltage drop observed after 100 hours of operation. Additional insights from APT suggests Zr aggregation on dislocations inside LSM and Mn aggregation on grain boundaries inside YSZ.

EI05.12

Unexpected Room-Temperature Conductivity on SrTiO₃ Single Crystal Surfaces Induced by Adsorbed Water Layers [Matthäus Siebenhofer](#)^{1,2}, Juergen Fleig¹ and Markus Kubicek¹; ¹Technische Universität Wien, Austria; ²Center for Electrochemistry and Surface Technology CEST, Austria

The conductivity of undoped SrTiO₃ (STO) has been studied extensively for many decades across the whole temperature range, from very high temperatures, where the conductivity is mainly electronic and charge carrier concentrations are largely controlled by Schottky equilibria down to lower temperatures, where ionic effects begin to dominate. Additionally, the effect of radiation on the conductivity of STO has been investigated with regard to classical electronic photoconductivity and photo-ionic effects, altering the conductivity by inducing stoichiometry changes.

In this contribution, a substantial conductivity increase of the in-plane conductivity of a (100) STO single crystal of up to 6 orders of magnitude was observed when decreasing the temperature below 100 °C. This conductivity anomaly was successfully correlated with the formation of a water adsorption layer on the single crystal surface which already entails substantial conductivity contributions (increase by 2 orders of magnitude) at a relative humidity as low as 10 %. The effect of UV light on the in-plane conductivity of STO single crystals at room temperature was investigated and the results show that, while in dry atmosphere, the conductivity increases significantly due to the well-known photoconductivity effect, the conductivity decreases slightly in humid atmospheres. What may be surprising at first can be explained by slight heating of the sample and therefore a depletion of the water adsorption layer. The implications of the results are twofold: STO single crystal surfaces could be well suited for the sensing of small amounts of humidity and

atmospheric humidity is an essential factor to consider in the investigation of the effects of illumination of STO single crystals at room temperature.

EI05.13

Non-Monotonic Electrochemical Conductivity Relaxation of Ce_{0.99}Gd_{0.01}O_{4-d} Yizhou Shen, Vincent Thor ton and Reidar Haugrud; Universitetet i Oslo, Norway

Electrochemical conductivity relaxation (ECR) is important for studies of surface exchange and chemical diffusion in oxides [1]. Principally, the electrical conductivity is measured as a function of time, relaxing to equilibrium upon a small perturbation in the reaction conditions, usually in the oxygen activity (for ideal cases the oxygen partial pressure, pO₂). The relaxation is driven by the chemical potential gradient and involves both surface and bulk processes, i.e. incorporation/excorporation and diffusion. It can be described mathematically by solving the differentials of Fick's second law with the appropriate boundary conditions. The response in the electrical conductivity may follow a different kinetic behavior depending on the processes involved retaining thermodynamic equilibrium [2]. For materials where a pair of interrelated point defects predominates, corresponding ambipolar transport yields a single-fold monotonic relaxation. However, if more than two charge carriers, that are not mutually in equilibrium contribute, a complex kinetic behavior is encountered; single-fold non-monotonic and two-fold non-monotonic relaxation. These two last modes are e.g. reported for mixed proton-oxide ion-electron conductors [3].

Cerium oxide, CeO₂, is an oxide with diverse and interesting properties in both a fundamental and technological perspective. This entails both pure surface catalytic and bulk properties, but also the combination of the two. The CeO₂-based materials are most often substituted with an aliovalent cation, among which acceptor substitution with a rare-earth cation, and particularly Gd, is widespread. The level of substitution is typically 10-20 atomic%. In the present study we aimed for a low doping level, but to avoid being destined by an unknown impurity level, 1% of Gd was added to CeO₂. The ECR measurements were performed in the temperature range 600-800 °C, under oxidizing conditions. The effects on the electrical conductivity of perturbations in pO₂ were relative minute, so to have reliable responses, a typical perturbation was between oxygen and air, or 0.01-0.05 atm. Depending on the reaction conditions single-fold monotonic, two-fold monotonic and two-fold non-monotonic relaxation were encountered. From a simple expectation that electron holes and oxygen vacancies are the predominating and interrelated defects in CeO₂, a single-fold monotonic relaxation should prevail. Under the present reaction conditions, the overall relaxation processes is presumably rate limited by the surface processes. This makes interpretation of the behavior more open. In the present contribution we, consequently, elucidate possibilities of the influence defect related surface processes leading to the diverse relaxation behavior observed for the electrical conductivity of 1%Gd doped CeO₂.

Acknowledgement

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EI05.14

Plasma Driven Exsolution for Nanoscale Functionalization of Perovskite Oxides Vasileios Kyriakou¹, Rakesh N. Sharma², Dragos Neagu², Floran Peeters², Stefan Welzel², Mauritius C.M. (Richard) van de Sanden² and Michalis N. Tsampas²; ¹Rijksuniversiteit Groningen, Netherlands; ²DIFFER, Netherlands

Perovskite oxides with dispersed nanoparticles on their surface are considered instrumental in energy conversion and catalytic processes. [1] Redox exsolution is an alternative method to the conventional deposition techniques for directly growing well-dispersed and anchored nanoarchitectures from the oxide support through thermochemical or electrochemical reduction. Herein, a new method for such nanoparticle nucleation through the exposure of the host perovskite to plasma is shown. To explore this new concept, we subjected a La_{0.43}Ca_{0.37}Ni_{0.06}Ti_{0.94}O_{3-d} (LCTN) perovskite (one of the few materials that has been successfully employed in both exsolution by gaseous hydrogen[2,3] and electrochemical plating [3]), capable of Ni exsolution, in the gas discharge of inert (N₂, Ar) gases, resulting in richer growth of metallic Ni NPs and at higher populations than under conventional gaseous hydrogen treatment. Interestingly, when N₂ plasma is used, apart from the electrons, the reduced N₂ charged species also participate in stripping oxygen from the perovskite, producing NO during the process. The formation of NO as the by-product adds value to this technology since it constitutes a key intermediate for the chemical industry, currently synthesized from complex and energy intensive processes. This can be considered as an alternative pathway to the reduction of metal oxides, in which nitrogen plasma is used for the reduction step and water (and/or carbon dioxide) for the oxidation with the simultaneous production of hydrogen (and/or carbon monoxide). We further demonstrate the applicability of this concept by exploiting the superior nanoarchitectures created after plasma treatment in a critical catalytic reaction for energy transition, such as the carbon dioxide hydrogenation. Our results not only prove that plasmas can enable nanostructuring of instrumental perovskite oxides but can also generate valuable chemical intermediates along the process as by-products, rendering the present approach even more attractive for future applications.

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EI05.15

Understanding Current Distribution at the Na Metal/NASICON Interface Through Surface Analysis Studies Sivakumaran Sukumaran¹, Stephen J. Skinner¹, Ainara Agudero^{1,2}, Richard Dawson³ and Joana Azevedo³; ¹Imperial College London, United Kingdom; ²Instituto de Ciencia de Materiales de Madrid, Spain; ³LiNa Energy Limited, United Kingdom

Abstract

Current perspectives on NASICON solid-electrolytes have focused on optimum conductivity through means of additive dopants¹ and optimising synthesis procedures². Yet, at present the fundamentals of interfacial inhomogeneities that affect the cyclability of these materials in full cells remain unknown. With consideration of the direct implications on conductivity that surface chemistry and diffusion mechanisms have, understanding of this is paramount. Thus, in this presentation the steps taken to highlight these mechanisms will be showcased and through which progress in further optimisation of the material can be established.

The primary means to evaluate the performance of the Na metal/NaSICON interface will have been achieved through assessing the chemical changes that take place at the surface and near-surface, through surface characterisation techniques that probe the area of interest at varying depths. This will be conducted on samples that have been electrochemically cycled and comparison will be made to samples in pristine condition. The compositions used to conduct this investigation are $\text{Na}_3\text{Zr}_2\text{Si}_2\text{PO}_{12}$ and $\text{Na}_{3.4}\text{Zr}_2\text{Si}_{2.4}\text{P}_{0.6}\text{O}_{12}$ – the latter of which has been shown to have the highest room temperature conductivity³. Through this, a 3D chemical map can be constructed to correlate surface chemical changes with electrochemical performance highlighting any changes that have taken place at the surface and near-surface of the NASICON materials. Thus, a preliminary means of understanding the fundamentals of diffusion mechanism will be established.

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EI05.16

Current Constriction at the $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ Interface Janis K. Eckhardt^{1,1}, Till Fuchs^{2,1}, Simon Burkhardt^{2,1}, Jürgen Janek^{2,1}, Peter J. Klar^{3,1} and Christian Heiliger^{1,1}; ¹Justus Liebig Universität Giessen, Germany; ²Justus Liebig Universität Giessen, Germany; ³Justus Liebig Universität Giessen, Justus Liebig Universität Giessen, Giessen, Hessen, DE, academic, Germany

The realization of the lithium metal anode may represent a new milestone in the development of novel battery technologies with higher energy densities and lifetimes. The theoretical capacity on the anode side can be increased approximately by a factor of 10 when replacing graphite with lithium. The side reactions occurring due to the high reactivity of lithium metals, however, are challenging. To suppress the growth of dendrites on the one hand and to reduce the flammability of the batteries on the other hand, a major research focus is on the consideration of solid electrolytes (SE) such as $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZO). The cycling behavior of the cell, however, is strongly influenced by the diffusion process on the metal anode side and the charge transfer driven morphological instability at the interface between both solids, i.e. lithium metal and LLZO. Thus, optimization of the kinetics at the interface is required for the development of solid-state batteries.

Impedance spectroscopy is particularly suitable to systematically investigate changes at the metal electrode|SE interface during operation. Individual impedance contributions such as the interface or transport signals, i.e. the grain boundary and bulk process, can be separated from each other if they differ in their frequency-dependent behavior. Krauskopf et al. recently demonstrated that the interfacial resistance is generally composed of a charge transfer (CT) and a constriction contribution.¹ The low exchange current densities frequently reported in the literature could be attributed to the pore formation at the interface since the CT resistance between lithium and LLZO is negligible. Despite the extensive study of the constriction effect in semiconductors or on solid|solid interfaces by Fleig and Maier^{2,3}, the phenomenon in ceramics with pronounced microstructure is not fully understood yet. Further research is required in order to understand the various dependencies of the phenomenon and how its behavior can be manipulated.

We developed an impedance network model to systematically investigate the impact of several factors such as the sample geometry, the microstructure of the SE or the interface design on the constriction effect and its derived transport quantities. Current constriction is not a migration process in the strict sense. It is related to the frequency dependent change of the electrode area actively contributing to the transport. The resistance is composed of constituents of all transport processes that occur around the interface. The activation energy is a mixture of the activation energies of the relevant transport processes. It is a geometric effect that has to be expected at different length scales. Stripping measurements were performed in order to compare the experimental behavior with the theoretical predictions. The results match quite well and the computations provide new insights into the dynamic change of the interface under anodic load.

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EI05.17

Single Side Interface Modification Layered Composite Electrolyte Pu-Yang Chen and Tzu-Ying Lin; National Tsing Hua University, Taiwan

All-solid-state electrolyte batteries have excellent safety and potentially higher volumetric energy densities through replacing the liquid electrolyte, which is regarded as the next-generation energy storage devices. Since the large-scale processing of electrolytes might encounter a brittle issue on the ceramic electrolyte sheet, the solid polymer electrolytes (SPEs) such as poly(ethylene oxide) (PEO) have great strength and bendable characteristics, which may widen the applications range and address the fragile concern. However, the low ion conductivity at room temperature and lower resistance against lithium dendrite growth are both the limitation of the PEO-based electrolyte. In this work, we use PEO and lithium bis (trifluoromethanesulfonyl) imide (LiTFSI) and mix garnet type Ta: $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZTO) ceramic particles to make a solid composite electrolyte. PEO matrix with LiTFSI can further improve the interface between the ceramic particles with PEO; in addition, LLZTO can improve the overall mechanical strength of the electrolyte and reduce the crystallinity of PEO. With different proportions of LLZTO powders, a layered structure with one side addition LLZTO particles in stacking is prepared. In the layered structure, the polymer layer has high flatness and adhesion at the electrolyte interface, and the composite layer doped with LLZTO can provide extra Lithium-ion channels and improve mechanical strength. In this way, the ionic conductivity of the composite electrolyte at room temperature can be improved and the ceramic particles also the inhibit lithium dendrite growth, which well combines the merits between solid and polymer electrolytes.

EI05.18

Effect of LiPF_6 concentration on lithium intercalation rate at LiCoO_2 / organic electrolyte interfaces characterized by neutron reflectometry Huangkai Zhou, Jun Izumi, Sho Asano, Kotaro Ito, Keisuke Shimizu, Kota Suzuki, Ryoji Kanno and Masaaki Hirayama; Tokyo Kogyo Daigaku Busshitsu Rikogakuin Oyo Kagaku, Japan

Gaining a thorough understanding of lithium intercalation at the cathode/electrolyte interfaces is critical for the development of next-generation Li-ion batteries with high energy density and high power density. Previous studies have mainly focused on the electrode-side interface such as electrochemical stability of the cathode surface and ionic conductivity of cathode electrolyte interphases (CEI) which could determine the lithium diffusion rate. On the other hand, there is few invaluable information about the interfacial structure at the liquid-electrolyte side. Neutron reflectometry (NR) is a powerful technique for gaining a nanoscopic understanding at solid/liquid interfaces as a function of the depth between the electrode and the electrolyte [1]. In this study, we analyzed the concentration gradient of ionic species from the Li_2ZrO_3 -modified LiCoO_2 cathode to the organic electrolyte using in situ NR. The 30 nm LiCoO_2 (104) films were epitaxially grown on Nb:SrTiO_3 (100) substrate and the 1~3 nm-thick Li_2ZrO_3 layer was modified on the LiCoO_2 (104) by pulsed laser deposition (PLD). The Li_2ZrO_3 -modified LiCoO_2 (104) film had very flat surface with the roughness of ~1.2 nm, which provided a model electrochemical interface with organic electrolytes. Charge-discharge tests were conducted using coin-type cells consisted of the film electrode, LiPF_6 containing EC:DEC (3:7 vol.) and Li metal anode. The rate capability of lithium intercalation improved with the increase in the electrolyte concentration from 1 to and 2 mol dm^{-3} , although the 2 mol dm^{-3} electrolyte has a lower ionic conductivity and a small transport number of Li^+ in the bulk region. The scattering length density (SLD) profiles at the $\text{LiCoO}_2/\text{Li}_2\text{ZrO}_3$ /electrolyte interface were analyzed using in situ NR data collected at charged 4.2 V and discharged 3.0 V. The interfaces showed different SLD values by changing the electrolyte concentration, which indicates the formation of the different ionic distribution. We will discuss on the crucial structure-parameters which determine the reaction rate in the interfacial regions. The depth-profile of the ionic distribution could give insight into research directions for electrode materials with highly-functional interfaces.

EI05.19

Experimental and Theoretical Study of Ir-Fe Bimetallic Electrocatalyst as an Excellent Anode in Both Electrolyte Cell and Fuel Cell Hyeonjung Jung and Jeong Woo Han; Pohang University of Science and Technology, Korea (the Republic of)

The electrolytic cell (EC), which can convert and store sustainable energy as hydrogen by water splitting, and the fuel cell (FC), which can obtain electricity from the chemical energy of hydrogen and oxygen, are key technologies for realizing a hydrogen energy society. Developing anode catalysts with high activity and durability for EC and FC is a major challenge in electrocatalysis. The EC's overall reaction rate is hindered by the slow kinetics of oxygen evolution reaction (OER) at the anode. A properly dynamic surface improves its catalytic activity, but excessive fluidity causes poor durability. The FC's hydrogen oxidation reaction (HOR) occurs at the anode under normal conditions. However, during start-up and shut-down (SU/SD) of an automobile, unintended air leakage into the anodic flow field can cause a parasitic oxygen reduction reaction (ORR) and an instantaneous potential jump at the cathode, resulting in cathode corrosion. Carbon corrosion can also occur at anode under fuel starvation conditions, and oxidizing water instead of carbon can be one solution. Therefore, an EC requires an anode material with high OER activity and durability, whereas an FC requires an anode material with high OER and HOR activity but low ORR activity.

In 2017, Kim et al. obtained a nanoporous Ir/IrO₂ catalyst by dealloying an Ir₂₅Os₇₅, and it showed very high Activity-Stability Factor (ASF) and electrical conductivity as an OER catalyst. [*Nature communications*, 8(1), 1-8] Inspired by this literature, we synthesized anode materials for EC and FC by alloying iridium with other 3d transition metals (TM = Mn, Fe, Co, Ni) and then oxidizing the surface. The synthesized Ir-TM catalysts consisted of an Ir@TM alloy core and a thin IrO_x shell. Interestingly, the Ir-Fe catalyst showed nearly zero Fe dissolution during OER, whereas quite large amounts of Co and Ni dissolution were observed in Ir-Co and Ir-Ni. Ir-Fe also exhibited higher current densities than Ir-Co and Ir-Ni, resulting in ~7 times higher ASF. It is ~14 times and ~17 times higher than the ASF of IrO_x and commercial OER catalyst IrO₂, respectively, suggesting that Ir-Fe is a promising EC anode material. On the other hand, Ir@Fe alloy showed lower half-wave potential for HOR than Ir@Mn, Ir@Co, Ir@Ni and commercial Pt-based catalysts. Ir-Fe also showed very low half-wave potential for ORR. The high activity of Ir-Fe for HOR and ORR and low activity for OER suggest that it is a suitable FC anode material with low corrosion problems due to SU/SD and fuel starvation.

Density functional theory (DFT) calculations were performed to reveal the TM-dependent activity and stability of Ir-TM catalysts. The surface model was constructed based on the experimental data that XRD represented a face-centered-cubic Ir@TM core and Ir 4f XPS represented a hydrous IrO_x shell. The electronic properties of the surface depending on the secondary metal added to Ir were confirmed through Bader charge analysis and density of states calculation. Here, the binding strength of the IrO_x shell to the Ir@TM core and the adsorption energy of the intermediates in the electrochemical reaction are different. The weak adsorption of the IrO_x shell to the Ir@TM core indicates the instability of the interfacial structure and leads to transition metal exposure by peeling of the shell. The weak hydrogen adsorption energy close to zero of Ir@Fe compared to other samples indicates a low potential barrier to HOR. Its moderate adsorption energy of oxygen containing intermediates (OCIs) results in a low potential barrier for OER and high potential barrier for ORR.

In this study, Ir-Fe was proposed as an excellent anode material for both EC and FC, and DFT calculations found the origin of its activity and durability from electronic structure analysis. Our results shed light on the design of electrocatalysts for oxygen and hydrogen evolution reactions.

SESSION EI06: Electrochemistry Fundamentals
Session Chairs: Christoph Baeumer and Sung-Yoon Chung
Tuesday Morning, July 19, 2022
Mezzanine Level, Second Floor, Berkeley/Clarendon

9:10 AM **EI06.01

Coupled Ion-Electron Transfer Reactions Between Solids, Liquids and Gas William C. Chueh; Stanford University, United States

Most non-metallic electrocatalysts and battery electrodes change composition during operation. This change in the composition directly modifies the kinetics of heterogeneous reactions at the electrode/electrolyte interface, whether it is the lithium intercalation reaction in Li_xFePO_4 , room-temperature oxygen evolution reaction in CoO_xH_y , or high-temperature oxygen incorporation in CeO_{2-x} . Such transformations and compositional changes in electrodes fundamentally alters the chemistry of the active site, impacting the local geometry and the electronic structure. In term, the microkinetic pathway becomes highly dependent on potential, beyond the standard treatment in Butler-Volmer or Marcus kinetics. As such, conventional electrochemical theories do not readily apply to these electrodes. In this talk, I will discuss how potential-dependent phase and composition variations can substantially alter the reaction pathway.

9:40 AM *EI06.02

Correlation of Local Structures and Electronic States with Oxygen Evolution Electrocatalysis in Oxides Sung-Yoon Chung; Korea Advanced Institute of Science and Technology, Korea (the Republic of)

As many actual devices based on electrochemical reactions for energy conversion and production operate at room temperature, the utilization of adequate electrocatalysts is imperative to significantly lower the activation barrier during the redox reactions. Hydrogen-evolution/oxygen-evolution reactions

(HER/OER) are key electrochemical processes at the cathode and anode sides, respectively, in electrolyzers for hydrogen production *via* water splitting. It is generally accepted that the activation barrier of the OER associated with transfer of multiple electrons and protons is very large, resulting in a comparatively higher anodic overpotential to split water. Therefore, the OER is a predominant pathway that can notably affect the overall efficiency of electrolysis. Furthermore, as acidic solutions are utilized in proton-exchange-membrane (PEM) electrolyzers usually showing high OER current at lower overpotentials, the durability of catalysts at the anode side is another significant issue in addition to the high catalytic activity. In this presentation, in addition to briefly summarizing the basic background and important descriptors of the OER, we focus on the correlation among the atomic structure, the electronic states, and the resulting OER in complex oxides to offer key insights toward achieving better catalytic activity and stability of oxide catalysts. In particular, advances in direct imaging and chemical analysis in scanning transmission electron microscopy (STEM) during the last two decades enabled atomic-level identification and visualization of the active sites. We thus demonstrate notable atomic-scale examples clarifying the strong relation between the local structure and the electronic states to achieve better OER performance.

10:00 AM **EI06.03

Chemical Capacitances at Electrochemical Interfaces in SOFC—The Origin and the Use for Characterization of Electrochemical Reaction Site Tatsuya Kawada¹, Keiji Yashiro¹, Kota Watanabe¹, Mirai Takeda¹, Masami Sato^{1,2}, Mayu Muramatsu³ and Kenjiro Terada⁴; ¹Tohoku University, Japan; ²Mechanical Design & Analysis Corporation, Japan; ³Keio University, Japan; ⁴Tohoku University, Japan

Frequency response analysis of electrochemical impedance often shows capacitive arcs in a Nyquist plot in solid state electrochemical cells as well as in liquid electrolyte cells. The origin of the capacitance can be purely electrical charge across the boundary or accumulation of chemical species such as adsorption around the interface or defect formation/annihilation in the electrode/electrolyte materials. The chemical origin often causes a large capacitance which, in some cases, gives a useful information on the electrochemical reaction site. In a typical mixed conducting oxygen electrode (La,Sr)CoO₃ (LSC), a Gerischer-type impedance appears according to the spreading reaction site into the electrode layer from the electrolyte boundary. With a porous LSC electrode on a doped CeO₂ electrolyte, impedance measurements were made with systematic variation of oxygen partial pressure, and the chemical capacitance was utilized as a measure of the thickness of the active reaction site. A careful analysis of the information led us to a conclusion that the surface reaction rate of a porous LSC was much faster than expected from a dense model electrode [1]. A similar analysis was possible to evaluate active site in Ni-ceria cermet anode using oxygen nonstoichiometry of doped CeO₂ [2]. Unlike those cases, the origin of the capacitance in a Ni-YSZ electrode was not clear so far. Model electrode experiments were made to find a quantitative explanation of the capacitance at Ni-YSZ boundary. Small circular electrodes with various diameters were deposited on a smooth surface of a YSZ pellet, and impedance responses were compared to their contact area and triple-phase-boundary (TPB) length or the periphery of electrodes. The observed resistance was inversely proportional to the TPB length, and the capacitance was proportional to the contact area. The area specific capacitance was much larger than an electrical capacitor with a single atom distance and thus attributed to a chemical origin. Then, the chemical capacitance of the electrolyte was evaluated from oxygen nonstoichiometry or electron concentration change in YSZ electrolyte. Finite element calculation was made to simulate the impedance responses with the model electrode/electrolyte geometry. Oxide ion and electron transport together with the oxygen nonstoichiometry of YSZ was considered in the calculation using an in-house code, SIMUDEL, that enables transient analyses of the oxygen potential distribution and local nonstoichiometry change in a solid system [3,4]. Contrary to our expectation, the calculated capacitance was larger than that observed in the experiments, which meant some presumption in calculation was not valid. After several trials, the calculation showed a reasonable match with the experiment when an existence of electron transfer barrier was assumed at the Ni/YSZ boundary. This result gives an important insight in the electrode reaction kinetics and active site width in Ni-YSZ cermet electrode.

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10:30 AM EI06.04

Operando Observation of Chemical Potential Distribution in Solid-State Ionics Devices by Using X-Ray Absorption Spectroscopy Koji Amezawa¹, Masaharu Yanagi¹, Yuta Kimura¹, Takashi Nakamura¹, Hirokazu Katsui², Kiyofumi Nitta³, Oki Sekizawa³ and Tatsuya Kawada¹; ¹Tohoku University, Japan; ²AIST, Japan; ³JASRI, Japan

Electrochemical devices using a solid-state ion-conducting material as the electrolyte can be expected as next-generation energy conversion and storage devices. Solid oxide fuel cells using a solid-state oxide ion or proton conductor and all-solid-state batteries using a solid-state lithium ion conductor are their typical examples. The driving force of these energy conversion and storage devices is the difference of chemical potentials between the anode and the cathode, which is maintained across the electrolyte. The chemical potential in the electrolyte often have great impacts on the properties and thermodynamic stability of the electrolyte, thus the device performance and durability. It is therefore important to understand the distribution of chemical potential in solid state ionics devices, particularly under operation, for optimizing designs and operating conditions of the devices or for ensuring thermodynamic and mechanical stabilities of the devices.

So far, a lot of numerical studies have been carried to clarify the distribution of chemical potential in solid state ionics devices. However, only a few studies have been reported to directly observe the distribution of chemical potential in an experimental manner. In particular, there exist no studies for its operando observation under device operation.

In this study, we aimed to experimentally evaluate the chemical potential distribution in solid state ionics devices. Challenges for this are how to detect the chemical potential change in the solid electrolyte and how to achieve operando measurement at desired temperature, in controlled atmosphere, under polarization, and preferably with high positional and temporal resolutions. In order to detect the chemical potential change, we embedded a potential probe into the electrolyte. In order to achieve operando measurement, we applied micro-beam X-ray absorption spectroscopy. In this study, yttria-stabilized zirconia, which is the most typical electrolyte (oxide ion conductor) for solid oxide fuel cells, was chosen as an example of solid electrolyte. Then, the distribution the oxygen chemical potential and its temporal change was experimentally evaluated, when electrochemical oxygen reduction/evolution was under progress at a porous Pt electrode on the electrolyte.

10:45 AM BREAK

Tuesday Morning, July 19, 2022
Mezzanine Level, Second Floor, Berkeley/Clarendon

11:00 AM *EI07.01

Electrochemical Characterization of the Effects of Nanocatalyst Infiltration on the Air Electrode Reaction Kinetics Using the Transmission Line Model Jaewoon Hong^{1,2}, Hohann Bae¹ and Sun-Ju Song¹; ¹Chonnam National University, Korea (the Republic of); ²University of Maryland at College Park, United States

The effect of nanocatalyst infiltration on the SOFC electrochemical performance was investigated by the application of electrochemical impedance (EI) spectroscopy. Anode-supported cell was fabricated using a YSZ electrolyte, and a mixed ionic electronic conductor $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ (LSCF6428) cathode. To study the electrode reduction reaction, the cathode-infiltrated cell was also prepared in which the LSCF6428 cathode was infiltrated by a monodispersed $\text{Sm}_{0.5}\text{Sr}_{0.5}\text{CoFe}_{3-\delta}$ (SSC55) nanocatalyst using a sol-gel method. The EI spectra were measured under various conditions ($0.02 \leq p\text{O}_{2,\text{cat.}}/\text{atm} \leq 1$; $0.2 \leq p\text{H}_2\text{O}_{\text{ano.}}/\text{atm} \leq 0.6$) in the temperature range of 600–800 °C. The results were analyzed by using the TLM to evaluate the effect of the nanocatalyst on the SOFC performance and electrode reaction characteristics. With the application of nanocatalyst infiltration, the parameters ($R_{s,\text{cat.}}$ and $R_{p,\text{cat.}}$) of the cathode were found to decrease by approximately one order and 40%, respectively. Similarly, $C_{p,\text{cat.}}$ also fell by approximately one order of magnitude. It suggested that SSC55 nanocatalyst had a greater effect on surface diffusion of ions adsorbed on the surface than diffusion of bulk ions.

In addition, by half-cell measurements of LSCF6428 air electrode with GDC electrolyte, impedance fitting was supplemented before and after infiltration under the same thermodynamic conditions. By measuring the AC impedance in the operating conditions, the rate determining reaction of the multi-stage electrode reaction in the air electrode was analyzed. The activation electrode resistance was separated by impedance fitting and converted into an activation polarization curve, which was analyzed by the Butler-Volmer equation. How the change in microstructure affects the oxygen reduction reaction was studied in terms of the dependence of the exchange current density on oxygen partial pressure and the change of the reduction transfer constant, indicating that the surface reaction and surface diffusion became more favorable due to the nanocatalyst infiltration.

11:20 AM EI07.02

Nanostructured LSC Thin-Film Electrodes with Improved Electrochemical Performance and Long-Term Stability Katherine Develos-Bagarinao¹, Ozden Celikbilek², Gwilherm Kerherve³, Sarah Fearn³, Stephen J. Skinner³ and Haruo Kishimoto¹; ¹National Institute of Advanced Industrial Science and Technology, Japan; ²Centre National de la Recherche Scientifique, France; ³Imperial College London, United Kingdom

Nanostructured $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_{3-\delta}$ (LSC) thin film electrodes exhibit exceptionally high oxygen surface exchange properties, surpassing those of conventional microscale electrode structures, which are desirable for application in solid oxide cells (SOC) [1-2]. On the other hand, the LSC nanostructures also tend to undergo significant morphological changes at typically high temperatures required for SOC operation, leading to rapid degradation in performance. Here, towards the goal of improving the long-term stability of electrochemical performance of nanostructured LSC thin films, a systematic investigation of the effect of processing temperatures on long-term stability was carried out [3]. By varying the deposition temperature (500 °C to room temperature), the as-grown characteristic nanostructures of LSC thin films prepared using pulsed laser deposition can be tuned from highly dense nanocolumnar grains to nanofibrous structures with high porosity. Variations in the deposition temperature also resulted to differences in the proportion of surface-bound/lattice-bound Sr and $\text{Co}^{2+}/\text{Co}^{3+}$ at the surfaces of the as-grown LSC thin films; however, prolonged annealing at 700 °C in air essentially transforms the surfaces to a final state with mostly lattice-bound Sr and Co^{3+} . Nevertheless, LSC films with initially nanofibrous structures are found to be less prone to the grain sintering effect occurring at high temperatures and exhibit less degradation of the electrode polarization resistance as compared to well-dense films. Using lower deposition temperatures, cation interdiffusion occurring at LSC/GDC interfaces is also significantly suppressed, thus leading to better interfacial stability as compared to those prepared at higher deposition temperatures. These results highlight the relationship between characteristic nanostructures of thin film electrodes and electrochemical performance and provide guidance on designing electrodes with improved long-term stability.

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11:35 AM *EI07.03

Multi-Doped Stabilized Bismuth Oxides as Functional Interlayers and Oxygen Electrode Components for Reversible Solid Oxide Cells at Reduced Temperatures Kang Taek Lee; Korea Advanced Institute of Science and Technology, Korea (the Republic of)

The singly doped-stabilized Bi_2O_3 (MSB) is known as a promising oxide ion conductor for reversible solid oxide cell (SOC) applications due to its excellent ionic conductivity compared to other conventional oxide ion conductors such as doped CeO_2 and stabilized ZrO_2 . Despite its superior ionic conductivity at reduced operating temperatures below 700 °C, the MSB has not been a practical choice for an electrolyte material for SOFCs because its time-dependent conductivity degradation below 650 °C. In this work, we developed highly stable stabilized bismuth oxides via substituting Bi^{3+} with very small amounts of the secondary iso/aliovalent dopants. In order to investigate the effect of the multi-doping on enhancing ionic conductivity and suppressing the kinetic degradation mechanism, ionic conductivity and the cation diffusivity of the samples were evaluated by electrochemical impedance spectroscopy, and Boltzmann-Matano method, respectively. Further, chemical and structural changes of the samples by extended annealing were also investigated. Moreover, our novel double-doped stabilized bismuth oxides were incorporated into conventional stabilized zirconia-based SOCs. The electrochemical performance and the stability of the SOCs with our novel bismuth oxides in fuel cell and electrolysis cell modes were evaluated with I-V characteristics and impedance spectroscopy.

11:55 AM EI07.04

Electrochemical Conversion of Methane to Ethylene Utilizing Highly Durable Barium Niobate Perovskites Kannan Ramaiyan, Luke Denoyer, Angelica Benavidez, Kyle Troche and Fernando Garzon; University of New Mexico College of Arts and Sciences, United States

Efficient conversion of methane to value added products such as olefins and aromatics has been in pursuit for the past several decades. The demand has increased further due to the recent discoveries of shale gas reserves. Electrochemical methane conversion is gaining attention due to its ability to control the oxide ion flux that will help reduce the over-oxidation of methane while also help activate methane via applied potential. High temperature electrolysis further benefits this process due to improved kinetics. Unfortunately, high temperature operation also leads to materials degradation, especially on the electrocatalyst, via sintering, crystal structure disproportion to thermodynamically more stable phases, and interfacial reactions that reduces the performance. For example, lifetime requirements for energy conversion technologies often times exceed 10 years of usage with no more than 20%

degradation.[1] Similarly, we demonstrated the chemical instability of $\text{Sr}_2\text{Fe}_{1.5}\text{Mo}_{0.5}\text{O}_{6-d}$ (SFMO) perovskite that was recently reported to show good methane activation properties.[2] [3] SFMO formed carbonates and coke upon exposure to CH_4 . Hence, the durability measurement results are often not reported for these catalysts under the extremely reducing or oxidizing high temperature environments. We have developed an exciting class of barium niobate perovskite materials with varying level of Mg/Ca and Fe co-doping that show good catalytic activity towards methane activation in the electrochemical and conventional heterogeneous oxidative coupling environment.[4] These catalysts further demonstrate durable electrochemical activities over five days of continuous operation. We have performed thermogravimetric, FT-IR and electrochemical linear sweep voltammetry methods to rapidly determine their stability under operationally relevant conditions and these results are compared to stability calculations. Stability determinations of our perovskite oxide electrocatalysts for EC-OCM offer an excellent example of our approach towards evaluation of materials durability under challenging temperature and reducing conditions. These perovskite materials could also serve as a support for a wide variety of catalyst materials for high temperature applications thus opening up new possibilities.

References

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12:10 PM **EI07.05

Recent Developments in Catalysts for Reversible Solid Oxide Cells Yucun Zhou, Nicholas Kane, Weilin Zhang, Zheyu Luo and Meilin Liu; Georgia Institute of Technology, United States

Solid oxide cells have potential to be the cleanest and most efficient option for the direct conversion of a wide variety of fuels to electricity and for efficient production of green hydrogen (or syngas) from the electrolysis of water (or co-electrolysis of water and CO_2). Thus, reversible solid oxide cells are ideally suited for large-scale energy storage and conversion, which is vital for the deployment of renewable energies. However, the commercialization of these systems hinges on the rational design of novel materials with exceptional functionalities at lower temperatures to dramatically reduce the cost while enhancing performance and durability. A key challenge is the development of highly active and durable catalysts. This presentation will highlight the critical scientific challenges facing the development of catalysts for a new generation of reversible solid oxide cells based on proton-conducting electrolytes, the strategies for enhancing durability and activity of electrode reactions, and the outlook for future-generation energy storage systems that exploit nano-scale materials with significantly improved performance.

SESSION EI08: Proton-Conducting Cells
Session Chairs: Meilin Liu and Sun-Ju Song
Tuesday Afternoon, July 19, 2022
Mezzanine Level, Second Floor, Berkeley/Clarendon

2:00 PM **EI08.01

Mixed Proton/Hole/Oxygen Vacancy Conductors—Bulk Defect Chemistry, Transport Properties and Surface Reaction Aspects Rotraut Merkle¹, Giulia Raimondi¹, Maximilian F. Hoedl¹, Andrew Chesnokov², Denis Gryaznov², Eugene Kotomin^{1,2} and Joachim Maier¹; ¹Max Planck Institute for Solid State Research, Germany; ²University of Riga, Latvia

Cathode materials for protonic ceramic fuel and electrolyzer cells (PCFC, PCEC) require sufficient proton conductivity to extend the reactive zone for oxygen reduction/water oxidation beyond the three-phase-boundary. The defect chemistry of perovskite oxides and related materials containing mobile protons, electron holes and oxygen vacancies ("triple conductors") is complex since defect interactions are non-negligible.[1,2] Several desired properties such as electronic and protonic conductivities are in conflict with each other and need to be balanced based on fundamental insight. Protonic defects are formed via dissociative hydration of oxygen vacancies: $\text{H}_2\text{O} + \text{V}_{\text{O}}^{\bullet\bullet} + \text{O}_{\text{O}}^{\text{x}} \rightarrow 2 \text{OH}_{\text{O}}^{\bullet}$. Triple conducting perovskites typically exhibit lower degrees of hydration than $\text{Ba}(\text{Ce},\text{Zr},\text{Y})\text{O}_{3-z}$ electrolyte materials, extensively investigated for $(\text{Ba},\text{Sr},\text{La})(\text{Fe},\text{Co},\text{Zn},\text{Y})\text{O}_{3-d}$ perovskites.[1] Interestingly, a partial substitution of Fe or Co by redox-inactive oversized ions such as Zn^{2+} , Y^{3+} drastically increases the proton uptake. A deeper understanding of the correlations between cation composition and proton uptake is obtained from EXAFS/XRS measurements and DFT calculations.[3,4] Fe-XANES and O-XRS spectra as well as the electronic density of states from DFT indicate a large degree of covalency of the Fe-O bonds, including partial hole transfer from Fe to O. This decreases the basicity of the oxide ions, which finally disfavors the hydration reaction. The EXAFS analysis shows that oversized Zn^{2+} , Y^{3+} dopants lead to a bending of the Fe-O-Fe connections, which decreases the Fe-O covalency. Owing to the predominant electronic conductivity, measurements of proton conductivity and mobility of triple conducting oxides are challenging. From the differences compared to $\text{Ba}(\text{Zr},\text{Y})\text{O}_{3-z}$ electrolytes (smaller lattice parameter, stronger local distortions, decreased B-cation charge etc.) no clear prediction for lower or higher proton mobilities can be derived. Proton migration barriers in $(\text{Ba},\text{Sr})\text{FeO}_{3-d}$ are calculated by DFT, and correlations with local geometry and electronic structure explored.[5] Proton mobilities extracted from chemical diffusion experiments indicate that they are slightly lower than in $\text{Ba}(\text{Zr},\text{Y})\text{O}_{3-z}$ electrolytes.

Regarding the surface oxygen reduction to water, systematic kinetic and mechanistic investigations on geometrically well-defined model electrodes on protonic ceramic electrolyte substrates are scarce. The estimated proton conductivity of Ba-rich cathode materials is expected to suffice to activate the whole thin-film electrode surface area for the oxygen reduction reaction. This is supported by microelectrode measurements.[6] The observed negative pH_2O dependence further indicates that protons are not involved before or in the rate-determining step. A strong surface hydroxylation might rather block oxygen vacancies which had been proven important for SOFC cathode kinetics in dry conditions. Approaches for improving the oxygen reduction rate on PCFC cathode materials will be discussed.

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2:30 PM EI08.02

Hydration, Stability and Electrochemistry of A- and B-Site Substituted Double Perovskite Cobaltites [Ragnar Strandbakke](#)¹, Maria Balaguer², Alfonso J. Carrillo², Sebastian Wachowski³, Iga Szpunar³, Aleksandra Mielewczyk-Gryn³, Magnus H. Sørby⁴, Øygarden Vegar⁵, Einar Vøllestad⁵, Maria Gazda³, Jose M. Serra² and Truls Norby¹; ¹Universitetet i Oslo, Norway; ²Instituto de Tecnologia Química, Spain; ³Politechnika Gdanska Wydział Fizyki Technicznej i Matematyki Stosowanej, Poland; ⁴Institutt for energiteknikk, Norway; ⁵SINTEF Industry, Norway

Mixed Proton and Electron conducting Ceramics (MPEC's) are central in the development of efficient electrodes for Proton Ceramic Electrochemical Cells. Mass transfer overpotential is limiting the electrode performance, and the interplay between catalytic activity and the inherent partial proton conductivity determines the electroactive surface. The electronic conductivity is important for low ohmic overpotential, but mobile electronic defects also affects proton stability. The stability of protons correlates with anion basicity, and electron structure and mobility is therefore essential with respect to both red-ox activity and partial proton conductivity. A wide range of double perovskites with A- and B-site substitutions has been investigated for proton concentration, stability in high steam pressures and electrochemical performance. Thermogravimetric Analysis (TGA) has been used to investigate proton concentrations and Electrochemical Impedance Spectroscopy (EIS) under positive, zero and negative DC bias was used to investigate polarization resistance for model electrodes and porous electrodes in both anodic and cathodic operation. The results reveal that while acceptor doping on the B-site promotes hydration and oxygen reduction, donor doping promotes hydrogenation and anodic water oxidation. Stability in high steam pressures is closely related to the A-site ionic radii ratio (IRR), where increased IRR gives increased oxygen non-stoichiometry, increased hydration and lowered stability in steam. Some of the reported MPEC materials¹ are therefore not stable at 600°C and 10 bar H₂O. They may, however, be stabilised for high steam pressures, and we present several ways to do so while maintaining MPEC functionality.

Acknowledgements: The Research Council of Norway (Grant 272797 "GoPhy MiCO" and 299736 "FunKey Cat")

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2:45 PM *EI08.03

Determination and Suppression of Electronic Leakage in Proton-Conducting Cells [Hiroshige Matsumoto](#) and Leonard Kwati; Kyushu Daigaku, Japan

Solid oxide cells consisting of proton-conducting solid electrolytes are interested for efficient energy conversion between fuel and electricity. Operation of fuel cells and steam electrolysis using proton-conducting perovskites have been reported so far with enhanced performance and/or reduced operation temperature. One of their challenges is the electronic leakage originated from electron-hole conduction in the electrolyte materials that lead to lower faradaic efficiency. In this paper, methods to determine and suppress the leakage are shown and discussed.

For the determination, one method is to measure the steam/hydrogen generation at the anode and cathode. The information is useful to determine proton and oxide-ion transport numbers as well. Another method is to use Hebb-Wagner polarization state under which ions have no electrical driving force to move in the electrolyte.

For the suppression, one idea is to introduce an interlayer that block the electronic leakage. Introduction of less leaking material is one example and the effect of more complicated layered electrode will be demonstrated.

3:05 PM *EI08.04

Importance of Anode Functional Layer for Protonic Solid Oxide Electrolysis Cells [Yoshitaka Aoki](#), Chunmei Tang and Hiroki Habazaki; Hokkaido Daigaku, Japan

Decarbonizing the planet is one of the goals set by countries around the world for 2050. To achieve this, one of the key measure is decarbonizing the production of hydrogen, resulting in "green" hydrogen, as this process is currently responsible for more than 2% of the total global CO₂ emissions. Steam electrolysis has some advantages in comparison to water electrolysis based on the thermodynamic aspects of the water splitting reaction. Hence, protonic solid oxide electrolysis cells (H-SOECs) based on proton-conducting perovskites, that is, Ba(Ce, Zr, M)O_{3-δ} (M = Y, Yb, etc.) are recently attractive as a steam electrolyzers operating in the intermediate temperature region (400–600 °C). When the mixed oxide ion and electronic conducting materials, such as La_{0.6}Sr_{0.4}Co_{1-x}Fe_xO_{3-δ} (LSCF), were used as anodes of H-SOECs, the anode reaction area is limited to the gas-electrode-electrolyte triple phase boundary (TPB) due to the mismatch of ionic carriers between electrolyte and anode. To extend the effective reaction area, it is strongly desirable to design anode materials with conducting proton, oxide ion and electron, and thus the H⁺/O²⁻/e⁻ triple conducting phases, such as BaCo_{0.4}Fe_{0.4}Zr_{0.1}Y_{0.1}O_{3-δ} (BCFZY), PrNi_{0.5}Co_{0.5}O_{3-δ} (PNC), PrBa_{0.5}Sr_{0.5}Co_{2-x}Fe_xO_{5+δ} (PBSCF), have been intensively studied.

In more recent year, several groups reported on the importance of functional layer between electrolyte and anode in order to improve the performances of P-SOECs. The ohmic losses of BaZr_{0.4}Ce_{0.4}Y_{0.1}Yb_{0.1}O_{3-δ} (BZCYYb4411) base cell decreased by 50% with H⁺/O²⁻/e⁻ triple conducting PBSCF interlayer (~100 nm) between PBSCF anode and electrolyte. The well-known double conducting oxide La_{0.5}Sr_{0.5}CoO_{3-δ} (LSC) was also promising as an anode functional layer.^[2] Both ohmic and polarization resistances of BaZr_{0.6}Ce_{0.2}Y_{0.1}Yb_{0.1}O_{3-δ} (BZCYYb6211) abse cells could be decreased by more than 50% with a use of LSC anode functional layer (AFL). In this study, we conducted a broad survey for optimal AFL materials and approached to the role of AFL in anode reaction of H-SOECs. [1] S. Choi, T. C. Davenport and S. M. Haile, *Energy Environ. Sci.*, 2019, **12**, 206–215. [2] C. Tang, K. Akimoto, N. Wang, L. Fadillah, S. Kitano, H. Habazaki and Y. Aoki, *J. Mater. Chem. A*, 2021, **9**, 14032-14042.

3:25 PM *EI08.05

A Discussion on the Electrochemistry of Positrodes in Proton Ceramic Electrochemical Cells [Einar Vøllestad](#); SINTEF, Norway

Proton ceramic electrochemical cells (PCECs) are emerging as a promising energy conversion technology for clean production of power (fuel cells), hydrogen (electrolyser) and chemicals (i.e., NH₃ synthesis) – particularly due to their potential for intermediate temperature of operation (400–500°C).¹ One of the main obstacles towards realizing intermediate-temperature operation is the kinetics of the O₂/H₂O-electrode (positrode). An emergence of novel positrodes based on mixed proton electron conducting oxides have resulted in excellent performance with electrode resistances below 0.5 Ωcm² at temperatures above 500°C.^{2,3} However, the fundamental electrochemistry of positrode reaction mechanisms and the rate limiting surface reactions are not well understood. A rational design of improved positrodes for intermediate temperature operation (≤ 500°C) necessitates fundamental understanding of the interplay between the electrochemistry of PCECs, the surface and material chemistry of the positrode material, and the interfacial processes at the electrode-electrolyte interface.

This presentation aims to shed some light on a few fundamental and unanswered questions within PCEC electrochemistry:

To what extent can we link thermodynamic bulk properties measured under equilibrium conditions to the electrochemical and kinetic activity of the electrode as the system is driven away from equilibrium? Is there a difference in the rate-limiting reaction mechanisms between fuel cell (oxygen reduction) and electrolysis (oxygen evolution) operation? Most studies to date have been conducted under open-circuit (equilibrium) conditions and little is

known regarding the electrode mechanisms when they are electrochemically driven away from equilibrium.

How will the positrode reaction mechanisms be impacted by an increased presence of surface protonic species when operated at lower temperatures (and higher relative humidity)? Will surface proton conductivity contribute to an expanded electrochemical area, or will the increased surface hydroxyl concentration effectively block active surface sites for either oxygen evolution or oxygen reduction?

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2. Duan, C. *et al.* Highly efficient reversible protonic ceramic electrochemical cells for power generation and fuel production. *Nature Energy* **4**, 230 (2019).
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3:45 PM BREAK

SESSION EI09: Solid-Liquid Interfaces
 Session Chairs: Hiroshige Matsumoto and Einar Vøllestad
 Tuesday Afternoon, July 19, 2022
 Mezzanine Level, Second Floor, Berkeley/Clarendon

4:00 PM EI09.01

High-Performance Anion Exchange Membrane Water Electrolyzers Enabled by Highly Active Oxygen Evolution Reaction Electrocatalysts—Synergistic Effect of Doping and Heterostructure [Chuancheng Duan](#) and Yoo Sei Park; Kansas State University, United States

Anion exchange membrane (AEM) water electrolyzers exhibit the potential to become a key technology for renewable hydrogen production. The AEM water electrolyzer allows using PGM-free electrocatalysts, especially the electrocatalysts for oxygen evolution reaction (OER) that typically have sluggish kinetics. Transition metal-based layered double hydroxides (LDHs) are known as the best OER electrocatalysts. Particularly, CoFe-LDH and NiFe-LDH have exceptional OER activity compared to other electrocatalysts; thus, the activation loss ascribed to OER can be dramatically reduced if these two electrocatalysts are applied on AEM electrolyzers. As a result, high-performance AEM electrolyzers can be demonstrated. However, the low electrical conductivity, a chronic problem of LDH electrocatalysts, causes Ohmic loss of the AEM electrolyzers, which acts as an obstacle to achieving high-performance AEM electrolyzers. Here, we developed an approach to modulating the composition of LDH and creating oxide-LDH heterostructure, which improves its conductivity and OER activity. The AEM electrolyzer catalyzed by the optimized LDH exhibits reduced Ohmic loss and improved kinetics, and achieves high performance of 3.0 A/cm² at 1.8 V_{cell}, which outperforms the state-of-the-art IrO₂ electrocatalyst. Our study suggests the performances of AEM electrolyzers with PGM-free OER electrocatalysts can be comparable to proton-exchange membrane (PEM) electrolyzers.

4:15 PM *EI09.02

Interface Properties of Model Perovskite Oxide Electrocatalysts [Christoph Baeumer](#)^{1,2}; ¹Universiteit Twente Faculteit Technische Natuurwetenschappen, Netherlands; ²Forschungszentrum Julich GmbH, Germany

Energy storage through the electrocatalytic generation of chemical fuels such as hydrogen is an attractive pathway for storing intermittent renewable energies, and perovskite oxides are among the most attractive candidate materials to catalyze the kinetically limiting half reaction, the oxygen evolution reaction (OER). OER activity is typically correlated to electronic and atomic structure parameters. But the catalyst surface – i.e. where the reaction happens – changes during the reaction. To design next-generation electrocatalysts, a detailed understanding of the relationships between catalytic activity, stability and atomic-level surface properties during the reaction is required.

Epitaxial thin films are a direct route for single crystalline model electrocatalysts that can be fabricated with atomically-tailored surface composition. These offer the ideal platform to derive structure-property-function relationships, track the evolution of the surface properties with applied potential and enable direct comparison to the surfaces investigated in density functional theory.

In this talk I will summarize our recent findings for the role of surface termination, surface contamination, point defects and transformation pathways during the reaction and the role of solid/solid interfaces in proximity of the solid/liquid interface. For LaNiO₃ thin films, which are atomically flat both before and after application as electrocatalysts for the OER during water electrolysis, we selectively tuned the surface cationic composition. The Ni-termination is approximately twice as active for the OER as the La-termination. Using a suite of ex situ, in situ and operando spectroscopy tools, we found that the Ni-rich surface undergoes a surface transformation towards a catalytically active Ni hydroxide-type surface.¹ If LaNiO₃ surfaces are exposed to the ambient, however, surface carbonate groups form, which prohibit the formation of the active phase, leading to an activity decrease compared to the clean surfaces.²

Our work thus demonstrates tunability of surface transformation pathways by modifying a single atomic layer at the surface and it shows that active surface phases only develop for select as-synthesized surface terminations, highlighting the instructional value of epitaxial model electrocatalysts. It also confirms that we need to further explore the three-step relationship between as-prepared surface, transformation under applied potential, and electrocatalytic activity.

References

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4:35 PM EI09.04

Operando Spectroscopic Studies on the Interfacial Chemistry of Oxygen Evolution Reaction Electrocatalysts [Allen Yu-Lun Liang](#)^{1,2}, Christoph Baeumer³, J. T. Mefford^{1,2} and William C. Chueh^{1,2}; ¹Stanford University, United States; ²Stanford Linear Accelerator Center, United States; ³Universiteit Twente, Netherlands

Green hydrogen generated from water electrolysis has massive potential in deep-decarbonizing our society. However, such a process suffers sluggish

efficiency at the counter oxygen evolution reaction (OER). Even with the state-of-the-art catalysts, the large overpotential limits water electrolysis from being economical for wide application. Thus, efforts are dedicated to understanding the OER reaction mechanism on catalysts to improve energy efficiency. Herein, we proposed to expand the capability of benchtop operando UV-Vis spectroscopy and observe the surface structure evolution on nickel-based electrocatalysts.

When the bulk material has relatively weak optical density change, the surface observation is fairly straightforward. Using epitaxial Lanthanum Nickel Oxide (LNO) film as a model system, UV-Vis can track the overall optical density changes at various DC biases. Varying the epitaxial film thickness and terminations reveals a spontaneous surface reconstruction to nickel hydroxide-like structure at the OER condition.

However, separating a surface signal from a strong bulk absorption requires some novel techniques. Nickel hydroxide film is our chosen model system for this purpose. In an operando UV-Vis setup, we propose to perturb the applied potential with an AC signal. By sweeping the AC frequency, we can control the transport depth of ions into the film, effectively tuning the probing depth of the operando UV-Vis setup. With the help of modeling, we demonstrate nickel hydroxide's distinct surface absorption spectrum under the OER conditions.

4:50 PM EI09.05

Advancing the Fundamental Understanding of MgCO₃ Formation in the Liquid/Solid Interface of Molten Salt-Promoted MgO During CO₂ Capture Alexander Hansen Bork¹, Margarita Rekhina¹, Elena Willinger¹, Jakub Drnec², Norbert Ackerl¹, Joakim Reuteler¹, Sachin Jog¹, David Gut¹, Robert Zboray³, Paula Abdala¹ and Christoph R. Mueller¹; ¹Eidgenossische Technische Hochschule Zurich, Switzerland; ²ESRF, France; ³Swiss Federal Laboratories for Materials Science and Technology, Switzerland

Solid oxide based sorbents are well-suited for CO₂ capture at large point sources such as power plants. Among the different solid sorbents considered for CO₂ capture, magnesium oxide (MgO) is an attractive candidate due its abundance, high CO₂ uptake per mass of sorbent and a comparatively low energy requirement for regeneration. However, MgO requires a promoter, typically a salt in its molten state (e.g. NaNO₃, LiNO₃, KNO₃), to have sufficiently fast carbonation kinetics. To improve the performance of MgO-based sorbents through rational design criteria a deeper understanding of the mechanisms that govern the CO₂ absorption reaction is required. [1]

A key scientific question is to determine where and how MgCO₃ forms during CO₂ capture. To address this question we used a MgO(100) single crystal coated with NaNO₃ as a model system and studied it under practically relevant CO₂ capture conditions via (in situ) X-ray reflectometry (XRR) coupled with grazing incidence X-ray diffraction, (ex situ) scanning electron microscopy, and high-resolution transmission electron microscopy. XRR revealed that a thin layer of ca. 7 Å thickness forms when bare MgO(100) is exposed to a flow of CO₂, thus limiting CO₂ capture to surface sorption. In contrast, when MgO(100) is coated with NaNO₃ and exposed to CO₂ a dramatic change in the surface roughness occurs. In situ GIXRD shows that this surface roughness corresponds to the formation of large (micron-sized) MgCO₃ crystals at the liquid/solid interface. Morphological characterization of the MgCO₃ formed by scanning electron microscopy (SEM) shows that the crystals exhibited a two-dimensional sectored plate morphology (size of 10-50 μm; thickness of 2 μm). Further transmission electron microscopy analysis demonstrates that the crystals are formed with a preferential orientation with respect to the MgO(100) substrate and that the lattice mismatch between MgCO₃ and MgO is relaxed through lattice misfit dislocations.[2]

While we have established that MgCO₃ formation occurs in the molten salt-promoted MgO(100) interface it still remains an open question whether the nucleation of MgCO₃ occurs most favorably in the “buried” liquid/solid interface or at the triple phase boundary (TPB) (i.e. liquid/solid interface in contact with the gas phase CO₂). For this purpose, we fabricated a model system consisting of MgO grooves structured through ultra-short pulsed laser ablation, coated with NaNO₃ as the promoter, and subsequently exposed to CO₂ capture conditions. The location of nucleation and growth of MgCO₃ is identified and characterized by micro X-ray computed tomography, plasma focused ion beam SEM and optical profilometry. We show that MgCO₃ forms at the NaNO₃/MgO interface and not inside the molten salt. Moreover, there was no preferential nucleation of MgCO₃ at the TPB when compared to the buried interface. Additionally, the model system allowed for a comparison of MgCO₃ formation under a thin versus a thick molten salt promoter coating. The thinnest promoter coating of 6 μm resulted in a 10 times higher volume of MgCO₃ compared to the thickest coating (180 μm thickness).

Overall, the fundamental understanding gained in this work, shows that more effective MgO sorbents should maximize the buried liquid/solid interface area while minimizing the thickness of the molten salt to enhance the formation of MgCO₃. This can be achieved by manufacturing MgO particles with a thin conformal coating of the molten salt.

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5:05 PM EI09.06

Effects of Defects and Metal Ion Dopants in Low Dimensional Carbon Catalysts on Carbon Dioxide Electroreduction at Triphasic Interfaces Soumyabrata Roy¹, Ram M. Yadav¹, Zhengyuan Li², Jingjie Wu² and Pulickel Ajayan¹; ¹Rice University, United States; ²University of Cincinnati, United States

Renewable electricity powered reduction of carbon dioxide (CO₂) to fuels and chemicals has extensive potential to close the anthropogenic carbon cycle. The large spectrum of CO₂ electroreduction (eCO₂R) products offers great opportunity from an electro-synthetic standpoint, although its potential is still limited by low catalytic selectivity for specific key products. Metal catalysts majorly dominate the state-of-the-art scenario in eCO₂R. Cu leads the way with its ability to produce hydrocarbons and oxygenates beyond the 2e-reduction process, but unfortunately with a wide product distribution. On the other hand, Ag/Au and Sn/Bi produce C1 products like carbon monoxide (CO) and formate (HCOO⁻) respectively, with >90% Faradaic efficiency (F.E.). Methane (CH₄) which is one of the kinetically hindered 8e- electron eCO₂R product can be used both as a fuel and hydrogen carrier. Thus, the challenging CO₂-to-CH₄ conversion pathway has received considerable attention in the past few years as an important step in carbon capture and utilization roadmap.^{1,2} Interestingly, low dimensional carbon matrices provide a reasonable alternative to metal-systems as tunable catalysts for eCO₂R. Over the years our group has systematically investigated several avenues of defect engineering, N doping, amine functionalization, nominal metal ion doping etc. to develop important structure-activity correlations in carbon nano-catalysts (nanodots, CNTs, graphene etc.) for eCO₂R.³⁻⁷ In our current study, we present a general molecular tuning strategy- in-situ amine functionalization of nitrogen-doped graphene quantum dots (N-GQDs) for CO₂-to-CH₄ conversion at high efficiencies.⁸ Extending the scope of this study, we also look into the effects of single ion metal dopants in nitrogenated low dimensional carbon matrices. N-GQDs achieve a CH₄ Faradic efficiency (FE) of 63% and 46%, respectively, at CH₄ partial current densities of 170 and 258 mA cm⁻², matching to or even surpassing the performance of the state-of-the-art Cu-based catalysts (Figure 1).^{9,10} The N-GQDs also produce C₂ products comprising primarily ethylene (C₂H₄) and ethanol (C₂H₅OH) with a maximum FE of ~10%. eCO₂R in gas fed flow cells occurs in a triphasic interface inside gas diffusion electrodes, that can largely address the solubility and mass transport limitations of gaseous CO₂ in liquid electrolytes. The interfacial ionic interactions at the

solid-liquid interfaces are crucial to understand to develop meaningful insights into the catalytic role of the active sites, the mechanistic drive and the evolution of the catalyst, operando. Detailed structure-activity relationship studies reveal that the CH₄ yield varies linearly with amine group content and the nuclearity of the dopant metal sites, whereas the C₂ production rate shows a positive dependence on the pyridinic N dopant content. A holistic analysis of our collective studies provides meaningful insights into the routes and effects of controlled N-defect and metal ion doping strategy with specific N configurations, variable local chemical environments, and functionalization on eCO₂R outcomes. These works can guide the rational design of defect-engineered carbon nano-catalysts with CO₂-to-C₁ product conversion efficiency at the industrially relevant level.

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5:20 PM EI09.07

Operando Electrochemical Atomic Force Microscopy of Model Electrocatalysts [Andrew R. Akbashev](#); Paul Scherrer Institut, Switzerland

In situ studies of electrochemical processes in model materials are central to fundamental electrochemistry as they provide precise potential-dependent quantities that can be used to accurately assess theoretical models and predictions. Among such processes is the structural evolution of materials under highly oxidizing conditions, which represents a particular challenge. To gain the necessary insight into the surface behavior, one has to employ not only a combination of advanced *in situ* characterization techniques but also well-defined materials that can be directly compared to computational models.

In this talk, I will discuss how epitaxial oxide films can be used as model systems for real-time tracking of materials' evolution during electrocatalytic water splitting (OER). Specifically, I will show how *operando* **electrochemical atomic force microscopy** (EC-AFM) can be used to record tiny changes in the surface morphology during anodic corrosion of the perovskite SrIrO₃ surface. In the experiments, we employ epitaxial films of SrIrO₃ with a sharp step between the film and substrate, which allows us to precisely track the dissolution rates. The degradation of SrIrO₃ electrocatalyst was found to follow different potential-dependent leaching and dissolution profiles in acidic and basic electrolytes. Ultimately, our work shows that (1) Sr leaching is an essential step during electrochemical dissolution of the perovskite structure, with the leaching rate controlled by the both potential and electrolyte composition, and (2) the A-site stabilization is crucial for the successful prevention of the perovskite dissolution during electrocatalysis

SESSION EI10: Exsolution and Nanoparticles
Session Chairs: Min Hwan Lee and Ragnar Strandbakke
Wednesday Morning, July 20, 2022
Mezzanine Level, Second Floor, Berkeley/Clarendon

9:10 AM *EI10.01

Insights into the Exsolution Process Using Synchrotron Radiation Methods [Benedikt Ehrhardt](#), [Benjamin Rudolph](#), [Emna Fezai](#), [Filippo Colombo](#) and [Simone Mascotto](#); Universitat Hamburg, Germany

The process of metal exsolution attracts since several years the interest of the scientific community because it represents a smart approach to prepare advanced metal-oxide nanocomposites through dopant segregation from a mixed conducting oxide matrix for applications in energy conversion, catalysis, and data storage. In spite of the outstanding number of publications in the past 5 years, still little is known about the formation mechanism of exsolved metal nanoparticles, and particularly about the interplay between the different steps of the process, i.e. dopant reduction, nucleation and nanoparticle growth. To tackle this, synchrotron methods represent a unique opportunity because they enable comprehensive understanding of the nanoparticle segregation process due to their high statistical significance and real-time operation.

In the present paper, the analysis of the exsolution of mono and bimetallic nanoparticles will be addressed by combining small-angle X-ray scattering (SAXS), X-ray diffraction (XRD) and X-ray absorption spectroscopy (XAS). Due to the high complementary character of these techniques it was possible to understand the correlation between the reduction and growth mechanisms during the exsolution of bimetallic Fe-Ni nanoparticles. Also, the use of SAXS combined with XRD enabled to obtain information about the size, shape and distribution of both surface- and bulk-segregated nanoparticles in powder and thin-film materials, providing insightful morphological information at different scales. Finally, the execution of real-time experiments demonstrated to be a highly promising approach to tackle the kinetics of nanoparticle formation, dissolution and self-regeneration.

9:30 AM *EI10.02

Electrochemical Activity Switching of Exsolution Catalysts [Alexander K. Opitz](#), [Harald Summerer](#), [Andreas Nanning](#), [Melanie Maurer](#) and [Christoph Rameshan](#); Technische Universität Wien, Austria

A catalyst preparation route, which has recently attracted much attention, makes use of deliberate partial decomposition of perovskite-type oxides containing reducible transition metals. This technique is commonly called exsolution and leads to formation of metallic nanoparticles. If these catalytically active precipitates form at the surface of their parent oxide, they show very interesting properties such as a very high degree of dispersion, a high resistance towards coarsening, and the possibility of redox cycling for recovery after catalyst poisoning. Depending on temperature, during such an oxidative treatment the exsolved transition metal particles are either redissolved in their parent oxide or only oxidised but still residing on the surface of the perovskite.

If the perovskite-type parent oxide is a mixed ionic/electronic conducting electrode in a solid oxide electrochemical cell, the latter can be also done by applying a respective bias voltage to the electrode. Moreover, this electrochemical manipulation of the particle's oxidation state can also be reversed – i.e. the particles switched back into the metallic state (for example by applying a cathodic bias). This approach is especially interesting as it allows reversible switching between two states of different catalytic activity: highly active metal particles and oxide particles with low catalytic activity.

In this contribution, the process of electrochemical activity switching of iron particles on $\text{La}_{0.6}\text{Sr}_{0.4}\text{FeO}_{3.8}$ (LSF) is presented and the associated change in the surface chemistry of the electrode is investigated using *in-situ* methods. In addition, the kinetics of the switching process itself are studied in more detail. It turns out that the transition between metallic and oxidic state of the particles (and *vice versa*) is manifested by a hysteresis-like behaviour of the electrode's I-V-characteristics. This is explained by a "kinetic competition" between gas atmosphere and electrochemically pumped oxygen and a suitable model illustrating the switching of the particles' oxidation state is discussed.

9:50 AM EI10.03

Low Energy Ion Scattering Analysis of Fe Exsolution in LSF Philipp Br uner¹, Thomas Grehl¹, Alexander K. Opitz² and Jiayue Wang³; ¹IONTOF GmbH, Germany; ²Technische Universitat Wien, Austria; ³Massachusetts Institute of Technology, United States

Mixed conducting fuel electrode materials like $\text{La}_{0.6}\text{Sr}_{0.4}\text{FeO}_{3.8}$ (LSF) are promising candidates for improving the performance of solid oxide electrolysis cells (SOECs). The electrochemical activity of LSF is found to increase strongly after cathodic polarization of the electrode under reducing conditions. XPS and XRD studies relate this behaviour to the formation of metallic Fe nanoparticles on the electrode surface. These catalyst particles are especially interesting as their activity can be reversibly switched between a high and low activity state by applying a sufficiently cathodic or anodic overpotential, respectively [1, 2].

For this study, Low Energy Ion Scattering (LEIS) was used to analyze the surface composition of a thin polycrystalline LSF layer on a single crystalline yttria-stabilized ZrO_2 (YSZ) substrate. In LEIS, the energy spectrum of backscattered noble gas primary ions is recorded. These ions are selectively scattered in the outer atomic layer, which results in an unmatched surface sensitivity of just a single monolayer. We show how from the energy spectrum the elemental composition of the sample surface is determined and quantified using reference samples. This reveals valuable information about the surface termination of the perovskite-type LSF material, surface contaminants, the extent of Fe exsolution, and the oxidation state of the surface Fe.

The measurements show the appearance of Fe under reducing conditions, up to a surface coverage of 12 % Fe. After exposing the sample to oxidizing conditions, a total absence of Fe from the topmost atomic layer is detected. This change in the surface composition is reversible and was observed over several cycles, thus being in line with the abovementioned switching behavior. Sample treatment was performed quasi in-situ in the preparation chamber of the analytical instrument.

In addition, Ni-doped LSCrMn was analyzed in an attempt to study the exsolution of Ni. After the same reducing treatment, no such effect was observed. This may be due to the greater chemical stability of LSCrMn preventing the exsolution of Ni unless stronger reducing conditions are applied or a rather low mobility of Ni in LSCrMn. However, it is worth mentioning that the LSCrMn material shows a notably different surface termination than LSF.

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[2] Opitz et al. *Nat. Comm.* 2020, 11, 4801

10:05 AM EI10.04

Exsolution-Reoxidation Cycle in Ni & Co-doped Sr(Ti,Fe)O₃ Electrodes for Intermediate Temperature Symmetric-Solid Oxide Cells Mariano Santaya¹, Catalina Jimenez², Mauricio D. Arce^{2,1}, Horacio Troiani¹, Emilia Carbonio^{2,3}, Lucia Toscani¹, Yanet Mansilla¹, Axel Knop-Gericke^{3,4}, Regan Wilks², Marcus B ar^{2,5} and Liliana V. Mogni¹; ¹INN-CNEA-CONICET, Argentina; ²Helmholtz Zentrum Berlin, Germany; ³Fritz-Haber-Institut der Max-Planck-Gesellschaft, Germany; ⁴Max Plank Institute for Chemical Energy Conversion, Germany; ⁵Fredrich Alexander Universit at Erlangen N urnberg, Germany

The optimization of electrodes for Solid Oxide Fuel Cells (SOFC) for the Intermediate Temperature range (IT-SOFC) is fundamental in order to mitigate degradation issues and decrease the Balance of Plant costs. In this sense, mixed ionic electronic conductor perovskite oxides have been widely implemented as cathodes, and some have also shown promising results as anode materials, although still with lower efficiencies than Ni-cermet anodes. However, perovskite type anodes present enormous advantages when compared to Ni-cermets regarding tolerance to C-based fuels, poisoning by S containing impurities durability after redox-cycling. Moreover, the possibility of using the same material both as anode and cathode in a Symmetric design (S-SOFC) reduces manufacturing and operational costs, and provides the possibility of redox-cycling the atmosphere to mitigate the impact of contamination with C-deposits. A recently implemented strategy to improve performance of SOFC anodes is the in-situ nanoparticle exsolution from perovskite oxides. This method has been widely studied for mono-metallic and bi-metallic exsolution, and though advantages of tri-metallic particles have been reported in electrochemistry and catalysis systems[1,2], the possibility of *exsolving* tri-metallic alloy nanoparticles from perovskite oxides was not deeply explored until recently, as reported in a recent publication by our group[3]. The aim of using perovskite electrodes decorated with exsolved nanoparticles in a S-SOFC design makes it mandatory to study also the reoxidation process as well as the exsolution.

In this work, we compare the redox activity during surface exsolution-reoxidation cycle on $\text{Sr}_{0.93}(\text{Ti}_{0.3}\text{Fe}_{0.7})\text{O}_{3.8}$ (STF), $\text{Sr}_{0.93}(\text{Ti}_{0.3}\text{Fe}_{0.63}\text{Ni}_{0.07})\text{O}_{3.8}$ and (STFN), $\text{Sr}_{0.93}(\text{Ti}_{0.3}\text{Fe}_{0.56}\text{Ni}_{0.07}\text{Co}_{0.07})\text{O}_{3.8}$ (STFNC) electrodes for IT-S-SOFC in a complete redox-cycle induced by atmosphere at 700 °C. The formation of metallic Fe, bi-metallic Fe-Ni and tri-metallic Fe-Ni-Co NPs on STF, STFN and STFNC, respectively, was followed in-situ by Near-Ambient Pressure X-ray Photoelectron and Absorption Spectroscopies (NAP-XPS and NAP-NEXAFS) that are sensitive to oxidation states. These experiments were conducted at the BEIChem and ISSIS beamlines at the BESSY II synchrotron facility. Complementing laboratory-based techniques such as TPR, XRD, and electron microscopies helped to understand similarities and differences between STFNC, STFN and STF. Although many research's use the term 'exsolution' to describe Fe⁰ reduction in STF or (La,Sr)FeO₃ perovskites, we believe that there is a fundamental difference between exsolution, as observed in STFN and STFNC, and Fe⁰ segregation in STF, which is easily distinguished in the shape and anchoring of the nanoparticle/perovskite system. While exsolved nanoparticles remain in close contact with the surface, segregated nanoparticles detach from the original matrix. This difference affects the reabsorption of the particles upon reoxidation – mostly the amount of nucleation sites (which is bigger for exsolved samples) – showing nanoparticle densities of [endif]-> for NiFe and NiCoFe exsolution in STFN and STFNC, respectively, and only [endif]-> for Fe⁰ segregated particles in STF. Transmission electron microscopy and microanalysis were used to determine NP compositions and crystalline structure after reduction and reoxidation. In our contribution, we will in detail discuss our results focusing on establishing a structure-function relationship that will aid in the insight-driven optimization of these electrode materials.

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10:20 AM BREAK

10:50 AM **EI10.05

Mechanistic Study for the Concurrent Process of Phase Transition and Exsolution and Its Application on Thermal Catalytic Reactions Jeong Woo

Han; Pohang University of Science and Technology, Korea (the Republic of)

Metal nanoparticles (NPs) can be applied to the catalytic application such as water gas shift reaction (WGS), dry reforming of methane (DRM), and SOFC fuel electrode when they are well-dispersed on the support. Since catalyst degradation such as carbon coking and sintering often occurs during long-term operation for conventional loaded metal NPs, the stability of metal NP on the support is one of the most important issues to resolve.

Exsolution is an efficient method for forming well-dispersed metal NP on oxide support (mostly perovskite support). Unlike the loaded metal NP which is produced from the external metal source, exsolution uses metal cations inside the oxide support to create strongly confined NPs to the surface of the support in reduction condition. Due to the strong confinement of NPs on the surface of the support, exsolved NPs have stronger resistance on sintering and carbon coking than conventional loaded NPs [Nat. Commun., 6, 8120 (2015)]. In addition, exsolved NP was also applied in perovskite-based fuel electrode and showed improved cell performance than conventional perovskite-based fuel electrode without exsolved NP [Nat. Commun., 8, 15967 (2017)]. Despite of the high stability of exsolved NP, the restrictions on the total amount of exsolved NP and types of possible combinations of metal and support are still major issues to be solved. Although there are several novel methods (topotactic ion exchange, electrochemical switching) to accelerate exsolution [ACS Nano, 15, 81 (2021)], universal method has not yet been developed.

Herein, we focused on the concurrent process of phase transition and exsolution. When exsolution of metal NP occurred with phase transition of $\text{Pr}_0.5\text{Ba}_0.5\text{MnO}_3$ (PBMO) support to a layered double perovskite (L-PBMO), the exsolution was more facilitated than the conventional exsolution [J. Mater. Chem. A, 8, 3590 (2020)]. We performed the theoretical and experimental study of the acceleration of exsolution by the phase transition of PBMO support [Energy Environ. Sci., 14, 873 (2021)]. The theoretical study by density functional theory (DFT) calculations showed that the selective oxygen vacancy formation in PrO layer plays a key role in the phase transition of PBMO. Co doping promoted the phase transition of PBMO by making PBMO more reducible, and the phase transition promoted the exsolution of Co by making co-segregation of Co easier. These results were experimentally verified.

Exsolution can be further promoted by the phase transition to Ruddlesden-Popper perovskite (R-P, A_2BO_4), which is B-deficient phase more than perovskite and layered double perovskite. Based on the mechanistic study of the phase transition of PBMO, we proposed Gibbs free energy of oxygen vacancy formation in BO_2 layer as a key factor of the phase transition to R-P and found that the reduction in BO_2 layer can be promoted by A-site Sr doping [Nat. Commun., 12, 6814 (2021)]. In our DFT study of $\text{Pr}_0.5(\text{Ba}/\text{Sr})_0.5\text{MO}_3$ (M: transition metal), selective reduction in BO_2 layer in reduction condition was only possible for $\text{Pr}_0.5\text{Sr}_0.5\text{MnO}_3$ (PSMO) and $\text{Pr}_0.5\text{Sr}_0.5\text{FeO}_3$ (PSFO). In in-situ XRD measurement, we can show that the exsolution and the phase transition to R-P of $\text{Pr}_0.5\text{Ba}_0.5\text{FeO}_3$ (PBFO) is promoted by A-site Sr doping, as predicted in our DFT study.

By using the accelerated exsolution by phase transition, we could develop the highly stable catalysts for gas reforming reaction (WGS, DRM, CO oxidation). The developed catalysts showed higher catalytic activity as well as the higher stability than conventional perovskite and loaded metal NP catalyst. These results may guide further development of highly stable and active catalysts for thermal catalytic reactions.

11:20 AM *EI10.06

Gas Reactions on Electrodes for Reversible and Symmetrical Solid Oxide Fuel Cells Boosted by Deliberate Surface Design Liliana V. Moggi^{1,2,3}, Mariano Santaya^{1,2}, Catalina Jimenez⁴, Mauricio D. Arce^{4,1}, Horacio Troiani², Yanet Mansilla^{1,2}, Lucia Toscani^{1,2}, Emilia Carbonio^{4,5}, Axel Knop-Gericke^{5,6}, Regan Wilks⁴, Marianne van der Merwe⁴, Raul Garcia Diez⁴, Enggar Wibowo⁴ and Marcus Bär⁴; ¹CONICET Patagonia Norte, Argentina; ²Comision Nacional de Energia Atomica, Argentina; ³Instituto Balseiro, Argentina; ⁴Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, Germany; ⁵Fritz-Haber-Institut der Max-Planck-Gesellschaft, Germany; ⁶Max-Planck-Institut für chemische Energiekonversion, Germany

Finding a material able to work properly as air and fuel electrode alternatively, in a symmetrical solid oxide fuel cell (S-SOFC), is quite a challenge. Even more if this material must operate reversibly in Fuel Cell (FC) and Electrolyzer (E) modes. This would simplify cell operation and manufacturing by reducing the number of electrode/electrolyte interfaces, improving mechanical and chemical compatibility issues. A few sets of oxides offer good performances for both H_2 oxidation reaction (HOR) and O_2 reduction reaction (ORR). Surface functionalization by nanoparticle (NP) exsolution from ABO_3 perovskites is an interesting method to boost the solid-gas electrode reactions. The formation of metallic NPs when oxide is treated in reducing conditions, generates socketed NPs, creating a unique metal-oxide interaction with the supporting perovskite that pin the NPs, avoiding its coarsening while keeping a high density of triple phase boundaries. However, the exsolution process is complex. It is affected by the material's own parameters: microstructure, composition, crystal defects, etc; and by external parameters: temperature, gas composition, and applied voltage. In addition, when exsolution occurs, it generates modifications at the near surface region that do not always have a positive impact on the electrode reactions. In consequence, several questions emerge: Which factors controls the NP microstructure? Are there additional surface structural modifications? Is this a reversible process? What is the role of NPs in the fuel and air electrode reactions? Can we use redox cycles to refresh the electrode once it degrades over time? To answer these questions, we studied the exsolution/reoxidizing process and its effects on the solid-gas electrode reaction in Ni-doped $\text{Sr}(\text{Ti},\text{Fe})\text{O}_3$ perovskites. We analyzed the mechanism of HOR and ORR by impedance spectroscopy. The studies were complemented by TPR, TG, XRD, SEM and TEM. NP features depend both on final conditions and on the pathway for reduction; e.g. a high density of Fe-rich nanoparticles is obtained if exsolution occurs by switching from air to reducing atmosphere at 700 °C. Anyway, a different result is obtained if the temperature is slowly raised in reducing conditions. The presence of NPs always promotes the H_2 dissociative adsorption step. The ORR is improved once the electrode is reoxidized, mainly because there is a change of mechanism in the O-surface reaction. For deeper understanding additional operando X-ray spectroscopy experiments were performed. The operando conditions included switching between reducing and oxidizing atmosphere and high temperature and electrode polarization. We found that NPs exsolution and reoxidation are triggered and controlled by these parameters. The exsolution starts with a fast and complete reduction of Ni. This drags the Fe to form Ni-Fe nanoalloys and also a Sr-enrichment at the surface and the near surface regions occurs. At high anodic potential (FC mode) the NPs are oxidized, decreasing the current. Contrary, under cathode potential (E mode), the original NPs were retrieved and if the potential is too high the concentration of metallic Fe increases as well the Sr-surface concentration. Alternatively if the electrode is treated in oxidizing atmosphere (either in FC and E modes), the pristine condition is partially recovered: the Fe is reincorporated, Ni remains at the surface as NiO nanoparticles and Sr-concentration is recovered at the near surface region but not totally at the surface. Thus, by cycling the electrode between reducing and oxidizing conditions the electrode can partially be revived. Thus in our contribution we will paint a comprehensive picture of the chemical structure of Ni-doped $\text{Sr}(\text{Ti},\text{Fe})\text{O}_3$ perovskites and how it changes upon FC/E mode operation with a focus on how the surface properties impact the underlying working principle and how their deliberate design can be used to rationally optimize the electrode properties.

11:40 AM EI10.07

Clarifying True Value of Activated Oxygen Incorporation Reaction by Heterogeneous Catalyst Jinwook Kim, Geon Gug Yang, Yoonseok Choi, Hyunseung Kim, Seongwoo Nam, Jongsu Seo, Jun Kyu Kim and WooChul Jung; Korea Advanced Institute of Science and Technology, Korea (the Republic of)

Solid oxide cells (SOCs) are promising next-generation energy devices that convert chemical fuels and electrical power to each other with high efficiency. Despite many attempts to lower the operating temperature of the device to realize the commercialization of SOC, the insufficient oxygen incorporation

reaction (OIR) rate in air electrode remains a big issue. To lower high hurdles of activity toward oxygen incorporation reaction, various attempts were conducted to make high-performance cathodes. There have been researches to improve the activity of electrochemical reaction by introducing various catalysts to cathode electrode as a solution to solve this problem [1,2]. Most representatively, transition metal nanoparticles such as Pt, Pd, Ag, Cu, Ni, and Co, or oxide nanoparticles with high oxygen conductivity such as doped ceria were adopted [3,4,5]. Some of these studies have shown noticeable decreases in electrode resistance through the introduction of nanoparticle catalysts [3,4], while others have shown only minor effects [5]. Fundamental study of intrinsic characteristics of nanoparticles in the electrochemical reactions is very difficult due to the extremely high complexity of OIR in a typical SOFC electrode. The complex geometry of electrodes with uneven distribution of poly-dispersed nanoparticles, severe sintering of nanoparticles, or segregation of cathode material during the electrochemical performance measurement makes it impossible to evaluate an accurate role of each nanoparticle. In addition, the natural complexity of OIR which contains adsorbate species, ionic defects, and electronic defects makes it much hard for mechanism study. This study aims to quantitatively evaluate the electrode activity according to the type of nanoparticles, find the dominant reaction sites of the activated electrode by nanoparticles, define the activated mechanism by nanoparticles. In this research, geometrically and chemically well-defined model $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-x}$ electrodes with perfectly ordered arrays of monodisperse nanoparticles were adopted [6]. Electrochemical performance for OIR was analyzed by measuring partial oxygen pressure and over-potential dependent oxygen exchange current [7,8]. *In-operando*, synchrotron-based X-ray photoelectron spectroscopy analysis was used to explore the surface defect information [8].

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11:55 AM EI10.08

Controlling the Size of Au Nanoparticles on Reducible Oxides with Electrochemical Potential Dongha Kim, Georgios Dimitrakopoulos and Bilge Yildiz; Massachusetts Institute of Technology, United States

Controlling the size of Au nanoparticles (NPs) and their interaction with the oxide support is important for their catalytic performance in reactions of importance to fuels and chemicals synthesis, such as methane oxidation, CO oxidation, H_2O splitting, and water-gas shift. It is known that the oxygen vacancies at the surface of support oxides form strong chemical bonding with the Au NPs and prevent their deactivation due to sintering¹. The resulting Au/oxygen vacancy interface also acts as an active site for oxidation reactions. Small Au NPs are needed to increase the density of the Au/oxide interface and thus high catalytic activity. Given the chemical affinity between the surface oxygen vacancies of a support oxide and the Au NPs, it is intriguing to think whether one can also systematically control the size of Au NPs by controlling the surface oxygen vacancies. We expect an increase in oxygen vacancies can serve as an increase in nucleation sites, and at the same time stabilize a larger density and smaller size of particles. However, a way to control the size of the deposited Au NPs on an oxide support is not established. Here, we demonstrate an electrochemical method that allows us to control the size of the Au NPs by controlling the concentration of surface oxygen vacancies on the support oxide. Oxides with different reducibility, $\text{La}_{0.8}\text{Ca}_{0.2}\text{MnO}_{3-\delta}$ (LCM) and $\text{Pr}_{0.1}\text{Ce}_{0.9}\text{O}_{2-\delta}$ (PCO), are used as a support oxide. By applying electrochemical potential, we achieve a wide range of effective pO_2 (10^{-37} to 10^{14} atm) in the support oxide. Applying negative, cathodic potential creates a high concentration of oxygen vacancies and transforms the pre-sputtered Au layer into finely distributed Au NPs with sizes less than 10 nm at 770C in 10min. The Au NPs maintained their size even with prolonged annealing time (3h) under the same conditions. Such high thermal stability of Au NPs observed in this study is comparable to that of the Au/TiO₂ system achieved through an encapsulation strategy in a recent study². On the other hand, applying positive, anodic potential removes oxygen vacancies at the surface and transforms the pre-sputtered Au layer into bigger Au NPs with an average size of 20 nm. Also, the onset potential required to control the size of Au NPs depends strongly on the oxygen non-stoichiometry of the support oxide. The more reducible oxide, LCM, starts to create additional oxygen vacancies and form smaller Au NPs at a lower negative potential (-0.3 V) than PCO (-1.5 V).

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12:10 PM EI10.09

Deposition and Stabilization of Bimetallic Oxide Nanoparticles for Enhanced Electro-Catalytic Activity of $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_3$ SOFC Cathode Nikolai Tsvetkov and WooChul Jung; Korea Advanced Institute of Science and Technology, Korea (the Republic of)

One of the major barriers to build solid oxide fuel cells (SOFCs) with high power output at intermediate, 500-700 °C, temperature range is the slow oxygen reduction reaction (ORR) rate on the SOFC cathode. The activity for oxygen reduction reaction (ORR) of the cathodes can be enhanced by the deposition of the highly reactive metal or metal oxide nanoparticle (NPs). However, at the high temperature operation conditions of cathode the transition metal oxides such as Cu, Co or Ni oxides have tendency for agglomeration and dissolution in perovskite oxide material of cathode. This is considered as the major obstacle for application of this strategy for SOFCs [1]. Thus, the NP-focused studies in SOFC field are mostly related with the utilization of nanocatalysts based on large cations such as Pt, Ce or Ag, however the possible role of abundant transition metal NPs is not investigated.

Recently it was demonstrated that the chemical passivation of the surface of perovskite oxide electrodes with low reducible cations such as Hf, Ti or Al can improve the electrode surface stability itself as well as the stability of nanoparticles [2,3]. In this work we further developed this strategy to use surface passivation approach to prevent transition metal oxide nanoparticle dissolution and agglomeration.

We performed the infiltration and stabilization of the various transition metal binary oxide and bimetallic metal oxide nanoparticles with the size below 10 nm on the surface of the porous $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_3$ (LSC) electrode. The effects on the NPs of different types on the ORR processes was investigated. Our results have shown that utilization of n-type oxide NPs such as ZnO leads to significant decrease in the ORR rate step related with the oxygen diffusion/incorporation processes but slows down the charge transfer step. The negative effect of ZnO NPs on charge transfer was suppressed when bimetallic NiZn oxide NPs were used. Thus, we have demonstrated how the optimization of the surface structure can significantly decrease the electrode area specific resistance reaching the values below than 0.1 Ohm/cm² for bimetallic NiZn oxide NPs. Moreover, the electrode with NPs have shown the good stability during more than 100h of operation at 600°C in humidified air atmosphere. Post-analysis reveals the stability of NPs at the electrode surface even some increase of NPs size up to 20 nm was taking place.

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12:25 PM EI10.10

Effects of Surface Additives on Electrochemical Performance and Chemical Capacitance in Mixed Conducting Oxides Han Gil Seo¹, Anna Staerz¹, Dino Klotz^{2,1} and Harry Tuller¹; ¹Massachusetts Institute of Technology, United States; ²Kyushu Daigaku, Japan

The oxygen non-stoichiometry of mixed ionic and electronic conducting (MIEC) oxides plays a central role in a variety of energy applications including energy conversion and storage devices (solid oxide fuel/electrolyser cells (SOFCs/SOECs), oxygen permeation membranes, batteries, and gas sensors, facilitating the surface oxygen exchange reaction. Oxygen non-stoichiometry can be formally quantified by the chemical capacitance, defined as the ratio of the change in charge oxygen vacancy concentration to the corresponding change in chemical potential. Although extensive studies on the enhancement or degradation of oxygen exchange kinetics of MIEC oxides have been investigated, their correlation with changes in surface chemical capacitance remains unclear. Recently, we observed that the rate of oxygen exchange of the MIEC $\text{Pr}_{0.1}\text{Ce}_{0.9}\text{O}_{2.8}$ (PCO) SOFC cathode material can be markedly influenced by surface additives. Indeed, we demonstrated systematic variations in exchange coefficient by over 6 orders of magnitude by controlling the acidity of additives that ranged from strongly acidic to strongly basic [1]. The increase or decrease in exchange kinetics was attributed to the induced relative accumulation (basic) or depletion (acidic) of surface electrons, respectively, potentially leading in turn to changes in near surface oxygen non-stoichiometry.

Here, we systematically investigate the effect of surface additives on electrochemical performance and chemical capacitance of mixed conducting SOFC cathodes using electrochemical impedance spectroscopy (EIS). Symmetric cells (cathode|electrolyte|cathode) were prepared by screen-printing and pulsed laser deposition (PLD) methods, followed by infiltration with basic and acidic additives. Changes in area-specific resistance (*ASR*) and chemical capacitance (C_{chem}) induced by the additives were monitored by AC impedance spectroscopy. While basic additives led to decreased *ASR* as expected, they also led to enhanced values of C_{chem} , while the reverse trends were observed for acidic additives. These preliminary findings appear to be consistent with changes in surface oxygen non-stoichiometry corresponding to the relative accumulation or depletion of electrons near the surface. These observations suggest that the engineering of surface chemical capacitance can be used as a mean of predicting and ultimately controlling electrochemical performance.

SESSION EI11: Solid-State Batteries I
 Session Chairs: Kisuk Kang and Kazunori Takada
 Thursday Morning, July 21, 2022
 Mezzanine Level, Second Floor, Berkeley/Clarendon

9:10 AM **EI11.01

Kinetics and Stability of Anode and Cathode Interfaces in Thiophosphate Based Solid-State Batteries Jürgen Janek^{1,2}; ¹Justus Liebig Universität Giessen, Germany; ²Karlsruher Institut für Technologie, Germany

The electrode interfaces are the Achilles heels of solid-state batteries based on thiophosphate solid electrolytes. Due to the relatively narrow thermodynamic stability range of these electrolytes - P(V+) is easily reduced and S(II-) is easily oxidized - the formation of interphases strongly influences the long term behavior of both anodes and cathodes. In this keynote, the state of research on the lithium metal anode and on cathode materials with high potential (layered oxide compounds like NCM or NCA) is discussed and own recent results will be presented.

At the lithium metal anode thiophosphate solid electrolytes are reduced and decomposed, leading to the growth of an interphase (SEI) and an increasing anode impedance. Combining various experimental techniques, i.e. impedance spectroscopy, dc measurements, X-ray photoelectron spectroscopy (XPS), time-of-flight secondary ion mass spectrometry (ToF-SIMS) and focused ion beam cross sectioning, we obtain comprehensive information on the chemical composition and the microstructure of the SEI, including quantitative information on the thickness. In contrast to previous reports, the SEI can be relatively thick, which has important implications for application. In addition to these stability issues, the plating and stripping behavior is considered in detail, pore formation and the role of the SE crystallinity is discussed.

The cathode interface of uncoated cathode material also suffers from serious degradation of the solid electrolyte, caused by oxidation. Based on a systematic analytical study using a similar set of techniques as in the case of the anode interface, two different degradation mechanisms are found. At low and medium potentials, the thiophosphate SE is oxidized by simple loss of lithium, leading primarily to oxidation of the sulfur atoms and oligomerization of PS_4 structural units. At higher potentials, the oxide cathode active materials can lose oxygen which enters into the oxidation reactions and leads to the formation of sulfate/phosphate species and strong impedance increase. These degradation reactions can only be avoided effectively by protective coating of the cathode active material. In this keynote, the current state of research on cathode coatings is briefly reviewed and novel own results are presented. Halide solid electrolytes will be highlighted as a novel type of potential coating materials.

Finally, the kinetics of both anode and cathode degradation will be analyzed from the viewpoint of solid state reactivity. Quantitative measurements of the impedance increase and the degree of reduction/oxidation at different SOC and temperature offer deep insight into the underlying mechanisms. In both cases, the rate of degradation is governed by diffusion control, thus parabolic rate laws can be proven. The resulting rate constants are analyzed quantitatively, which allows far-reaching conclusions on the properties of the interphases formed at anode and cathode.

The prospect of solid-state batteries with thiophosphate electrolytes is analyzed, and future research directions are suggested.

9:40 AM *EI11.02

Drastic Reduction of Solid Electrolyte–Electrode Interface Resistances Taro Hitosugi; Tokyo Institute of Technology, Japan

Solid-state Li batteries are promising energy storage devices owing to their high-energy densities with improved safety. However, the large interface resistance at the interface of solid-electrolytes and electrodes hinders the development of solid-state Li batteries.

By fabricating the interfaces using thin-film technology, we demonstrated that Li_3PO_4 - LiCoO_2 interface resistances could become $\sim 5 \Omega\text{cm}^2$ [1,2]; the value is much smaller than that of liquid-electrolyte-based Li-ion batteries [3]. We also confirmed that Li_3PO_4 - $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ [4,5], Li_3PO_4 - $\text{LiCo}_{0.5}\text{Mn}_{1.5}\text{O}_4$ [6], Li_3PO_4 - $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ [7], and Li_3PO_4 - $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_4$ [8] interfaces also show low interface resistances. These studies strongly encourage solid-state Li battery research by demonstrating a very low interface resistance leading to fast charging and discharging.

We have recently revealed a method to drastically reduce the electrical resistance at the interface of a solid electrolyte and a positive electrode [9]. It is well known that the interface resistance increases when the electrode surface is exposed to air. However, an effective method of reducing this resistance has not been developed. Our study demonstrates that a drastic reduction of the resistance is achievable by annealing the entire battery cell. Exposing the LiCoO₂ positive electrode surface to H₂O vapor increases the resistance by more than ten times (to greater than 136 Ωcm²). The magnitude was reduced to the initial value (10.3 Ωcm²) by annealing the sample in a battery form. First-principles calculations reveal that the protons incorporated into the LiCoO₂ structure are spontaneously deintercalated during annealing to restore the low-resistance interface. These results provide fundamental insights into the fabrication of high-performance all-solid-state Li batteries.

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10:00 AM EI11.03

Electrochemical Stability of Electrode/Electrolyte Interfaces in Metal Borohydride Solid Electrolytes Matthew Ko, Yiliang Li and Yet-Ming Chiang; Massachusetts Institute of Technology, United States

To meet the promise of all-solid-state batteries, solid electrolytes that are electrochemically stable at both low and high potential, have high metal ion conductivity, low electronic conductivity, and sufficiently high critical current density to avoid metal dendrite penetration are required. Metal borohydrides are a relatively new class of compounds that is being explored for its potential as solid electrolyte materials. Here, we examine the electrochemical stability and critical current density of sodium amide borohydride (Na₂NH₂BH₄, or NNB) over the potential range 0 to 5 V vs. Na/Na⁺, using electrodynamic methods, X-ray photoelectron spectroscopy (XPS) characterization of the interfacial reaction products¹, and electron microscopy characterization of microstructure. We observe SEI and CEI layers that appear to passivate the NNB electrolyte over a wide voltage range. XPS measurements indicate that the passivating SEI and CEI layers are composed of a family of sodium hydrides and borohydrides whose specific stoichiometries agree with reaction products predicted by DFT calculations². Impedance spectroscopy shows that with appropriate formation cycles, the passivating layers contribute <10% to electrolyte resistance in the test cells.

Acknowledgements: This work was supported as part of the Joint Center for Energy Storage Research, an Energy Innovation Hub funded by the U.S. Department of Energy, Office of Science, Basic Energy Sciences.

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10:15 AM EI11.04

Quantitative Investigation of the Resistances at the Interfaces of Sulfide Electrolytes and Positive Electrodes Kazunori Nishio¹, Daisuke Imazeki¹, Kosuke Kurushima², Yuki Takeda¹, Ryo Nakayama¹, Ryota Shimizu¹ and Taro Hitosugi¹; ¹Tokyo Kogyo Daigaku, Japan; ²Kabushiki Kaisha Toray Research Center Kenkyu Bumon Shiga, Japan

A low interface resistance between the sulfide solid electrolyte and the electrode is critical for developing all-solid-state Li batteries. However, the origin of interface resistance has not been well established. This study reports the resistance values across the interface between an amorphous Li₃PS₄ solid electrolyte and a LiCoO₂(001) epitaxial-thin-film positive electrode in a thin-film Li battery. At the Li₃PS₄-LiCoO₂(001) interface, a high interface resistance is observed (3.5 × 10⁴ Ωcm²), which is attributed to the spontaneous formation of an interfacial layer between the solid electrolyte and positive electrode upon contact. In contrast, the introduction of a 10 nm thick Li₃PO₄ buffer layer between the solid electrolyte and positive electrode layers suppresses the formation of the interfacial layer, thereby leading to a 2,800-fold decrease in the interface resistance (12.6 Ωcm²). These results clearly indicate the role of the buffer layer and reveal the origin of interface resistance; the origin is mainly due to the chemically formed interphase layer. The results negate the model for space charge layer formation as the origin of interface resistance. The investigation shows that the interfacial layer significantly increases the interface resistance. Further, this result is contrary to the previous reports that claim the interphase layer is formed by electrochemical reactions; this study reveals that the layer spontaneously forms upon contact.

10:30 AM BREAK

11:00 AM **EI11.05

Lithium Plating-Stripping Reaction on Li⁺ Conductive Solid Electrolyte Yasutoshi Iriyama and Munekazu Motoyama; Nagoya Daigaku, Japan

Lithium metal has been expected as an anode material of next-generation rechargeable batteries, such as all-solid-state batteries (SSBs), Li-air batteries, Li-S batteries, etc. Li metal anode has been successfully used in thin-film SSBs, and stable charge-discharge reactions are repeated for over ten thousand cycles. Application of in-situ formed, that is, electrochemically grown, Li has also been proposed to simplify the battery manufacturing process. Thus, it is important to understand fundamental aspects of Li plating-stripping reaction on solid electrolytes for applying Li metal anode well in the above-mentioned advanced batteries.

The author's group has focused on lithium plating-stripping reactions on lithium phosphorus oxynitride glass electrodes, LiPON, as a model system. The LiPON/LATP/LiPON multi-layered cell was formed, where LATP is flat-textured Li⁺ conductive solid electrolyte (Ohara Inc.) but unstable with Li, and then LiPON is used as a protective layer. Current collector thin films (CC) were deposited on one side of LiPON film, and the Li metal film was opposite side. The Li nucleation and growth reaction at the CC/LiPON interface depends on the current densities, temperature, mechanical properties, current collector species, etc. Some of those reactions were observed by operando SEM analysis. During the Li stripping process at high current densities, voids are formed at the Li/LiPON interface and then parts of electrochemically-grown Li are disconnected and then degrade the coulomb efficiency.

In this presentation, the authors would like to discuss on Li plating-stripping reaction on solid electrolytes focusing on electrode/solid electrolyte interface

using some of operando SEM movies.

11:30 AM EI11.06

Electrochemical Protocols for Failure Mitigation and Safe Operation of All-Solid-State Batteries [Ruhul Amin](#), Anand Parejiya, Marm Dixit, Rachid Esschli and Ilias Belharouak; Oak Ridge National Laboratory, United States

Solid-state batteries (SSB) have several interfaces such as anode | solid electrolyte (SE), cathode | SE, catholyte | active material, etc. These interface properties vary depending on the contact condition, energy states, type defects, and chemical/electrochemical stability. SSB life and performance rely largely on these interfaces since dendrite formation, Li-depleted space-charge layer generation, and spatial variation in interfacial adhesion originates at the interfaces, which leads to battery failure. Stabilizing anode | SE interface is crucial for the development of high-energy-density solid-state batteries. Current approaches in Li metal stabilization employ the energy and cost-intensive protocols that have a detrimental impact on the techno-economic feasibility of the SSBs. This presentation will focus on the facile, electrochemical protocol for improving the interfacial impedance and contact at the Li | $\text{Li}_{6.25}\text{Al}_{0.25}\text{La}_3\text{Zr}_2\text{O}_{12}$ (LALZO) interface. Applying a fraction of second short-duration high voltage pulse to a poorly formed interface leads to a sustained improvement in contact impedance and lower overpotentials for electrodeposition and electro-dissolution [1]. The theoretical simulations support that the high local current density in the vicinity of pores at the interface can lead to Joule heating leading to the improvement of the interface. This high pulse protocol does not induce the formation of dendrites on the symmetric cells. This electrochemical protocol has direct application in battery formation cycles as well as online management systems for SSBs. This presentation will also discuss the dendrite healing process by using the current-voltage protocol to revive the battery cell from the failure state [2].

Reference

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11:45 AM EI11.07

Elucidation of the Kinetics at the $\text{Na}|\text{Na}_{3.4}\text{Zr}_2\text{Si}_{2.4}\text{P}_{0.6}\text{O}_{12}$ Solid-State Battery Electrode Interface [Till Ortmann](#)^{1,1}, Simon Burkhardt^{1,1}, Janis K. Eckhardt^{1,1}, Ziming Ding^{2,3}, Joachim Sann^{1,1}, Marcus Rohnke^{1,1}, Qianli Ma⁴, Olivier Guillon^{4,5}, Christian Kübel^{2,2} and Jürgen Janek^{1,1}; ¹Justus Liebig Universität Giessen, Germany; ²Karlsruher Institut für Technologie, Germany; ³Technische Universität Darmstadt, Germany; ⁴Forschungszentrum Jülich GmbH, Germany; ⁵JARA, Germany

Much effort has been made in recent years to use alkali metal anodes in combination with solid electrolytes to increase the energy density of next generation batteries. Due to its high ionic conductivity, $\text{Na}_{3.4}\text{Zr}_2\text{Si}_{2.4}\text{P}_{0.6}\text{O}_{12}$ is a promising candidate as solid electrolyte for solid-state sodium batteries. Beside the ionic conductivity, the thermodynamic stability as well as the interfacial kinetics are key knowledge for developing sodium metal anodes. Since the stability of $\text{Na}_{3.4}\text{Zr}_2\text{Si}_{2.4}\text{P}_{0.6}\text{O}_{12}$ vs. sodium was not studied so far, the material has been investigated by time resolved impedance analysis in combination with in situ X-ray Photoelectron Spectroscopy (XPS) revealing the formation of a kinetically stabilized interlayer. Despite this interlayer, only an increase of the overall impedance resistance of $2 \Omega\text{cm}^2$ is observed while no assignable interfacial contribution in the impedance data can be detected within the equivalent circuit. The morphology of the $\text{Na}|\text{Na}_{3.4}\text{Zr}_2\text{Si}_{2.4}\text{P}_{0.6}\text{O}_{12}$ interface was visualized by Focused Ion Beam Scanning Electron Microscopy (FIB-SEM) as a function of the external pressure. Already at low pressures of 1.7 MPa a near-ideal interfacial contact without gaps is obtained supporting the fact that no interfacial resistance can be detected by impedance analysis. Based on pressure and temperature dependent impedance analysis, we conclude that the $\text{Na}|\text{Na}_{3.4}\text{Zr}_2\text{Si}_{2.4}\text{P}_{0.6}\text{O}_{12}$ interfacial kinetics is limited by current constriction rather than by the charge transfer process. Finally, the anodic dissolution of sodium at the $\text{Na}|\text{Na}_{3.4}\text{Zr}_2\text{Si}_{2.4}\text{P}_{0.6}\text{O}_{12}$ interface was studied at various external pressures. We prepared cross sections by FIB-SEM to visualize the formed pore structure due to the accumulation of sodium metal vacancies near the interface. At extremely low pressures ($p=10^{-3}$ Pa) lenticular structures are observed, whereas at 0.3 MPa no regular pore structures are discovered. By means of time resolved impedance spectroscopy, conclusions are drawn about the morphological development of the pore structure after anodic dissolution. Even under extremely low external pressures a reduction of the total impedance of more than $100 \Omega\text{cm}^2$ is observed indicating dynamic changes of the interfacial structure which is attributed to vacancies diffusion. By increasing the external pressure the regeneration of the interfacial contact is more pronounced which can be explained by higher dislocation climbing/movement (creep) besides metal vacancy diffusion.

12:00 PM EI11.08

Surface Modifications as a Route Towards Improved Solid-State Sodium Metal Batteries [Wojciech Zajac](#), Aleksandra Boron, Weronika Sordyl and Michal Chmiest; Akademia Gorniczko-Hutnicza imienia Stanislawia Staszica w Krakowie, Poland

Energy storage belongs to the central topics in power supply chains, especially when intermittent renewables, such as wind and sun, take the lead among various energy sources. As electrochemical batteries offer short response time, high energy and power density, along with high efficiency, they became one of the most promising energy storage techniques. Currently lithium batteries are the first choice when portable electronics, electric vehicles and grid energy storage are concerned. However, due to limited reserves of raw materials various alternatives are considered. Among them solid state sodium metal batteries recently attracted vivid interest in the scientific community due to utilization of abundant raw materials, high energy density and increased safety. A key factor determining performance and safety of the sodium metal electrochemical cell are the interfaces between the solid state electrolyte and the electrodes, as it is where the charge transfer, a limiting step for operation of an electrochemical cell, occurs. In this work we aim to verify a hypothesis that wettability of a solid state electrolyte by metallic sodium, and in a more general sense interfacial properties, are critical factors governing plating and stripping behavior of sodium metal electrode as well as dendrite growth inside a ceramic electrolyte.

Four alloying additives to sodium metal: silicon, antimony, tin and indium were selected as agents affecting contact angle, and investigated in symmetrical all-solid-state Na/solid electrolyte/Na cells with two ceramic solid electrolytes: $\beta\text{-Al}_2\text{O}_3$ and NaSICON $\text{Na}_3\text{Zr}_2\text{Si}_2\text{PO}_{12}$. Moreover, the effects of various surface treatments of the solid state electrolyte on the solid electrolyte/Na interface are discussed: grinding and polishing, heat treatment under inert, oxidizing and reducing atmospheres, surface impregnation, as well as vacuum sputtering with gold and platinum particles.

Charge transfer resistance of the electrode/electrolyte interface was measured for symmetrical Na/solid electrolyte/Na cells using electrochemical impedance technique (EIS) including distribution of relaxation times (DRT) analysis. Interface stability and critical current density before short circuit was measured using galvanostatic method. Contact angle between each of the molten alloys and two of the electrolytes was measured under argon atmosphere using static sessile drop technique. X-ray Photoelectron spectroscopy (XPS), Raman microscopy and scanning electron microscopy (SEM) were applied to investigate solid electrolyte's surface before contact with the sodium metal electrode. Correlation between surface chemical composition, contact angle and electrochemical performance is discussed in this work.

Acknowledgements:

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12:15 PM EI11.09

Anion Control of the Electrolyte $\text{Na}_{3-x}\text{SbS}_{4-x}\text{Br}_x$ Extends Cycle Life in Solid-State Sodium Batteries Xin Zhang and [Stefan Adams](#); National University of Singapore, Singapore

Among the solid electrolytes studied for all-solid-state sodium batteries Na_3SbS_4 (NAS) appears particularly promising due to its unique combination of high ionic conductivity and compatibility with humid air, which lowers the cost of processing and facilitates large-scale industrial application. Considering that partial substitution of sulfur by halide ions increases the number of mobile sodium vacancies, we developed a low-cost structural modification to NAS by integrating a doping step with the aqueous synthesis. Through a highly feasible low-cost aqueous synthesis approach, bromide anions were effectively doped into Na_3SbS_4 , as demonstrated by Rietveld refinement of site occupancy and unit cell increase, as well as a variation of the NMR chemical shift. Here we focus predominantly on investigating how Bromine doping affects the microstructure and kinetic electrochemical stability of the electrode:solid electrolyte interfaces [1]. The Br-doped sodium electrolyte demonstrates enhanced ionic conductivity, greatly reduced ionic migration barrier, and improved sodium compatibility.

Extent, location and homogeneity of Br doping are clarified by NMR, XRD and electron microscopy analysis. The impact of doping on the ion transport properties is studied by static energy landscape analyses as well as molecular dynamic simulations. Our Br-doped NAS exhibits greatly reduced activation energy down to 0.12 eV. Thereby, the total ionic conductivity is more than doubled allowing for solid state batteries with lower overpotentials. The crystal structure and ^{23}Na local chemical environment analysis reveal that Br partially substitutes S modifying the Na^+ migration pathways. The sodium released to balance the charge on Bromide doping preferably comes from the 8-fold coordinated Na2 site rather than the 6-fold coordinated Na1 site. Molecular dynamics simulations demonstrate that the high ionic conductivity with low activation energy is of extrinsic nature and the low migration energy is caused by dynamic rotational disorder of the tetrahedral polyanion building blocks.

Bromide doping is found to facilitate the densification and smoothens the surface of cold-pressed pellets, which further enhances the achievable total ionic conductivity. Maybe even more important than the enhancement of the ionic conductivity is the strongly enhanced kinetic stability of our Bromine-doped electrolyte in contact with both sodium metal and alloy anodes, which along with the improved interface morphology allows to enhance both rate performance and cycle life of solid-state batteries at the same time. Stable cycling profiles of the doped NAS vs. both sodium-metal anodes and sodium-tin alloy anodes evidenced a major enhancement of the electrochemical stability and thus a path towards longer cycle life all-solid-state sodium metal batteries.

[1] X. Zhang, K. C. Phuah and S. Adams, *Chem. Mater.* **33** (2021) 9184–9193.

SESSION EI12: Solid-State Batteries II
Session Chairs: Taro Hitosugi and Jongwoo Lim
Thursday Afternoon, July 21, 2022
Mezzanine Level, Second Floor, Berkeley/Clarendon

2:00 PM *EI12.02

Electron and Ion Transfer at Solid-Solid Interface—DFT-Based Electrochemistry with Explicit Interface Model [Yoshitaka Tateyama](#); National Institute for Materials Science, Japan

Interfacial resistance and degradation is one of the most essential issues for realization of solid-state battery (SSB). To understand the mechanisms on the atomic scale, we have recently developed an efficient sampling method for probable solid-solid interface structures with explicit interface model [1]. Using this method with accurate density-functional-theory (DFT) calculations, we have explored the electronic and ionic behaviors of various solid-solid interfaces on the atomic scale to acquire guiding principles to control the interfacial problems.

In this talk, we first introduce the study on the interfaces of NASICON-type oxide $\text{Li}_{1+x}\text{Al}_x\text{Ti}_{2-x}(\text{PO}_4)_3$ (LATP) Solid Electrolyte (SE) with LiCoO_2 (LCO) cathode and Li metal anode, as a representative example of phosphate SE [2]. Adopting $x=0.17$, we investigated the electron and ion transfer behaviors at the interfaces by the Li standard chemical potential and the electronic band offsets. Especially, we considered the model situations of (1) upon contact, (2) after annealing and (3) during charging. For the LATP/LCO interface, the results indicated the Li-ion transfer from LCO to LATP upon contact until a certain electric double layer is formed under equilibrium, in which LCO is partially reduced. The calculation results agree well with experimental observations. Co–Ti exchange was also found to be favorable where the Li ion moves with Co^{3+} to LATP. We also explored the possible interfacial processes during annealing by simulating the oxygen removal effect and found that oxygen vacancy can be more easily formed in the LCO at the interface. It implies that partial Li ions move back to LCO for the local charge neutrality. The calculation results are well in line with the experiments. We also demonstrated higher Li standard chemical potential around the LATP/LCO interfaces, leading to the dynamical Li-ion depletion upon charging.

We also discuss the coating layer effect of LiNbO_3 (LNO) in the LCO/b- Li_3PS_4 (LPS) interfaces [3]. The coating layers usually mitigate the interfacial resistance and degradation. The calculated electronic states indicate that the LNO layer prevents the electron transfer between LCO and LPS, leading to the suppression of the SE oxidation. In addition, to examine the interfacial Li-ion transport, we evaluated the position-dependent energy profile of Li-ion, the Li-ion standard electrochemical potential in our definition, by using the electronic band offset, associated with the electronic electrochemical potential, and the Li standard chemical potential (Li vacancy formation energy). Note that the DFT calculation condition was regarded as the standard condition. Consequently, the electronic adjustment was found dominant in the LNO layer, which provides the rather smooth Li-ion standard electrochemical potential around the interfaces. This approach provides a microscopic electrochemistry picture based on the DFT calculations.

These works were done in collaboration with Dr. Bo Gao and Dr. Randy Jalem in NIMS, Japan and Prof. Hong-Kang Tian in National Cheng Kung University, Taiwan, and partly supported by MEXT as “Program for Promoting Researches on the Supercomputer Fugaku” (Fugaku Battery & Fuel Cell Project) and JSPS KAKENHI “Interface IONICS” Grant Number JP19H05815.

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2:20 PM EI12.03

In Operando Characterization of Interface Between Al doped $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ Garnet Solid Electrolyte and $\text{LiNi}_{0.6}\text{Mn}_{0.2}\text{Co}_{0.2}\text{O}_2$ Cathode by Soft X-Ray Absorption Spectroscopy [Younggyu Kim](#) and Bilge Yildiz; Massachusetts Institute of Technology, United States

All-Solid-State Li-ion Batteries have multiple advantages over conventional batteries based on liquid electrolytes such as higher capacity, higher power, and non-flammability. $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ is particularly promising as a solid electrolyte due to its chemical stability with Li metal anode. However, cathode side instability of $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ still remains an issue. Computational studies predict instability between layered oxide cathodes and $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$, and formation of secondary phases with low Li-ion conductivity at the cathode/solid electrolyte interface during cycling. This causes irreversible capacity loss and overpotential increase during cell operation. Despite the importance of the issue, experimental validation of computationally predicted phases and their onset condition is still missing. Conventional characterization method such as X-Ray Diffraction is not suitable to capture onset conditions, as they are not appropriate for characterizing phases with small quantity and low crystallinity. Development of in-operando characterization method with high sensitivity is necessary.

Soft X-ray Absorption Spectroscopy (XAS) offers precise chemical characterization of phases as it is sensitive to both oxidation states and local chemical environment of elements. This made soft X-ray Absorption Spectroscopy a popular technique for characterizing degradation of cathodes in liquid environment. However, there had been only limited attempts on using soft XAS on characterization of cathode/solid electrolyte interface due to difficulty of characterizing buried interface with the technique. Major challenge comes from the limited detection depth of soft XAS.

We designed a model cell consisting thin film cathode and thin film current collector to solve the issue. The cathode/solid electrolyte interface is within detection depth of soft XAS in this design, so we could investigate interfacial chemistry with the technique. We chose $\text{LiNi}_{0.6}\text{Mn}_{0.2}\text{Co}_{0.2}\text{O}_2$, which is a high-voltage and high-capacity cathode, for the experiment. The model cell was cyclable at room temperature without applied pressure, which made the cell compatible with experimental setup at the beamline (23-ID-2 (IOS), NSLS-II). With this cell, we present the first in-operando soft XAS data of layered oxide cathode/ $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ interface during electrochemical cycling.

2:35 PM BREAK

3:00 PM **EI12.04

Thin-Film Solid-State Batteries with Epitaxial LiCoO_2 Films Kazunori Takada and Tsuyoshi Ohnishi; Busshitsu Zairyo Kenkyu Kiko, Japan

Use of solid electrolytes is anticipated to provide high reliability to lithium-ion batteries, which is beneficial for large-sized batteries, because batteries for electric vehicles and energy storage need high durability such as extremely long cycle life. On the other hand, there are new demands arising for small batteries, e.g., IoT, MEMS etc. Another aspect of solid-state and thin-film batteries is model systems for the fundamental research on battery materials.

Interfaces between the battery materials

Battery reactions in solid-state systems are simple, because only lithium ions are mobile to take part in the electrochemical reactions. The single-ion conduction suppresses side reactions, and electrode materials never dissolve into the electrolytes. In addition, geometry of the electrochemical systems is also simplified in thin-film systems: interface between the electrode and electrolyte is flat, and ionic diffusion can be regarded as one dimensional. Interfaces are attracting much attention in the research on solid-state batteries, because the highest conductivities in solid electrolytes have become comparable to that of liquids, and the interfaces are often rate-determining and govern the battery performance. However, complicated geometry of interfaces in bulk-type batteries is a difficulty in research on interfaces, which will be eliminated in thin-film systems. Since the surface forming the interface should be defined for the study, crystal orientation of the films should be controlled, which can be achieved by epitaxial growth.

We have been synthesizing battery materials into epitaxial films and successfully obtained LiCoO_2 films with different crystal orientations [1]. A LiCoO_2 epitaxial film with (001) orientation exhibits extremely-high rate capability due to the accessible interlayer galleries. On the other hand, rate capability of a (001)-oriented film is much lower, and the differences in the electrode properties are attributable to anisotropic ionic diffusion in LiCoO_2 , which have been widely expected from its layered structure but rarely revealed experimentally [2]. In addition, a thin-film battery unveils clear relation between phase transition and cycling properties, which has been blurred by side reactions in liquid electrolytes [3].

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3:30 PM EI12.05

High Voltage Bipolar Stacking of Sulfide Based All Solid-State Batteries Hongli C. Zhu; Northeastern University, United States

All solid-state lithium batteries (ASLBs) are regarded to deliver higher energy density and safety than conventional lithium-ion batteries (LiBs). The higher energy density was because of employing high energy electrodes and unique battery structure designs, like bipolar stacking. In contrast to the conventional LiBs that are sealed separately and then packed together, the solid electrolyte (SE) enables ASLBs to be directly connected without extra packing materials. The bipolar stacking design could minimize the using of inactive material in the batteries resulting a greatly increased energy density. Moreover, if the batteries are connected in series, a high voltage output could be obtained. In addition, the adjacent ASLBs could share one current collector. The shortened electron conduction paths between cells benefit lower resistance and increased power density. Sulfide SEs which are highlighted with ultrahigh ionic conductivity, are one of the most promising electrolytes to produce the bipolar stacked ASLBs. However, the report on sulfide-based ASLBs is rare. The main reason is the lack of reliable laminated electrodes and electrolytes layers. Herein, based on sulfide SE, we successfully assembled bipolar stacked ASLBs through facilely stacking freestanding cathode, electrolyte, and anode layers. A Li_3SiO_3 coated single crystal NMC 811 was utilized as cathode. A Silicon composite anode was used as anode. Benefiting from the excellent compatibility among sulfide SE, toluene, and ethyl cellulose, a vacuum filtration method is successfully used to prepare freestanding, flexible, and robust cathode, electrolyte, and anode layers. A stainless steel foil was utilized as the current collector for both cathode and anode. As a result, the bipolar stacked ASLBs was successfully fabricated. The doubly stacked cells deliver a high voltage of 8.2 V and cell level energy density of 204 Wh kg^{-1} which is much higher than the 189 Wh kg^{-1} of ASLBs in conventionally stacked. Our work will pave the way to use sulfide SE to fabricate ASLBs with bipolar stacking designs.

3:45 PM EI12.06

Surface Tension of Melted Electrolytes at Nanostructural Cathode Interfaces and Their Effect on Lithium-Ion Transport Properties in Lithium-Metal Solid-State Batteries Abu Md Numan-Al-Mobin, Ian Kasten, Karen Ly, Greydon Shangreux and Alevtina Smirnova; South Dakota School of Mines and Technology, United States

Solid-state battery technology is fast emerging due to the limited capabilities of conventional batteries with liquid electrolytes, especially regarding their flammable nature and lack of electrochemical stability in presence of lithium metal. Compared to batteries with liquid electrolytes, solid-state batteries have their own challenges and the limited interfacial contact at cathode/electrolyte interfaces is one of them. These interfaces are essential in reducing ionic and electronic transport between the layers and increasing the overall electrochemical cell performance. One of the ways to address this challenge is by using low-melting-point lithium halides or oxyhalides with low surface tension at the solid-state interface with cathodes. Our current study demonstrates that the surface tension of solids in a liquid state defines their ability to form improved interfaces with metal oxides upon solidification. A comparative study is presented for a few commercial cathodes in comparison to new cathodes with decreased surface tension. The scanning electron microscopy, energy

dispersive spectroscopy, and impedance spectroscopy applied to the newly created architectural designs confirm that low surface tension of the melted solid-state electrolyte is a key factor for improved morphology and electrochemical cell performance. Electrochemical cell testing results performed at different C-rates and temperatures justifies the initial hypothesis regarding the importance of surface tension adjustment for creating functional cathode-solid electrolyte interfaces.

SESSION EI13: Batteries
Session Chairs: Yasutoshi Iriyama and Yoshitaka Tateyama
Friday Morning, July 22, 2022
Mezzanine Level, Second Floor, Berkeley/Clarendon

9:10 AM **EI13.01

New Battery Chemistry from Conventional Layered Cathode Materials for Advanced Lithium-Ion Batteries Kisuk Kang; Seoul National University College of Engineering, Korea (the Republic of)

The discovery of layered TiS_2 and LiCoO_2 compounds has led to the proliferation of modern lithium-ion batteries, exploiting the lithium-ion insertion/deinsertion chemistry toward the high-energy-density battery system. For the past decades, extensive efforts have been placed in improving the performance of these layered compounds for cathodes such as by compositional tuning and structural modifications. One of the notable approaches in recent years is to adopt excess amounts of lithium-ions in the layered materials, which surprisingly revealed that the specific capacity can be boosted in the layered cathodes via the shift from the conventional cationic redox reaction relying on transition metals (Co, Ni and Mn) to the cumulative cationic and anionic (oxygen) redox reaction. In this journey to explore the ‘lithium-excess layered cathodes’, various new findings have been disclosed. In this talk, I will present our recent understandings on these materials with respect to the lithium insertion mechanism that differs from what have been observed in conventional layered materials and the effect of the layered stacking sequences, and discuss on the outlook on the lithium-excess layered cathodes.

9:40 AM *EI13.02

Manipulating Phase Transformation During Electrochemical Reactions—Lithium-Ion Batteries and Battery-Inspired Electrocatalysis Jongwoo Lim; Seoul National University, Korea (the Republic of)

Electrochemically dynamic environment in lithium-ion batteries and water electrolysis often makes phase transition of electrode unpredictable. Lithium-ion insertion kinetics fundamentally hinges upon phase transformation behavior during (dis)charging at high cycling rates. Ni-rich NCM, one of the most widely investigated cathodes, shows strong phase-separating behavior as cycling rate increases. However, the origin of phase separation remains unclear and inconsistent, complicating quantitative analysis. On the other hands, surface reconstruction of electrocatalysts during water electrolysis determines the active species and the catalytic performance. However, rationally modulating the dynamic surface restructuring and generating active surface species remain tremendous challenges. In the first part of my talk, I will present how we can redirect the detrimental two-phase behavior to single-phase at a fast cycling rate during lithium-ion battery operation. Electrochemically manipulating the lithium-ion distribution within the NCM particles could effectively induce facile lithium diffusion and solid-solution phase behavior. The second half of my talk will present a novel cationic redox-tuning method to redirect the *in-situ* surface reconstruction of a transition-metal-oxide electrocatalyst for the oxygen evolution reaction (OER). Cl-doping lowered the potential to trigger in situ cobalt oxidation and lithium leaching, which induced the surface of $\text{LiCoO}_{1.8}\text{Cl}_{0.2}$ to transform into a self-terminated amorphous (oxy)hydroxide phase during the OER. We further demonstrated that surface-restructured $\text{LiCoO}_{1.8}\text{Cl}_{0.2}$ outperformed many state-of-the-art OER catalysts and demonstrated remarkable stability.

10:00 AM EI13.04

The Impact of Alkali Metal Ion Intercalation on Redox Chemistry and Mechanical Deformations—A Case Study on Intercalation of Li, Na, and K Ions into FePO_4 Cathode Bertan Özdoğru¹, Younghwan Cha², Behrad Koohbor³, Bharat Gwalani⁴, Vijayakumar Murugesan⁴, Min-Kyu Song² and Ömer Ö. Çapraz¹; ¹Oklahoma State University, United States; ²Washington State University, United States; ³Rowan University, United States; ⁴Pacific Northwest National Laboratory, United States

Electricity become the backbone of modern society with the rapid increase in the human population in the latter part of the 20th century. While the majority of the electricity is coming from fossil fuels, global warming forces society to harvest electricity from renewable sources. While direct utilization of renewable power is possible with the current electricity grid, their intermittent nature requires the utilization of either mechanical or chemical energy storage technologies. As a chemical method, Li-ion batteries (LIBs) are predominantly used for energy storage today, large-scale usage of such systems are not economically viable due to the demand and price of Li metal. For these applications, cheaper alternatives compared to LIBs are needed. Sodium-ion batteries (NIBs) and potassium-ion batteries (PIBs) are possible candidates to replace LIBs. However, NIBs and PIBs suffer from low cycling stability, primarily caused by mechanical and chemical instabilities due to higher reactivity and larger ionic radius of sodium and potassium metals¹. Intercalation and removal of these ions result in phase transitions and rapid lattice parameter changes in the intercalation electrodes. This causes volume changes, fractures, and pulverization in the electrode particles, reducing the cyclability of the electrode. Understanding this mechanism is crucial to improving the performance of Na-ion and K-ion batteries.

In this study, we aim to understand the effect of alkali ions (Li^+ , Na^+ or K^+) on the mechanical response of a cathode material during electrochemical alkali ion insertion and removal. Electrochemically delithiated iron phosphate (FePO_4) is used to investigate the effect of different alkali metals since it can be cycled with Li, Na, and K metals². Composite electrodes are cycled in a custom battery cell, and electrochemical strain evolution is calculated using Digital Image Correlation (DIC) technique. Intercalation of Li-ion or Na-ion shows a nearly linear relationship between strain and state of charge/discharge (SOC/SOD), with a near-constant strain rate with the exception of the first sodiation cycle. During K-ion intercalation into FePO_4 , nonlinearity is observed between strain and SOC/SOD, as well as a larger strain rate throughout the cycling. Our in situ strain measurements suggest that the strain rate, instead of absolute strain is the cause of amorphization of the crystalline FePO_4 electrode during the K-ion intercalation³. Amorphization of FePO_4 electrode is also demonstrated with in-situ XRD and TEM analysis⁴.

This work was supported by the U.S. Department of Energy, Office of Science, Basic Energy Sciences (Award number DE-SC0021251).

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10:15 AM EI13.05

Ion Exchange at the Liquid-Solid Interface in Spinel Oxide Thin-Film Model Cathode for Multivalent Batteries Jae Jin Kim¹, Bilash KC², Haesun Park³, Guennadi Evmenenko⁴, Bruce Buchholz⁴, Robert Klie², Peter Zapol³, Brian Ingram¹ and Timothy Fister¹; ¹Argonne National Laboratory, United States; ²University of Illinois at Chicago, United States; ³Argonne National Laboratory Materials Science Division, United States; ⁴Northwestern University, United States

Among “beyond lithium ion battery” technologies, systems based on the intercalation of multivalent (MV) ions have attracted substantial research effort, because they can, in principle, deliver 2 or 3-fold enhanced energy capacity with di- or trivalent charge carrier ions, respectively, compared to monovalent lithium ion chemistry. Furthermore, the theoretical energy density at cell level can be significantly increased when coupled with MV metal anodes, given that, compared to lithium, they are considered to be less vulnerable to dendrite growth upon stripping and plating. Natural abundance of elements such as Al, Ca and Mg, which have been actively investigated as a charge carrier, is another attractive merit with possibly offering low costs and reliable supply. In practice, however, the search for an improved MV rechargeable batteries has been impeded by limited understanding and control of MV ion transport within both electrode and electrolyte and reactions at the interfaces. For example, unlike steady progress on development of new electrolytes for reversible plating/stripping of Ca and Mg on the anode side, there has been little improvement on the cathode side. This is, in large part, due to the lack of electrolyte capable of being both cathodically and anodically stable. However, even with anodically stable electrolyte, magnesium cathodes still show poor rate performance and significant hysteresis. As theoretical calculations and recent nuclear magnetic resonance studies on oxide spinels show that bulk Mg ion mobility is not a limiting factor, the overall transport is likely bottlenecked by a mechanism at the cathode/electrolyte interface.

In this presentation, we will compare the lithium and magnesium transport near the surface of one of the most well-known cathode materials: spinel structured lithium manganese oxide (LiMn₂O₄). We utilize thin film model electrodes with controlled structure and property, in order to obtain a mechanistic understanding of the electrochemical reactions at the interface. While lithium is electrochemically ion-exchanged for magnesium in a nanoscale thin film, real-time X-ray surface scattering is performed to monitor corresponding structural change. Using a combination of operando characterization and density functional theory calculations, we will discuss dissimilar transport kinetics during initial lithium extraction, magnesium insertion and subsequent extraction, structural stability of the charged Mn₂O₄ phase, and potential role of the inherent strain developed in a thin film, or even the surface region of a bulk cathode.

10:30 AM BREAK

11:00 AM EI13.06

In Situ Stress Generation During Oxygen Evolution and Reduction Reactions on Au Positive Electrode in Li-O₂ Batteries Hannah Dykes, Bertan Özdogru and Ömer Ö. Capraz; Oklahoma State Regents for Higher Education, United States

Li-O₂ batteries have received enormous interest from the scientific community due to its extremely high theoretical specific energy density, which is originated from the oxygen reduction reactions during discharge at the surface of the cathode electrode. Unfortunately, the commercial implementation of this technology is hindered by the poor cycling performance, mostly due to the sluggish oxygen evolution/reduction kinetics and the nature of the discharge reaction product. The lithium peroxide (Li₂O₂) is the discharge reaction product and its insulating nature limits to harvest the theoretical capacity of the Li-O₂ batteries practically. The impact of the salt and solvent species on the formation mechanisms of the discharge product has been reported widely. However, underlying mechanisms dictating the reaction pathway is still under debate.

In this study, we employed in situ stress measurement to investigate the impact of the electrolyte salt on nanoscale dynamic changes on the surface of the thin Au film cathode (1-D) during charge / discharge of Li-O₂ batteries. Stress measurements have been applied to various electrochemical and electrocatalytic application areas in order to probe the dynamic changes on the surface of the materials. The electrolyte was prepared by mixing 1 M LiTFSI or LiNO₃ salts in DMSO or Diglyme solvents. Electrolytes were saturated either with oxygen or argon prior to performing electrochemical measurements. In situ stress measurements were conducted using a multiple beam optical sensor (MOS). A custom cell was designed to monitor the physical response of the cathode during cycling while enabling optical access to the back of the substrate for stress measurements¹. In situ curvature evolution on Au thin film cathode was monitored during discharge and charge via galvanostatic cycling and cycling voltammetry.

In this talk, we will present the impact of the electrolyte salt on the potential-dependent surface stress generation during the formation and oxidation of electrochemical redox reaction products at nanoscale on the Au thin film cathode. Shortly, in situ stress measurements pointed out the contribution of charge-induced stress, electrostriction stress, and intrinsic stress associated with the formation of discharge reaction products. Revealing the mechanical response of the discharge products on cathode electrode will shed light into the formation mechanisms of these products, which is crucial to design new electrolyte and cathodes for Li-O₂ batteries.

Acknowledgement:

This work was supported by the Binational Science Foundation (#2018327), and we are thankful to both Dr. Malachi Noked and Rosy for fruitful discussions.

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11:15 AM EI13.07

Novel Double Perovskite Oxide-Based Bifunctional Electrocatalysts for Oxygen Evolution/Reduction Reactions Aman Bhardwaj, Thomas Fischer and Sanjay Mathur; University of Cologne, Germany

Metal-air batteries are one of the prominent energy storage devices of the present need, and the bifunctional oxygen evolution-reduction (OER/ORR) reaction electrocatalyst is their core-technology component. The non-precious metal-based perovskite oxides and derivatives are prototype materials for these applications and offer high terrestrial availability and high stability. Their electronic geometry and structure are often considered key factors in controlling the catalytic activity. Herein, we demonstrate the impact of M-O-M' interactions in double perovskite oxide electrocatalysts over its bifunctional electrochemical activity towards the oxygen evolution and reduction reactions. The materials synthesized through sol-gel chemistry were characterized for the physicochemical by various diffraction and spectroscopic techniques and further evaluated for electrochemical characteristics. A vibronic superexchange interaction resulting in a predominant M³⁺-O-M'³⁺ interaction was found to positively impact the electrocatalytic activity by enhancing the current densities and lowering the Tafel slope. Our finding presents a promising pathway for developing advanced precious metal-free catalysts and substantiating their suitability as the bifunctional oxygen electrode for metal-air batteries.

Plenary

Plenary
July 18 - July 22, 2022

* Invited Paper

SESSION PI01: Plenary I
Monday Morning, July 18, 2022
Mezzanine Level, Second Floor, Grand Ballroom A

8:00 AM PI01.01

Exemplary Tuning the Properties of Ionic Thin Films for Electronic and Energy Devices [Judith Macmanus-Driscoll](#); University of Cambridge, United Kingdom

Many current and emerging solid state devices for ICT, energy generation and storage involve electrochemical processes. Thin films, as well as being important components for several device types, can also provide new understanding of these processes. Furthermore, new ways of nanostructuring of thin films enable strong performance enhancements at the same time as materials stabilisation. Finally, combining functionalities into a single thin film materials system, e.g. ionicity and ferroelectricity, enables unprecedented multifunctional property enhancement. In this talk, using a range of oxide thin film systems, I give examples both of new understanding of nanoionic electrochemical processes as well as strong performance improvements, from cathodes and electrolytes for micro-solid oxide cells to solid state batteries to memristors.

SESSION PI02: Plenary II
Tuesday Morning, July 19, 2022
Mezzanine Level, Second Floor, Grand Ballroom A

8:00 AM PI02.01

The Key Role of Solid State Ionics in the Development of Li-Ion Batteries [M. Stanley Whittingham](#); Binghamton University SUNY, United States

TBD

SESSION PI03: Plenary III
Wednesday Morning, July 20, 2022
Mezzanine Level, Second Floor, Grand Ballroom A

8:00 AM PI03.01

Oxide Surfaces at the Atomic Scale [Ulrike Diebold](#); TU Wien, Austria

The functionality of energy materials is often driven by interface and defect chemistry. Surface science methods, combined with first-principles calculations, are ideal for obtaining mechanistic insights into elementary reaction steps. In the talk, I will give an overview of how one can model surface chemical reactions using atomically-resolved microscopy and surface spectroscopic techniques, using metal oxide single crystals and epitaxial films as samples.

SESSION PI06: ISSI Young Scientist Award
Wednesday Afternoon, July 20, 2022
Mezzanine Level, Second Floor, Grand Ballroom A

1:00 PM TO RECOGNIZE THE OUTSTANDING CONTRIBUTIONS MADE BY YOUNG SCIENTISTS TO THE FIELD OF SOLID STATE IONICS, THE INTERNATIONAL SOCIETY OF SOLID-STATE IONICS ESTABLISHED THE ISSI YOUNG SCIENTIST AWARD. THIS YEAR, FIVE YOUNG SCIENTISTS WILL BE AWARDED. DON'T MISS THE AWARD RECIPIENTS' TALKS FROM 1:00PM - 2:30PM IN GRAND BALLROOM A.

SESSION PI04: Plenary IV
Thursday Morning, July 21, 2022
Mezzanine Level, Second Floor, Grand Ballroom A

8:00 AM PI04.01

Strain Effects on Surface Activity and Oxide Ion Conductivity Tatsumi Ishihara; Kyushu Daigaku, Japan

Strain effects on ionic materials have been attracting much interest for increasing electrochemical performance of oxide ion conductor or mixed conductor. Tsvetkov et al. reported that the nickelates structure materials can improve high oxygen reduction reaction (ORR) activity by tensile strain in thin film [1]. However, these studies have been mainly performed by using the film which grows epitaxially. It seems that lattice strain has a significant effect on surface activity of catalyst from surface composition. In this talk, effects of strain on oxide ion conductivity and surface activity of $\text{PrNi}(\text{Cu}, \text{Ga})\text{O}_4$ (PNCG) will be introduced. Three-dimensional (3D) strain which was induced by thermal expansion mismatch between Au nano particles and PNCG, was studied and it was found that the cathodic overpotential was decreased significantly by dispersion of Au into PNCG bulk and this Au dispersion effects might be assigned to the tensile strain [2,3].

In this presentation, effects of three-dimensional strain induced by Au dispersion on oxide ion conductivity in Pr_2NiO_4 oxide will be also introduced. The oxygen permeation rate was increased by Au dispersion, in particular at lower temperature. This was assigned to the increased oxide ion conductivity by increased interstitial oxygen into rock salt block in Pr_2NiO_4 . In this study, analysis of such induced interstitial oxygen is also performed by XPS and TEM-EELS analysis. Both method shows reduced state of oxygen is formed by introduction of 3D strain by Au dispersion. Mapping of such reduced state oxygen by TEM-EELS shows location of these interstitial oxygen concentrated around dispersed Au. Thus, introduced strain by Au particles is origin of introduce interstitial oxygen resulting in the increased oxide ion conductivity, and oxygen reduction activity.

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SESSION PI05: Plenary V
Friday Morning, July 22, 2022
Mezzanine Level, Second Floor, Grand Ballroom A

8:00 AM PI05.01

Computational Design of Fast Oxygen Kinetics in Materials Dane Morgan; University of Wisconsin-Madison, United States

Rapid transport of oxygen across and through materials is at the heart of technologies from solid oxide fuel cells to gas separation membranes to memristors. Almost 200 years of experimental study and materials theory have given us a deep understanding of the mechanisms by which ions, and in particular oxygen, move through solid state systems, as well as significant quantities of data on relevant kinetic processes. In recent decades molecular simulations have complimented experiments and theory with extraordinary insights into oxygen's motion and even quantitative prediction of transport rates. However, computationally driven discovery and design of new fast oxygen materials remains an enormous challenge due to the structural, chemical, and kinetic complexity contributing to their properties. In this talk, I will use examples from my work and others to describe how new developments in computational approaches, including increased accuracy and high-throughput molecular simulations, and data-centric descriptor and machine learning methods, are helping overcome this challenge to aid the search for the next generation of fast oxygen materials.

I will focus on perovskites and closely related compounds and start by describing how basic properties, such as defect chemistry and oxygen transport, can now be accurately predicted for complex systems using ab initio methods and new machine learning potentials. As a concrete example, I will share our work on understanding mechanisms controlling fast ion conduction in perovskites and high-throughput screening approaches to discovering new fast oxygen conductors. I will then discuss the more challenging problem of surface exchange and how molecular simulations have provided new insights into the most active surfaces and rate limiting steps of oxygen exchange. I will also explain how we and others are overcoming some of the limitations of direct molecular simulations to rapidly predict complex properties, such as surface exchange rates, by using empirical correlations to descriptors, in particular the oxygen p-band. I will share our recent results where we screened about 2000 perovskites with oxygen p-band to find new stable oxides with high surface exchange. Finally, I will show how machine learning methods can take us beyond simple descriptors to provide a data-centric approach to discovering new active oxygen materials.