

SYMPOSIUM CM03

In Situ/Operando Analysis of Electrochemical Materials and Interfaces
November 26 - November 30, 2018

Symposium Organizers

Hao Ming Chen, National Taiwan University
Neil Dasgupta, University of Michigan
Matthew McDowell, Georgia Institute of Technology
Vanessa Wood, ETH Zürich

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* Invited Paper

SESSION CM03.01: Battery Interfaces
Session Chairs: Neil Dasgupta and Kelsey Hatzell
Monday Morning, November 26, 2018
Hynes, Level 3, Room 300

8:15 AM *CM03.01.01

Single Particles Cathode Material Electrochemical Properties from Micro-Pipets Methods Malak Dayeh¹, Micheal Snowden^{1,2}, Mohammadreza Ghavidel^{1,2}, Janine Mauzeroll¹ and Steen Schougaard²; ¹McGill University, Montreal, Quebec, Canada; ²NanoQAM and Département de Chimie, Université du Québec à Montréal, Montreal, Quebec, Canada.

Lithium ion batteries have demonstrated their importance in portable electronics and as alternative to fossil based portable energy in automotive applications.[1] This importance is expected to continue at least in the near and intermediated future. However, in the longer term electrode materials will need improved capacity and charge/discharge rates. As new anode and cathode materials are developed[2] they are typically screened for advantageous properties by assembly into a working battery. This typically involves film fabrication from a mixture of conductive material (e.g. carbon), a binder (e.g. polyvinylidene fluoride), and the active material of interest. How this film is cast onto the current collector, the ratio of the individual components of the film, the drying procedure for the film and the final assembly of the cell can significantly alter the performance of the battery.[3,4] In order to avoid misleading information about the effectiveness of a novel active material many cells are required to validate findings.

Here we present micro-pipet measurements[5,6] which demonstrate the suitability of the technique for probing lithium ion battery materials. Specifically, we probed dispersions of active materials to determine the oxidation and reduction potentials, and the charge capacity of the material. Data obtained on candidate materials by the micro-pipet method was compared to coin cell measurements, to critically assess this technique for characterization of active battery materials.

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8:45 AM CM03.01.02

In Situ/Operando Soft X-Ray Spectroscopy of Interfacial Processes in Energy Materials and Catalysis Yi-Sheng Liu, Liang Zhang and Jinghua Guo; Lawrence Berkeley National Lab, Berkeley, California, United States.

The energy materials and devices have been largely limited in a framework of thermodynamic and kinetic concepts or atomic and nanoscale. Synchrotron radiation based x-ray spectroscopic techniques, especially in-situ/operando capabilities, offer unique characterization in many important energy materials of energy conversion, energy storage and catalysis in regards to the functionality, complexity of material architecture, chemistry and interactions among constituents within.

It has been found that the microstructure and composition of materials as well as the microstructure evolution process have a great influence on performances in a variety of fields, e.g., energy conversion and energy storage materials, chemical and catalytic processes. In-situ/operando x-ray spectra characterization technique offers an opportunity to uncover the phase conversion, chemical environment change of elements and other very important information of solid/gas and solid/liquid interfaces in real time. We will present soft x-ray spectroscopy characterization techniques, e.g. soft x-ray absorption spectroscopy (XAS) and resonant inelastic soft x-ray scattering (RIXS), and the development of in situ/operando soft x-ray spectroscopy characterization of interfacial phenomena in energy materials and devices.

We will present a number of the experimental studies that successfully revealed the catalytic and electrochemical reactions in real time, e.g. solid (Au film)/liquid (water) electrochemical interface, Mg-ion and Li-S batteries, and solid-state hydrogen storage materials [1-5]. The experimental results demonstrate that in-situ/operando soft x-ray spectra characterization techniques provide the unique information for understanding the real reaction mechanism.

References:

1. "Mg deposition observed by in situ electrochemical Mg K-edge X-ray absorption spectroscopy", T. S. Arthur, P.-A. Glans, M. Matsui, R. Zhang, B. Ma, J.-H. Guo, *Electrochem. Commun.* **24**, 43 (2012).
2. "The structure of interfacial water on gold electrodes studied by x-ray absorption spectroscopy", J. J. Velasco-Velez, C. H. Wu, T. A. Pascal, L. F. Wan, J.-H. Guo, D. Prendergast and M. Salmeron, *Science* **346**, 831 (2014).
3. "Nucleophilic substitution between polysulfides and binders unexpectedly stabilizing lithium sulfur battery", M. Ling, L. Zhang, T. Zheng, J. Feng, J.-H. Guo, L. Mai, G. Liu, *Nano Energy* **38**, 82 (2017).
4. "Interfacial insights from operando sXAS/TEM for magnesium metal deposition with borohydride electrolytes", T. Arthur, P.-A. Glans, N. Singh, O. Tutusaus, K. Nie, Y.-S. Liu, F. Mizuno, J.-H. Guo, D. H. Alsem, N. Salmon, R. Mohtadi, *Chem. Mater.* **29**, 7183 (2017).
5. "Revealing the Electrochemical Charging Mechanism of Nanosized Li₂S by in Situ and Operando X-ray Absorption Spectroscopy", L. Zhang, D. Sun, J. Feng, E. Cairns, J.-H. Guo, *Nano Lett.* **17**, 5084 (2017).

9:00 AM CM03.01.03

Enabling Ultrafast Interfacial Li-Transport in Layered-Oxide Cathodes Bohua Wen, Ping-Chun Tsai, Menghsuan S. Pan and Yet-Ming Chiang; Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

In order to design electrode materials for optimal combinations of energy and power, it is essential to understand kinetic barriers at all applicable length scales and over a wide range of state-of-charge. Here, using a recently developed single-electrode-particle characterization method,¹ we investigate the rate-limiting transport mechanisms in NMC and NCA cathodes. EIS and PITT measurements have been performed on single secondary particles of ~25 μm size, as a function of charge voltage and liquid electrolyte composition. We find that with increasing charge voltage, transport is increasingly limited by surface reaction kinetics; thus increasing the exchange current density is critical to obtaining high capacity utilization at high voltage. Upon performing the single-particle measurements in electrolytes containing salts with different anion groups, we find that electrolytes containing LiTFSI salt have, surprisingly, an order of magnitude higher exchange current density compared to electrolytes containing LiPF₆ salt, and that this improvement is retained to high charge voltages. The improved interfacial kinetics lead to a significantly higher materials utilization during fast charge/discharge, in both the single-particle measurements and in experiments on macroscopic composite electrodes. Possible origins of the strong anion species dependence of interfacial kinetics, and interfacial characterization in these systems, will be presented.

This work was supported as part of the NorthEast Center for Chemical Energy Storage (NECCES), an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Basic Energy Sciences under Award # DE-SC0012583. P.-C. Tsai thanks the Ministry of Science and Technology, Taiwan (MOST 104-2917-I-006-006), for financial support.

Reference:

- [1] P.-C. Tsai, B. Wen, M. Wolfman, M.-J. Choe, M. S. Pan, L. Su, K. Thornton, J. Cabana, Y.-M. Chiang, *Energy Environ. Sci.*, **11** (4), 860-871.

9:15 AM CM03.01.04

Interfacial Studies of the Solid Electrolyte Interphase Hans-Georg Steinrueck¹, Chuntian Cao^{1,2}, Iwnetim I. Abate^{1,2} and Michael F. Toney¹; ¹SSLR Materials Science Division, SLAC National Accelerator Laboratory, Menlo Park, California, United States; ²Department of Materials Science and Engineering, Stanford University, Stanford, California, United States.

The solid electrolyte interphase (SEI) is an interfacial layer formed on lithium ion battery (LiB) anode surfaces due to electrolyte decomposition at low potentials outside the electrolyte's electrochemical stability window, and is a major source for capacity losses. Due to its electrically insulating and solvent diffusion prohibiting nature, its growth is in principle self-limiting. The ideal SEI can thus prevent further decomposition once formed, while allowing for ion conduction. However, in real systems, where electrodes experience volume and morphological changes, continued SEI growth renders LIB cyclability issues. Despite extensive research efforts to investigate the SEI, open questions still remain. These include the SEI formation processes, the SEI composition and thickness, as well as the structure-function relationship to the electrochemical cycling performance.

In a reductionist approach, we utilized simple and well-defined model systems to study SEI formation, growth, and evolution, in order to obtain an atomic scale fundamental understanding of the occurring processes. We have combined in situ x-ray reflectivity (XRR) and ex situ x-ray photoelectron spectroscopy (XPS) to probe the structure and chemistry of the SEI on two different substrates, i.e. oxide terminated crystalline silicon (Si) and pristine silicon carbide (SiC). We used various electrochemical cycling conditions, including galvanostatic, cyclic voltammetry and potential holds, for different electrolytes, such as lithium hexafluorophosphate (LiPF₆) in ethylene carbonate (EC)/dimethyl carbonate (DMC). Our results of the thickness, density, roughness, porosity, and composition of the SEI show significant differences between Si and SiC. Specifically, the formation of lithium fluoride (LiF) is significantly suppressed by the presence of a surface oxide, which we attribute to its electrically insulating nature. We compare and contrast our results with recent studies of the electrocatalytic formation of LiF on metal surfaces [1]. Through combining these observations with our findings that the SEI on silicon contains low ion-conductivity lithium silicates, we hypothesize the native oxide is beneficial if a thin and smooth SEI layer is desired, but may be counterproductive if a fast ion-conduction SEI is desired.

Furthermore, we compared our XRR and XPS results with electrochemical data using a cone-cell, which eliminates parasitic currents, and were able to "count" each electron/Li-ion passed into the Si and SEI. Thus, we uniquely disentangled the Si lithiation and SEI contributions to electrochemical current measurements, yielding ultra-sensitive insights into SEI properties. This approach is even more sensitive when a non-active material such as SiC is utilized.

- [1] Strmcnik et al., *Nature Catalysis* 2018, **1**, 255.

9:30 AM CM03.01.05

Investigating Molecular Structures at Interface Using Nanogap Surface-Enhanced Raman Spectroscopy Guang Yang¹, Robert Sacchi¹, Ilia Ivanov⁴, Rose Ruther², Kevin Hays², Yiman Zhang¹, Pengfei Cao³, Gabriel Veith¹, Nancy J. Dudney¹, Tomonori Saito³, Daniel Hallinan⁵ and Jagjit Nanda¹; ¹Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States; ²Energy and Transportation Sciences Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States; ³Chemical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States; ⁴Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States; ⁵Chemical & Biomedical Engineering Department, Florida State University, Tallahassee, Florida, United States.

Understanding the aprotic solution structures at the immediate vicinity of solid/liquid interface (SLI) is critically important for next generation lithium ion battery development. Yet, it is still challenging to investigate the carbonate profiles close to the diffuse layer (about 10 nm) at SLI due to the lack of a

highly surface sensitive tool. In this work, we demonstrate the structures of commonly used carbonate solvents (ethylene carbonate (EC) and diethyl carbonate (DEC)) and an carbonate additive (fluoroethylene carbonate (FEC)) in a Li-ion battery electrolyte can be determined at ~17 nm above the electrode surface. This is only enabled by a nanogap surface-enhanced Raman spectroscopy (SERS) technique. SERS stems from the amplification of local electromagnetic (EM) field generated by localized surface plasmons. The local EM-field is extremely intense within metallic nanogap (<10 nm) due to the coupling effect among adjacent nanoparticles. We have developed methods to assemble gold nanoparticles (Au NPs) into large area (cm²) monolayers, which ensures the formation of long-range ordered nanogap arrays. The interparticle gap can be tuned between 1 and 4 nm by surface ligands of different sizes. The SERS enhancement factor (EF) of the carbonates in this study was found to depend on the molecular polarizability, with the maximum EF at ~10⁵ found for EC and FEC. Compared to EC, several vibration modes in FEC, such as C-C skeletal deformation, ring breathing band and C=O stretching band, shift to higher frequencies because of the displacement of a hydrogen atom by a much heavier fluorine atom in a methylene bridge. This counterintuitive observation against the commonly used “ball and spring” model in vibrational spectroscopy is mostly due to the increased bond strength in the FEC ring versus that of EC. A second order empirical polynomial of a single indeterminate best describes the correlation between the SERS band integration of and EC molar fraction, which allows for quantifying the electrolyte species in the carbonate mixture at SLI using SERS. Our findings open up new opportunities for in-depth understanding of the electrolyte molecular structures at direct solid/liquid interface, which is closely related to the Li-ion battery performance such as energy density, life time and safety of the lithium rechargeable batteries.

Acknowledgment

This research was conducted at Oak Ridge National Laboratory, managed by UT Battelle, LLC, for the U.S. Department of Energy (DOE) under contract DE-AC05-00OR22725, was sponsored by the Office of Energy Efficiency and Renewable Energy (EERE) Vehicle Technologies Office (VTO). SERS measurements were performed at the Center for Nanophase Materials Sciences, which is a DOE Office of Science User Facility.

9:45 AM BREAK

SESSION CM03.02: Transformations in Battery Materials
Session Chairs: Neil Dasgupta and Kelsey Hatzell
Monday Morning, November 26, 2018
Hynes, Level 3, Room 300

10:15 AM *CM03.02.01

***In Situ* TEM Studies of Electrochemical Lithium Storage Mechanisms at Nanoscale** [Reza Shahbazian-Yassar](#); University of Illinois at Chicago, Chicago, Illinois, United States.

Design of safe lithium ion batteries require innovations in advanced characterization of electrochemical reactions at nanoscale. Real time microscopy provides new opportunities to observe and monitor lithium storage mechanisms at unprecedented resolutions. We demonstrate the shortage and gaps in the field of lithium ion batteries that require advanced real time microscopy. In particular we show that in-situ transmission electron microscopy (TEM) is fundamental to discover mechanisms of ion conductivity, structural degradation and transformations, and other structural phenomenon associate with the behavior of electrodes. Using liquid-cell TEM, we will show the charge and discharge mechanisms in lithium-air batteries depends on the contribution of electrical conductivity and ionic conductivity to allow Li₂O₂ decomposition. We also show that the oxygen release from oxide cathodes can trigger structural transformations that results in thermal runaway chain events. Using open-electrochemical cell TEM, we demonstrate lithium storage through conversion, intercalation, and alloying mechanisms.

10:45 AM CM03.02.02

Visualizing Intercalation Events in Ultrathin Graphite Electrodes [Madeline Stark](#), Hailey Kim, Judy Cheng and Scott C. Warren; University of North Carolina at Chapel Hill, Chapel Hill, North Carolina, United States.

Near the atomic limit, layered materials such as graphite, transition metal dichalcogenides, and black phosphorus demonstrate enhanced transparency, conductivity, and storage capacity, making them attractive electrode materials for battery and optoelectronic applications. To develop sustainable energy storage devices, however, it is critical to understand electrode-electrolyte interactions. In particular, elucidating the mechanisms of intercalation, SEI formation, and ion transport are areas of active research. To explore these processes *in-situ*, we have developed a planar battery cell that enables us to visualize intercalation events during charge and discharge cycles. In this work, we focus on the electrochemical intercalation of bisulfate into ultrathin graphite as a model for aqueous intercalation. This compound is of interest, since it exhibits well-defined staging and can be reversibly cycled, paralleling battery technologies, but in an aqueous environment. Our work highlights the important factors to consider when designing an electrochemical cell for aqueous intercalation, specifically in a strongly oxidizing electrolyte, and describes a cell design that enables *in-situ* optical imaging of both bulk and ultrathin graphite. Qualitatively, we image the intercalation process under an optical microscope, and observe intercalation, deformation, and degradation of the material during cyclic voltammetry and galvanostatic cycling. By visualizing the process of intercalation *in-situ*, we can acquire and analyze complex image sequences to extract information about the rate of ion transport and diffusion in bulk and ultrathin graphite. To correlate optical images with charge transfer, we perform *in-situ* reflectance measurements as well as Raman spectroscopy at distinct locations in the bulk crystal and on individual graphite flakes. By coupling optical images with *in-situ* spectroscopic techniques, we gain insight into how intercalation events and charge transfer occur in a bulk crystal compared to a few-layer electrode. In addition, our observation of differences in color and charge transfer between bulk and ultrathin flakes of varying morphologies highlights the importance of understanding the factors that affect intercalation. The presence of edge sites and grain boundaries are of particular interest since they present a likely pathway to initiate intercalation. Defects within the layers can also lead to degradation and non-uniform charging of the material. However, the role that edges, grain boundaries, and defects play in the ion transport mechanism between the layers of ultrathin materials is not well understood. Thus, we can utilize transmission electron microscopy to study these features in individual graphite flakes prior to intercalation. Combining highly-resolved information about intrinsic defects with spatially-resolved dynamics through optical imaging would provide critical insight into the mechanism of intercalation in 2D electrodes.

11:00 AM CM03.02.03

Insertion and Conversion Based Electrochemical Energy Storage Systems—Complementary Insights from *Ex Situ*, *In Situ* and *Operando* Spectroscopy, Diffraction and Electrochemistry Studies [Amy C. Marschilok](#)^{1,2}, Kenneth Takeuchi¹ and Esther Takeuchi^{1,2}; ¹Stony Brook University, Stony Brook, New York, United States; ²Brookhaven National Laboratory, Upton, New York, United States.

Conceptually, there are two related electrochemical storage mechanisms for electrochemical energy storage materials: insertion where an ion inserts into a structure on reduction and then is removed from the structural lattice upon oxidation, and conversion where there is a chemical reaction leading to a new material or phase. For some materials, each of these mechanisms may participate at different stages of the electrochemical redox process, where the kinetics for ion and electron transport can play a deterministic role regarding which process dominates at a particular state of (dis)charge. Complementary insights gained from ex situ, in situ, and operando spectroscopy, diffraction and electrochemistry studies will be highlighted in this presentation, emphasizing materials which undergo both insertion and conversion processes.

11:15 AM CM03.02.04

In Situ Investigation of Multi-Step Lithiation of Tin Sulfide Sooyeon Hwang¹, Zhenpeng Yao², Lei Zhang³, Maosen Fu⁴, Kai He², Liqiang Mai³, Christopher Wolverton² and Dong Su¹; ¹Brookhaven National Laboratory, Upton, New York, United States; ²Northwestern University, Evanston, Illinois, United States; ³Wuhan University of Technology, Wuhan, China; ⁴Northwestern Polytechnical University, Xi'an, China.

Materials adopting two-dimensional (2D) layered structure have been actively explored as electrode for lithium ion batteries since their unique crystal structures is beneficial for lithium ions to be intercalated between layers[1]. Metal chalcogenides which have 2D layered structure have demonstrated intriguing multi-step reaction with lithium ions; for example, it is known that lithiation of tin disulfide (SnS₂) takes place *via* intercalation, conversion, and alloying[2]. As electrochemical properties are highly dependent on how these complicated reactions proceed, investigation of the reaction pathways with *in situ* analysis is of importance to improve the electrochemical properties of electrode materials. However, thorough understanding of each reaction mechanism of SnS₂ is still missing and full scenario of lithiation dynamics remains elusive.

In this work, we examine the dynamic lithiation process of tin disulfide using *in situ* transmission electron microscopy (TEM) and first-principles calculations[3]. Structural evolutions induced by lithium insertion are reflected in diffraction peak shift, appearance and disappearance of peaks; thus, we could distinguish reaction steps by the modifications in diffraction profiles. We find 4 sequential steps of lithiation reaction: intercalation, disordering, conversion and alloying, which is different from well-known three stages. Disordering step is suggested for the first time. After Li ions are intercalated between S-S layer, rock-salt phase is formed by the disordering of Sn and Li cations. As all the octahedral sites are filled with cations in rock-salt phase, intercalation channel can be restricted. In order for further lithiation, decomposition of rock-salt phase may be inevitable, resulting in a conversion reaction. First principles calculations are conducted not only to elucidate the ground state reaction pathways but to validate the founding from experiments. Due to discrepancies between lithiation reactions at equilibrium state and empirical results, we simulate non-equilibrium reaction pathways using non-equilibrium phase searching method [4]. Calculation results corroborate that rearrangement of cations would not increase the energy of whole system and the formation of rock-salt phase is energetically more favorable than other LiSnS₂ polymorphs, which is well-matched with real-time TEM observation.

References:

[1] J.-M. Tarascon, M. Armand, Nature **414** (2001), P. 359.

[2] T.-J. Kim *et al.* J. Power Sources **167** (2007) p. 529.

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[5] This work is supported by the Center for Functional Nanomaterials, Brookhaven National Laboratory, which is supported by the U.S. Department of Energy (DOE), Office of Basic Energy Science, under Contract No. DE- SC0012704.

11:30 AM CM03.02.05

In Situ S/TEM of SnO₂ Nano-Clusters for Li-Anodes Katherine L. Jungjohann¹, Shalini Tripathi^{2,4}, Subrahmanyam Goriparti¹, C. B. Carter^{2,3,1} and Narayanan Ravishankar⁴; ¹Sandia National Laboratories, Albuquerque, New Mexico, United States; ²Electrical and Computer Engineering, University of Connecticut, Storrs, Connecticut, United States; ³Chemical and Biomolecular Engineering, University of Connecticut, Storrs, Connecticut, United States; ⁴Materials Research Center, Indian Institute of Science, Bangalore, India.

Nanoparticles for Li-ion battery anodes provide high surfaces areas to mediate fast ion transport between the electrode and electrolyte. HRTEM has been used to show that porous nanoparticles can be produced by wet chemistry. The porous morphology of these nanoparticles is then advantageous in mitigating electrode degradation of high theoretical capacity materials such as Si and Sn that are known to undergo significant volume changes and pulverization when the particle sizes are above ~ 150 nm. Therefore, tuning the nanoparticle geometries can be exploited to increase the rate of Li-ion insertion and abstraction, increase the amount of Li-ion storage, and obtain the ideal nanoparticle volume fraction to mitigate material degradation at the individual nanoparticle level and for the anode composite. In this work, we have tested SnO₂ nanocrystalline hollow nanoparticle clusters, where the nanocrystalline particle sizes are tuned separately from the hollow nanoparticle cluster size. In this geometry, the nanocrystallites were tested in a range from 6 – 30 nm, which composed larger hollow nanoparticle structures of 70 – 100 nm in diameter. SnO₂ nanocrystalline cluster nanoparticles were tested in an open-cell configuration using the Nanofactory STM-TEM holder at 300 kV in a TEM. A direct electron detection camera (Gatan K2-IS) attached to a Titan 300kV TEM can be used to monitor the volume changes in the anode hollow nanoparticles during charge cycling. Small nanocrystalline clusters observed even volume expansion and contraction during charge cycling, with no fracture observed within the nanoparticle structure. This nano-anode morphology is promising for the fast Li-ion transport required for fast charging of portable electronic devices.

NR and ST acknowledge the Department of Science and Technology (DST), India, for support, and the Advance Facility for Microscopy & Microanalysis (AFMM) in IISc, Bangalore, for TEM facilities. ST is now at UConn. This work was performed, in part, at the Center for Integrated Nanotechnologies, an Office of Science User Facility operated for the U.S. Department of Energy (DOE) Office of Science. Sandia National Laboratories is a multi-mission laboratory managed and operated by National Technology and Engineering Solutions of Sandia, LLC., a wholly owned subsidiary of Honeywell International, Inc., for the U.S. DOE's National Nuclear Security Administration under contract DE-NA-0003525. The views expressed in the article do not necessarily represent the views of the U.S. DOE or the United States Government.

11:45 AM CM03.02.06

Structural Characterization of the Atomic and Electronic Evolution of Complex Metal Oxides in High-Rate Energy Storage Kent J. Griffith¹, Kamila Wiaderek², Giannantonio Cibirri³, Lauren Marbella¹ and Clare Grey¹; ¹University of Cambridge, Cambridge, United Kingdom; ²Argonne National Laboratory, Argonne, Illinois, United States; ³Diamond Light Source, Didcot, United Kingdom.

The maximum power output and minimum charging time of a lithium-ion battery – key parameters for its use in, for example, transportation applications – depend on mixed ionic– electronic diffusion. While the discharge/charge rate and capacity can be tuned by varying the composite electrode structure, ionic transport within the active particles represents a fundamental limitation. Thus, to achieve high rates, particles are frequently reduced to nanosize dimensions despite this being disadvantageous in terms of volumetric packing density as well as cost, stability, and sustainability considerations. As an alternative to nanoscaling, we show that complex niobium tungsten oxides with topologically frustrated polyhedral arrangements and dense μm -scale particle morphologies can rapidly and reversibly intercalate large quantities of lithium. Multielectron redox, buffered volume expansion, and extremely fast lithium transport approaching that of a liquid lead to extremely high volumetric capacities and rate performance as very recently reported in both crystallographic shear structure and bronze-like niobium tungsten oxides[1]. The active materials Nb₁₆W₅O₅₅ and Nb₁₈W₁₆O₉₃ offer new strategies toward

designing electrodes with advantages in energy density, scalability, electrode architecture/complexity and cost as alternatives to the state-of-the-art high-rate anode material $\text{Li}_4\text{Ti}_5\text{O}_{12}$.

Characterisation of these phenomena and complex material evolution will be presented with structural and chemical insights from *operando* X-ray diffraction and multi-edge X-ray absorption spectroscopy as well as neutron diffraction and nuclear magnetic resonance spectroscopy. The direct measurement of solid-state lithium diffusion coefficients (D_{Li}) with pulsed field gradient NMR demonstrates room temperature D_{Li} values of 10^{-12} – $10^{-13} \text{m}^2 \times \text{s}^{-1}$ in the niobium tungsten oxides, which is several orders-of-magnitude faster than typical electrode materials and corresponds to a characteristic diffusion length of $\sim 10 \mu\text{m}$ for a 1 minute discharge. Materials and mechanisms that enable lithiation of μm particles in minutes have implications for high power applications, fast charging devices, all-solid-state batteries, and general approaches to electrode design and material discovery.

[1] Griffith, Kent J.; Wiaderek, Kamila M.; Cibir, Giannantonio; Marbella, Lauren E.; Grey, Clare P. Niobium Tungsten Oxides for High-Rate Lithium-ion Energy Storage. *Nature*, **2018**, *559*, 556–563.

SESSION CM03.03: Solid-State Electrolytes I
Session Chairs: Katherine Jungjohann and Dong Su
Monday Afternoon, November 26, 2018
Hynes, Level 3, Room 300

1:30 PM *CM03.03.01

When Lithium Travels in Solid-State Disorder for Novel Device Prototypes to Store Energy, Sense the Environment or Emulate Data Jennifer L. Rupp^{1,2}; ¹Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States; ²Department of Electrical Engineering and Computer Science, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

Next generation of energy storage and sensors may largely benefit from fast Li^+ ceramic electrolyte conductors to allow for safe and efficient batteries and real-time monitoring anthropogenic CO_2 . Recently, Li-solid state conductors based on Li-garnet structures received attention due to their fast transfer properties and safe operation over a wide temperature range. Through this presentation basic theory and history of Li-garnets will first be introduced and critically reflected towards new device opportunities demonstrating that these electrolytes may be the start of an era to not only store energy or sense the environment but also to emulate data and information based on simple electrochemistry device architecture twists.

In the first part we focus on the fundamental investigation of the electro-chemo-mechanic characteristics and design of disordered to crystallizing Li-garnet structure types and their description. Understanding the fundamental transport in solid state and asking the provocative question: how do Li-amorphous to crystalline structures conduct? As well, as how can we alter their charge-and mass transport properties for solid electrolytes and towards electrodes is discussed. Here, we firstly present new Li-garnet battery architectures for which we discuss lithium titanate and antimony electrodes in their making, electrochemistry and assembly to full battery architectures. Secondly, new insights on degree of glassy to crystalline Li-garnet thin films are presented based on model experiments of the structure types. Here, the thermodynamic stability range of maximum Li-conduction, phase, nucleation and growth of nanostructure is discussed using high resolution TEM studies, near order Raman investigations on the Li-bands and electrochemical transport measurements. The insights provide novel aspects of material structure designs for both the Li-garnet structures (bulk to films) and their interfaces to electrodes, which we either functionalize to store energy for next generation solid state batteries or ... make new applications such as Li-operated CO_2 sensor tracker chips. As a final part we review in a more holistic picture how one can use such materials and change the electrochemistry from energy storage, chemical sensing to data emulation for which we see prospect for electric vehicles, the Internet of Things or hardware in artificial intelligence.

2:00 PM CM03.03.02

X-Ray Tomography Studies of Ceramic Solid Electrolytes for Solid-State Battery Applications Kelsey B. Hatzell, Marm Dixit and Fengyu Shen; Vanderbilt University, Nashville, Tennessee, United States.

All solid-state batteries are promising solutions for high energy density storage devices. Absence of volatile liquid elements in the system mitigates the safety hazards encountered in conventional batteries. Ceramic electrolytes have showcased outstanding ionic conductivities and high shear modulus, however have stability and processing challenges still exist. While theoretical studies suggested that solid electrolytes with shear moduli greater than 8.5 GPa can mitigate Li dendrite formation, recent experiments have shown contradictory results. So far, the studies to understand the failure mechanism in ceramic electrolytes have been primarily surface based ex-situ characterization/imaging techniques. Toward the goal of understanding processing-structure relationships for practical design of solid electrolytes, the present study tracks structural transformations in solid electrolytes processed at three different temperatures (1050, 1100, and 1150 °C) using synchrotron X-ray tomography. A subvolume of $300 \mu\text{m}^3$ captures the heterogeneity of the solid electrolyte microstructure while minimizing the computational intensity associated with 3D reconstructions. While the porosity decreases with increasing temperature, the underlying connectivity of the pore region increases. Solid electrolytes with interconnected pores short circuit at lower critical current densities than samples with less connected pores. These insights provide insight into the importance of microstructure on device performance.

2:15 PM CM03.03.03

Multi-Modal Characterization of $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ Solid Electrolyte Stability in Solid-State Lithium Metal Batteries Andrew L. Davis¹, Kevin N. Wood², Regina Garcia-Mendez³, Kuan-Hung Chen³, Eric Kazyak¹, Jeff Sakamoto^{1,3}, Glenn Teeter² and Neil P. Dasgupta¹; ¹Mechanical Engineering, University of Michigan, Ann Arbor, Michigan, United States; ²National Renewable Energy Laboratory, Golden, Colorado, United States; ³Materials Science and Engineering, University of Michigan, Ann Arbor, Michigan, United States.

Solid-state batteries based on ultra-high ionic conductivity solid electrolytes are a promising technology to increase battery lifetime and capacity, and reduce safety concerns associated with usage of a flammable liquid electrolyte. In recent years, sulfide solid electrolytes such as $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ (LGPS) have achieved ionic conductivities comparable to or higher than that of traditional liquid electrolytes. Despite these promising breakthroughs, viable high capacity and high energy density sulfide solid-state batteries have proved elusive. The small electrochemical stability window of sulfide electrolyte materials leads to undesirable reactions at the electrode/electrolyte interface against both high voltage cathode materials and Li metal anodes. This forms a solid electrolyte interphase (SEI), which dramatically degrades battery performance.

To gain a deeper fundamental understanding of the dynamic evolution of the SEI, as well as its spatially varying composition and phase, the LGPS-Li metal interface was characterized by electrochemical measurements, *operando* X-ray photoelectron spectroscopy (XPS), *in-situ* auger spectroscopy, scanning electron microscopy (SEM), and optical microscopy. This allowed for quantitative evaluation of time dependent degradation of the interface, which occurs due to the evolution of a variety of decomposition by-products. *Operando* XPS was used to correlate distinct decomposition products with

corresponding increases in overpotential. *In-situ* Auger, SEM and optical Mapping of the surface shows spatial inhomogeneities leading to preferential lithium plating and corresponding $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ breakdown. By performing complementary electrochemical measurements of bulk solid-state batteries employing Li metal, electrochemical signatures associated with interfacial degradation can be identified. Using these techniques and the new mechanistic insights gained, rational interfacial design strategies are identified that can provide a pathway to limit interfacial instability and improve battery performance.

2:30 PM *CM03.03.04

***In Situ* Scanning Electron Microscope Observations of Li Plating/Stripping Reactions on Oxide Solid Electrolytes** Munekazu Motoyama, Takayuki Yamamoto and Yasutoshi Iriyama; Nagoya University, Nagoya, Japan.

The theoretical capacity of Li metal anode (3860 mAh g^{-1}) is more than ten times greater than those of other practical anodes such as graphite and $\text{Li}_4\text{Ti}_5\text{O}_{12}$ for lithium ion battery. However, Li dendrites cause short-circuit in liquid electrolytes during cycles of Li plating/stripping. On the other hand, since inorganic solid electrolytes (e.g. $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$) have been expected to prevent dendrite growth, all-solid-state-lithium battery (SSLB) has been regarded to innovate battery technology and enable the use of Li metal anode. Hence, it is important to obtain the fundamental understanding of Li plating/stripping processes on solid-state electrolytes.

We have studied the Li plating/stripping reactions with lithium phosphorous oxynitride (LiPON) glass electrolyte and $\text{Li}_{6,6}\text{La}_3\text{Zr}_{1,6}\text{Ta}_{0,4}\text{O}_{12}$ [LLZ(Ta0.4)] coated with thin current collector (CC) films of Cu, Ni, W, and Pt [1]. The Li nucleation sites are supposed to exist at solid/solid interfaces in "lithium-free"-thin-film SSLB [2]. Hence, the nuclei must push either electrode or electrolyte to create their own spaces. This process is associated with generation of significant strain energies.

This study applies an *in-situ* scanning-electron microscope (SEM) observation technique to the investigation on the Li nucleation/growth and dissolution processes with various CC films (Cu, Ni, W, Pt, Au). Cu, Ni, and W are unable to form specific alloy phases with Li. Pt and Au form alloy phases with Li. The top and bottom surfaces of a $\text{Li}_{1-x-y}\text{Al}_x(\text{Ti, Ge})_{2-x}\text{Si}_y\text{P}_{3-y}\text{O}_{12}$ (LATP) sheet (Ohara Co.) were coated with 2.5- μm -thick LiPON layers by RF magnetron sputtering. Additionally, a LLZ(Ta0.4) plate (Toshiba Manufacturing Co. Ltd.) with a thickness of 0.5 mm was used as an electrolyte [3].

A current collector film (i.e. Cu, Ni, W, Pt, Au) was deposited on the top LiPON surface and LLZ(Ta0.4) surface by pulsed laser deposition (PLD). A Li film with a thickness of 2 to 3 μm was deposited within an area of 9.0 mm in diameter on the other side of a cell as the counter electrode by vacuum evaporation.

The results of dynamic observations of Li plating/stripping and Li alloying/dealloying on LiPON and LLZ(Ta0.4) coated with thin metal CC films via an *in-situ* SEM technique will be discussed.

The authors gratefully acknowledge JSPS 17H04894 and ALCA-SPRING for the financial supports.

[1] M. Motoyama *et al.*, *Electrochemistry*, **82**, 364 (2014); *J. Electrochem. Soc.*, **162**, A7067 (2015); *J. Electrochem. Soc.*, **165**, A1338 (2018).

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3:00 PM BREAK

SESSION CM03.04: High Capacity Battery Electrodes

Session Chairs: Katherine Jungjohann and Dong Su

Monday Afternoon, November 26, 2018

Hynes, Level 3, Room 300

3:30 PM *CM03.04.01

Multimodal X-Ray Characterization of Operating Electrochemical Energy Storage Systems Johanna N. Weker; SLAC National Accelerator Lab, Menlo Park, California, United States.

The shift from fossil fuels toward clean, renewable energy will require significant improvements in rechargeable battery technology for electric vehicles. Current battery technology limits electric vehicles to a short travel range, slow recharge, and costly price tag. Li-ion batteries promise the high specific capacity required to replace the internal combustion engine with a number of possible earth abundant electrode materials; however, setbacks such as capacity fading hinder the full capability of these rechargeable batteries. In the search for better electrode materials, multimodal X-ray characterization spanning many relevant length scales during typical battery operation is vital in understand and overcoming the failure mechanisms of these materials. We will discuss our multimodal approach combining information from high resolution X-ray microscopy and spectra-microscopy, micro- and nano-tomography, X-ray diffraction, and X-ray absorption spectroscopy to track electrochemical, morphological, and structural changes in the electrode material in real time during typical battery operation.

4:00 PM CM03.04.02

Revealing Nanoscale Passivation and Corrosion Mechanisms of Reactive Battery Materials in Gas Environments Yuzhang Li and Yi Cui; Stanford University, Stanford, California, United States.

Lithium (Li) metal is a high-capacity anode material ($3,860 \text{ mAh g}^{-1}$) that can enable battery chemistries beyond Li-ion. However, Li metal is highly reactive and repeatedly consumed when exposed to liquid electrolyte (during battery operation) or the ambient environment (throughout battery manufacturing). Studying these corrosion reactions on the nanoscale is especially difficult due to the high chemical reactivity of both Li metal and its surface corrosion films. Here, we directly generate pure Li metal inside an environmental transmission electron microscope (TEM), revealing the nanoscale passivation and corrosion process of Li metal in oxygen (O_2), nitrogen (N_2), and water vapor (H_2O). We find that while dry O_2 and N_2 (99.9999 vol%) form uniform passivation layers on Li, trace water vapor (~1 vol%) disrupts this passivation and forms a porous film on Li metal that allows gas to penetrate and continuously react with Li. To exploit the self-passivating behavior of Li in dry conditions, we introduce a simple dry- N_2 pretreatment of Li metal to form a protective layer of Li nitride prior to battery assembly. The fast ionic conductivity and stable interface of Li nitride results in improved battery performance with dendrite-free cycling and low voltage hysteresis. Our work reveals the detailed process of Li metal passivation/corrosion and demonstrates how this mechanistic insight can guide engineering solutions for Li metal batteries.

[1]: Y. Li, *et al.* "Revealing nanoscale passivation and corrosion mechanisms of reactive battery materials in gas environments," *Nano Letters* 17.8 (2017):

4:15 PM CM03.04.03

Operando Characterization of Lithium Metal Plating and Stripping Using Grazing Incidence Small Angle X-Ray Scattering Robert M. Kasse^{1,2}, Natalie R. Geise^{3,2}, Hans-Georg Steinrueck² and Michael F. Toney²; ¹Materials Science and Engineering, Stanford University, Stanford, California, United States; ²Stanford Synchrotron Radiation Lightsource, SLAC National Accelerator Laboratory, Menlo Park, California, United States; ³Chemistry, Stanford University, Stanford, California, United States.

Emerging technologies such as electric vehicles, which rely on high energy density batteries, necessitate the development of advanced materials to replace those currently being used in traditional lithium ion devices. Anodes employing lithium metal are the most promising given their high specific capacity (3,860 mAh/g) and low electrochemical potential (-3.04 V vs SHE). However, lithium metal is highly unstable with large irreversible capacity losses occurring during plating and stripping due to electrolyte decomposition and formation of electrochemically inactive 'dead' lithium. To allow for the intelligent design of lithium protection strategies, a fundamental understanding of the plating and stripping behavior is needed, particularly during the first cycle.

These dynamic processes occurring during battery operation require *operando* characterization. Thus, we have performed grazing incidence small angle X-ray scattering (GISAXS) during the lithium plating and stripping process in order to probe the morphology of plated lithium. Investigating the surface of a copper film in an operating lithium-copper cell, we are able to determine the lithium metal growth mechanism and particle growth rates as a function of relevant battery parameters including electrolyte composition and cycling protocol. The nucleation and growth mechanism is very sensitive to electrolyte impurities and cycling protocol, due to the different solid electrolyte interphase (SEI) formed on the copper surface under different conditions. Fluorine-containing SEI components formed at high potentials due to impurity decomposition create a more uniform current distribution leading to monodisperse columnar growth of Li metal, compared to nonuniform deposition in a baseline electrolyte. A fundamental understanding of the effect of such parameters on lithium plating can be used to engineer high energy density batteries with enhanced safety and cycle life.

4:30 PM CM03.04.04

Multiscale Modeling and In Situ Visualization Analyses of Electrodeposition in Nanostructured Electrolytes Snehashis Choudhury and Lynden Archer; Cornell University, Ithaca, New York, United States.

Electrochemical cells based on alkali metal (Li, Na) anodes have attracted significant recent attention because of their promise for producing large increases in gravimetric energy density for energy storage in batteries. To facilitate stable, long-term operation of such cells a variety of structured electrolytes have been designed in different physical forms, ranging from soft polymer gels to hard ceramics, including nanoporous versions of these ceramics that host a liquid or molten polymer in their pores. In almost every case, the electrolytes are reported to be substantially more effective than anticipated by early theories in improving uniformity of deposition and lifetime of the metal anode. These observations have been speculated to reflect the effect of electrolyte structure in regulating ion transport to the metal electrolyte interface, thereby stabilizing metal electrodeposition processes at the anode. In this work, we create and study model structured electrolytes composed of covalently linked polymer grafted nanoparticles that host a liquid electrolyte in the pores. The electrolytes exist as freestanding membranes with effective pore size that can be systematically manipulated through straightforward control of the volume fraction of the nanoparticles. By means of physical analysis and direct visualization experiments using advanced optical microscopy, we report that at current densities approaching the diffusion limit, there is a clear transition from unstable to stable electrodeposition at Li metal electrodes in membranes with average pore sizes below 500 nm. We show that this transition is consistent with expectations from a recent theoretical analysis that takes into account local coupling between stress and ion transport at metal-electrolyte interfaces.

References:

1. Choudhury, S., Mangal, R., Agrawal, A. & Archer, L. A. A highly reversible room-temperature lithium metal battery based on crosslinked hairy nanoparticles. *Nat. Commun.* **6**, 10101 (2015).
2. Choudhury, S. *et al.* Confining electrodeposition of metals in structured electrolytes. *Proc. Natl. Acad. Sci.* (2018).

4:45 PM CM03.04.05

Coupling Operando Techniques for Unravelling the Electrochemical and Structural Mechanism of High-Performance Lithiated Nitrides as Negative Electrode Material for Li-Ion Batteries Nicolas Emery and Jean-Pierre Pereira-Ramos; ICMPE-GESMAT UMR 7182, Thiais, France.

Comprehension of redox processes and their influence on structural properties of electrode materials is a key point to improve Li-ion batteries efficiency. The rise of *operando* techniques leads to a better insight into these reactions due to the *real-time* observation of the process. In this work, we will mainly develop two examples of lithiated transition metal nitrides studies where different operando techniques were combined.

Our group has clearly demonstrated layered lithiated transition metal nitrides can be considered as genuine Li intercalation compounds and possible negative electrode materials for Li-ion batteries [1-2]. In particular attractive properties for optimized Co and Ni contents in the Li-M-N system were proved with for instance $\text{Li}_2\text{Ni}_{0.67}\text{N}$ exhibiting a specific capacity of 200 mAh g^{-1} and an excellent cycle life. After a precise determination of the chemical composition using NRA technique, its structural mechanism under operation was studied and solved using operando XRD upon successive discharge-charge cycles [2]. A solid-solution behaviour is shown with a very limited volume variation, less than 1% which well explains electrochemical features. A superstructure is mandatory to clearly describe the *operando* XRD data set recorded here. Indeed, the presence of vacancies in the Li_2N^- planes allows a slight displacement of interlayered nickel ions cell inducing a negligible swelling process of the host lattice in line with a remarkable cycle life.

With a specific capacity of 280 mAh g^{-1} at C rate available around 1.2 V vs Li^+/Li , a 3D Li_7MnN_4 has been proved to be a credible alternative to $\text{Li}_4\text{Ti}_5\text{O}_{12}$ for moderate to high power applications. The redox-mechanism and structural response upon a full electrochemical oxidation/reduction cycle have been studied using XAS and XRD *in-situ operando* techniques. The charge curve composed of two successive plateaus and a continuous potential increase, is well explained by two diphasic domains and a solid-solution behaviour [3]. After a MCR-ALS analysis of the Mn K-edge absorption spectra data set, three different environments related to three different Mn oxidation states involved in redox processes were isolated [4]. Using the simple concept of coordination charges and comparison with available data for appropriate reference oxides, the oxidation states of each environment were ascribed and fully explained the achieved specific capacity. By combining these two methods, a comprehensive scenario has been proposed to explain the attractive electrochemical performances of Li_7MnN_4 with the role of Mn 5+, Mn 6+ and Mn7+ ions here stabilized by the nitride framework.

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[3] N. Emery *et al.*, *J. Power Sources*, **247** (2014) 402-405

[4] D. Muller-Bouvier, N. Emery *et al.*, *PCCP* **19** (2017) 27204-27211

8:15 AM *CM03.05.01

Correlative Imaging of Electrochemical Devices Over Multiple Time and Length Scales Paul Shearing; University College London, London, United Kingdom.

Electrochemical device is a term used to describe a group of technologies including fuel cells, batteries, electrolysers and super-capacitors. Whilst many of these technologies are already in common daily usage, for example Li-ion batteries that power our mobile phones, in the future electrochemical devices will play an increasing role in our lives – from fuel cells that can power our homes to high performance batteries for our cars.

At a microscopic length scale, these devices can be considered as one of a general class of porous materials, whereby the physical microstructure will influence a range of phenomena, including diffusion, catalysis and conductivity – our ability to engineer these microscopic features to maximize performance can be translated to substantial improvements in macroscopic device design. At macroscopic length scales the robustness of device design will influence the system energy and power density and its ability to safely store/convert energy over extended periods of time.

As these materials are likely to evolve over time, in response to range of processing and environmental conditions (sintering, corrosion, failure etc); understanding how these changes in microstructure can be linked to understanding of degradation and failure is pivotal to improving device lifetime and safety.

Over the past 10 years the increasingly widespread use of X-ray imaging and tomography has revolutionized our understanding of these materials; with increasing sophistication researchers have been able to characterize samples over multiple time and length scales from nm to mm and from ms to days. Here we consider examples of our work to explore these materials in three and “four” dimensions, to examine materials evolution with time. We will explore case studies that utilize both laboratory and synchrotron X-ray sources across a range of spatial and temporal domains, and examine how improvements in these imaging techniques, alongside correlative spectroscopy, is providing unprecedented insight into these materials and devices.

8:45 AM CM03.05.02

Monitoring Capacity Losses Through *Operando* X-Ray Diffraction in Lithium Metal Anodes Natalie R. Geise^{1,2}, Robert M. Kasse^{3,2}, Hans-Georg Steinrueck² and Michael F. Toney²; ¹Chemistry, Stanford University, Stanford, California, United States; ²Stanford Synchrotron Radiation Lightsource, SLAC National Accelerator Laboratory, Menlo Park, California, United States; ³Materials Science, Stanford University, Stanford, California, United States.

Li-metal is a promising, high-capacity anode that can be incorporated into Li-ion, Li-S, and Li-air battery systems to meet the need for energy-dense batteries. Coulombic efficiency losses remain a major challenge to adoption and commercialization. These losses are driven by loss of lithium to the solid electrolyte interphase (SEI) and into metallic lithium deposits that become electrically disconnected (“dead” Li) due to complex morphological changes. While protection methods, such as coatings and electrolyte additives, have yielded improved efficiencies, fundamentally understanding how these improvements are realized will allow for optimization of their design.

Here, we have developed a method of monitoring lithium metal in the anode through plating and stripping cycles via *operando* X-ray diffraction (XRD). We obtain quantitative results on the reversible lithium metal, dead lithium development and evolution with cycling, and lithium corrosion. Our results show the lithium metal efficiency, measured through XRD, is higher than the electrochemical Coulombic efficiency measurements. Additionally, the contribution of “dead” lithium to the overall Coulombic efficiency varies much more across electrolytes and cycling conditions than the SEI does. This new experimental methodology and the understanding on the origins of capacity loss in lithium metal anodes which it enables will lead to better-designed protection layers and electrolytes which improve anode performance.

9:00 AM CM03.05.03

Plan-View *Operando* Video Microscopy of Li Metal Anodes Adrian J. Sanchez, Kuan-Hung Chen, Eric Kazyak and Neil P. Dasgupta; University of Michigan Ann Arbor, Ann Arbor, Michigan, United States.

Improving the safety and performance of Li metal anodes is key to enabling next generation batteries such as Li-Air and Li-Sulfur. However, the mechanisms governing poor performance of Li metal anodes are not fully understood, which hinders our ability to characterize, diagnose, and rationally design solutions to problems including dendrite growth and low Coulombic efficiency. *In situ* and *operando* analyses are well suited to study the mechanisms of battery degradation, as they avoid any sample alteration due to the disassembly of a cell.

Herein, we present a multifunctional *operando* visualization platform that synchronizes optical recordings with cycling electrochemistry. This platform was initially used to understand the origins of the “peaking” behavior exhibited in the voltage traces of Li symmetric cells [1]. However, by limiting the viewing angle to a cross sectional perspective, the impact of electrode surface variations, including microstructure, flaws, and chemical inhomogeneities cannot be fully accounted for. To address this, in this study, a plan view optical visualization cell was designed that maintains a highly uniform current distribution along the electrode surface and avoids mechanical deformation of the electrode. This enables correlation of dendrite nucleation location to surface features. Dendrite nucleation and pitting nucleation density are quantified as a function of current density on a Li metal surface. Additionally, the impact of pitting on the performance of a Li metal anode is directly observed. The impact of surface modifications on Li plating, including protective coatings and mechanical deformation, are also quantified. Finally, the knowledge generated on the coupled morphological and electrochemical behavior of Li metal deposition will be discussed as a potential pathway to develop battery failure diagnostics.

1. K. N. Wood, E. Kazyak, A. F. Chadwick, K. H. Chen, J. G. Zhang, K. Thornton, N. P. Dasgupta, *ACS Central Science* **2**, 790 (2016)

9:15 AM CM03.05.04

***In Situ/Operando* Grazing Incidence Small Angle X-Ray Scattering of Model Oxide Nanostructures for Li-Ion Battery Conversion Electrodes** Jae Jin Kim¹, Byeongdu Lee¹, Chun Zhou², Hyo Seon Suh², Anil Mane¹, Jeffrey Elam¹, Paul Nealey², Paul Fenter¹ and Tim Fister¹; ¹Argonne National Laboratory, Lemont, Illinois, United States; ²The University of Chicago, Chicago, Illinois, United States.

Conversion reactions in Li ion batteries, such as the electrochemically-driven phase separation of a transition metal oxide into metal nanoparticles and lithium oxide species, are well-known to have specific capacities far beyond typical intercalation materials. However, these types of reactions invariably suffer from irreversibility and hysteresis due to their substantial volume change and kinetic barriers. Oxides also tend to have substantially lower redox potentials than thermodynamically expected values, limiting their practical use. Given the complex network of metal-rich and lithia domains evolved during lithiation, interfacial processes must play a critical role in the nucleation of the overall conversion reaction and charge/mass transport. In contrast to the complex network of nanoparticles that form during lithiation, we have studied electrode surfaces with periodic tungsten oxide nanostructures, whose dimensions can be tuned to test the mechanical and kinetic properties of conversion reactions. Our fabrication approach uses the selective growth of ALD on block copolymers, in this case producing arrays of oxide nano-cylinders or their inverse, a film with periodic hole patterns. These electrodes are well-suited for grazing incidence small angle X-ray scattering (GISAXS), which can be used to assess the size, density, and spacing of the electrodes during the reaction. Using *operando* GISAXS, we find that nanoscale (50 – 80 nm) oxides undergo conversion reactions at 1.4 – 1.7 V, which is close to the theoretical value (1.65 V) and well above the discharge plateau of 0.8 – 0.9 V for micron-sized bulk powders. Insights from this study can bring a new perspective on enhancing the energy density and reversibility of conversion reactions and provide strategies for improving their overall performance.

9:30 AM CM03.05.05

Reaction with Larger Ions Avoids Fracture in a Conversion Battery Material—*In Situ* TEM Investigation [Matthew G. Boebinger](#)^{1,2}, Baolin Wang^{1,3}, Marc Papakyriakou^{1,3}, Shuman Xia^{1,3}, Ting Zhu^{1,2,3} and Matthew McDowell^{1,2,3}; ¹Georgia Institute of Technology, Atlanta, Georgia, United States; ²School of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, Georgia, United States; ³The George W. Woodruff School of Mechanical Engineering, Georgia Institute of Technology, Atlanta, Georgia, United States.

Demand for cheap energy storage systems has led to growing interest in the development of sodium- and potassium-ion battery systems. Conversion and alloying-type electrode materials with high specific capacity are attractive options for these batteries, but the larger volumetric expansion during reaction with sodium and potassium compared to lithium is thought to limit cycle life. The nanoscale reaction mechanisms of many electrode materials with Na⁺ and K⁺ ions are unknown, however, and they must be investigated to understand how to engineer Na and K-battery materials to undergo minimal mechanical damage due to volume changes. In this study, *in situ* transmission electron microscopy (TEM) experiments are used to examine the nanoscale transformations of cube-shaped FeS₂ nanocrystal electrode materials as they undergo reaction with Li⁺, Na⁺, and K⁺. Although the FeS₂ nanocrystals underwent a conversion-type reaction via a two-phase mechanism with a sharp reaction front in all cases, fracture was only observed to occur during lithiation, despite the larger volumetric changes associated with sodiation and potassiation. This difference was ascribed to dissimilar shapes of the two-phase reaction fronts during the reaction processes. Specifically, reaction fronts during lithiation were found to retain rectangular shapes with sharp corners, while sodiation and potassiation caused the reaction front to take an oval shape with blunted corners. Chemomechanical modeling of stress evolution during reaction showed that the differences in the evolution of the shape of the two-phase reaction front led to higher tensile stress concentrations and particle fracture during lithiation. The results indicate that even though larger volumetric expansions take place in Na- and K-ion battery materials, these volume changes may be managed through understanding and control of nanoscale reaction mechanisms and do not necessarily cause failure of individual particles.

9:45 AM BREAK

SESSION CM03.06: Solid and Liquid Interfaces
Session Chairs: Neil Dasgupta and Matthew McDowell
Tuesday Morning, November 27, 2018
Hynes, Level 3, Room 300

10:15 AM *CM03.06.01

Scanning Electrochemical Microscopy of Battery Interfaces—Versatile Imaging Using Novel Ionic Probes and Multimodal Raman Interrogation Zachary Gossage, Noah Schorr, Jingshu Hui, Zachary Barton and [Joaquin Rodriguez-Lopez](#); University of Illinois at Urbana Champaign, Urbana, Illinois, United States.

Designing advanced battery interfaces requires visualizing ionic, electronic, and redox pathways that indicate how local surface activation and site-specific differential reactivity impact ion-intercalation and interfacial evolution with cycling. This presentation will discuss new in-situ analytical tools based on the scanning electrochemical microscope (SECM) that incorporate functions for imaging surface redox reactivity, spectroelectrochemistry, and ionic transfer reactions for species such as Li⁺, Na⁺ and K⁺ at interfacial and bulk nanostructures in non-aqueous electrolytes.

In ionic measurements, the principle is based on SECM probes that integrate mercury micro- and nano- cap electrodes on which alkaline ions can be detected by means of fast-scan anodic stripping voltammetry. The probe potential provided chemical specificity while the probe current enables the measurement of ionic fluxes with excellent stability and linearity. We will demonstrate how these probes were used for the measurement of ion insertion sites on graphene, graphite, and silicon nanostructures. When combined with redox modes using the SECM (e.g. feedback), these probes provide a comprehensive view of how interfacial processes impact charge transfer across operating interfaces.

Complementing these powerful measurements, we will discuss how the combination of SECM with Raman spectroscopy via colocalized and simultaneous measurements of operating electrodes enables real-time correlation of electrochemical and structural information. We will show how our system is used for simultaneous imaging and time-resolved experiments of interfaces of interest for energy storage, such as redox polymers and graphene with a resolution of ~1 micron, sub-second resolution, and high signal to noise ratio. We hope our techniques will contribute to a new understanding of interfacial processes on battery structures, allowing the measurement of ionic reactivity, and elucidating the impact of interfacial processes on single reacting sites. SECM mapping reveals aspects of surface reactivity that are lost during averaging in conventional battery testing.

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10:45 AM CM03.06.02

Cryo-Electron Microscopy for Battery Materials Yanbin Li and Yi Cui; Stanford University, Stanford, California, United States.

Cryo-electron microscopy (cryo-EM) received the 2017 Nobel Prize in Chemistry for its ability to elucidate the nanostructure of biomolecules in their native state, revolutionizing the field of structural biology. Here, we pioneer an approach to utilize this powerful technique to enable new discoveries for batteries¹ (Y. Li*, **Y. Li***, Y. Cui, et al. *Science* 2017, DOI: 10.1126/science.aam6014) and show that cryo-EM can potentially have a similar impact in materials science.

Whereas conventional transmission electron microscopy (TEM) studies are unable to preserve the native state of chemically-reactive and beam-sensitive battery materials (e.g. Li metal) after operation, such materials remain pristine at cryogenic conditions. It is then possible to atomically resolve individual Li metal atoms and their interface with the solid electrolyte interphase (SEI). We observe that dendrites in carbonate-based electrolytes grow along the <111> (preferred), <110>, or <211> directions as faceted, single-crystalline nanowires. These growth directions can change at kinks with no observable crystallographic defect. Furthermore, we reveal distinct SEI nanostructures formed in different electrolytes that explain why certain additives lead to better performance. With cryo-EM, we open up exciting new opportunities for scientific discovery, which will be critical for providing fundamental insight to battery materials design.

Yuzhang Li*, **Yanbin Li***, A. Pei, K. Yan, Y. Sun, C-L Wu, L-M, Joubert, R. Chin, A.L. Koh, Y. Yu, J. Perrino, B. Butz, S. Chu, Y. Cui. “Atomic structure of sensitive battery materials and interfaces revealed by cryo-electron microscopy,” *Science* (2017) DOI: 10.1126/science.aam6014

*Denotes equal contribution

11:00 AM *CM03.06.03

Electrochemical Interfacial Properties Revealed by Synergistically Combining Ambient Pressure XPS with Theory Ethan J. Crumlin^{1,2}; ¹Advanced Light Source, Lawrence Berkeley National Laboratory, Berkeley, California, United States; ²JCESR, Lawrence Berkeley National Laboratory, Berkeley, California, United States.

Interfaces play an essential role in nearly all aspects of life and are critical for electrochemistry. Electrochemical systems ranging from high-temperature solid oxide fuel cells (SOFC) to batteries to capacitors have a wide range of important interfaces between solids, liquids, and gases which play a pivotal role in how energy is stored, transferred, and/or converted. This talk will focus on our use of ambient pressure XPS (APXPS) to directly probe the solid/gas and solid/liquid electrochemical interface. In particular, I will discuss how we synergistically combine this powerful experimental technique with DFT theoretical insight to reveal a mechanistic understanding of electrochemical interfaces. I will highlight some of our recent investigations into CO₂ adsorption phenomena on various metals. *In situ* APXPS and DFT together provide a comprehensive understanding of the initial adsorption processes and how oxygen and water transform CO₂'s adsorption behavior. Additionally, I will highlight how theory/modeling has enhanced our knowledge of *in situ/operando* solid/liquid APXPS investigations including electrochemically promoted dissolution and the interaction of a magnesium electrode in a non-aqueous electrolyte. Information gained from these studies will aid in the guided design and control of future electrochemical interfaces.

11:30 AM CM03.06.04

Illuminating the Oxygen Cathode Interface of the Non-Aqueous Metal Oxygen Battery Iain Aldous and Laurence Hardwick; Univ of Liverpool, Liverpool, United Kingdom.

Improving energy storage, beyond Li-ion batteries, is an important opportunity to provide solutions for varying applications.¹ A family of emerging battery chemistries are non-aqueous metal oxygen cells. Ideally, the cathodic reactant (oxygen) is provided from the atmosphere and electrochemically reduced in the presence of alkali metal cations to form reduced oxygen species (ROS) such as peroxides and superoxides. On charge, the formed ROS are then electroxidised and the oxygen returned to the atmosphere and alkali metal cations reduced at the alkali metal anode to form alkali metal (Li, Na, K and Ca). Combining electrochemistry and spectroscopy has provided an understanding of how to control this mechanism through the solvation of O₂⁻, LiO₂²⁻, NaO₂^{3,4} and CaO₂⁵. This is achieved via the manipulation of the local chemical environment of these species within the electrolyte. Additives such as water⁶ and organic redox mediators⁷ can be used to great effect in increasing capacity, rechargeability and decreasing the over potential of the system.

This talk will focus on the group's research and findings on how to manipulate the direction of the oxygen reduction reaction in non-aqueous metal-oxygen batteries. Using *in situ/ex situ* surface enhanced Raman spectroscopy and UV/Vis spectroscopy to characterise the electrochemical reactions occurring at the cathode interface demonstrates the group's findings. Discussion will touch upon how oxygen electrochemistry relates to the electrode substrate and electrolyte composition, as well as the use of electrolyte additives.

References:

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11:45 AM CM03.06.05

Electrified Solid/Liquid Interface Studied by Nanoelectrical and Nanoelectrochemical Atomic Force Microscopy Zhuangqun Huang¹, Peter De Wolf¹, Antoine Dujardin^{1,2}, Bede Pittenger¹ and Thomas Mueller¹; ¹Bruker Nano Surfaces, Goleta, California, United States; ²Cellular Microbiology and Physics of Infection Group, Lille Centre for Infection and Immunity, CNRS UMR8204, INSERM U1019, Lille Regional Hospital University Centre, University of Lille, Institut Pasteur de Lille, Lille, France.

Atomic force microscopy (AFM) has been adopted for *in situ* and *in operando* electrical and electrochemical (EC) studies with nanometer resolution at electrified solid-electrolyte interfaces. Recent developments include PeakForce EC-AFM for topographic and nanomechanical imaging during EC reactions on the surfaces of Li ion battery anodes [1] and PeakForce scanning electrochemical microscopy (SECM) for the simultaneous acquisition of local EC and conductivity information at electrified solid/liquid interfaces of nanoparticle-catalysed photoelectrodes for water splitting [2 - 3]. In this work, we introduce these recently-developed techniques with a variety of examples in energy, biological, and semiconductor applications.

We have also developed DataCube SECM to provide highly-dimensional, big-data results allowing us to perform in-depth data mining for improved electrochemical kinetic quantification, 3-D nano-EC and nanomechanical characterization. This mode is based on the fast force volume mapping method, providing a force-distance spectrum in each pixel. With each probe ramping cycle, an SECM probe approach curve (PAC) is acquired. This method overcomes the limitation of conventional SECM methods where only few PACs are inefficiently captured from a single or very few point locations. By direct analysis of the experimentally achieved data cube, one can greatly improve the quantification accuracy. It also allows plotting the SECM current images at different tip-sample distances with nm step accuracy. In addition, during each force-distance cycle, the probe can be held on the surface for a user-defined dwell time. This enables nanocontact EC studies such as local surface EC potential measurement. [4-5]

In addition, many applications require performing nanoelectrical studies in electrolyte solutions, e.g. battery, bioelectricity, and bioelectromechanics. However, these are technically challenging. The general implementation requires avoiding electrical shorting, liquid spilling and chemical corrosion. Minimal parasitic electrochemistry and stray capacitance are also needed. With the use of nanoelectrode AFM tips (~25 nm active tip apex), we have developed a suite of solutions to conduct multi-dimensional nanoelectrical measurements in liquid, including piezoelectric response, conductivity, and Kelvin Probe mapping. The DataCube method has been also integrated with these implementations. For example, DataCube-Piezo Force Microscopy characterizes piezoelectric materials, where pixelwise frequency-based spectra allow studying the contact resonance properties of bio-mimic materials. [6]

[1] Kuma et al., *ACS Appl. Mater. Interfaces*, **2017**, *9*, 28406

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[3] Jiang et al., *ChemSusChem* **2017**, *10*, 4657

[4] Nellist et al., *Nat. Energy*, **2018**, *3*, 46

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[6] Cui et al., *Phys. Rev. Lett.*, **2018** submitted

SESSION CM03.07: Photoelectrochemistry
Session Chairs: Ethan Crumlin and Matthew McDowell
Tuesday Afternoon, November 27, 2018
Hynes, Level 3, Room 300

1:30 PM CM03.07.01

***In Situ* Raman Investigation of Doped Ceria Redox Mechanisms Under Solar-to-Fuel Conversion Schemes** Claire Halloran¹, Alfonso J. Carrillo¹, Eva Sediva^{1,2} and Jennifer L. Rupp¹; ¹Massachusetts Institute of Technology, Cambridge, Massachusetts, United States; ²ETH Zürich, Zurich, Switzerland.

Solar-to-fuel technology promises to play a key role in realizing a carbon-neutral future by enabling renewable fuel processing for capacity-independent storage beyond current battery technologies [1]. Metal oxide catalysts enable the two-step thermochemical cycle by catalyzing the reduction of H₂O and CO₂ to produce H₂ and CO. Currently, ceria is the reference material due to its rapid kinetics, crystallographic stability, and abundance [1]. To address the low fuel production of ceria, doping with tetravalent cations and co-doping with 3+/5+ combinations are used to enhance oxygen release and thus increase maximum fuel yield [2]. However, the reaction mechanisms and kinetics of oxygen vacancy formation in doped-ceria are still unclear, and this understanding will be crucial to developing improved redox materials that will make solar-to-fuel technology economically viable.

This novel investigation utilizes *in situ* Raman spectroscopy under redox cycling schemes to illuminate the reaction mechanisms of oxygen vacancy formation and annihilation in 10mol% doped ceria solid solutions of the composition Ce_{0.9}(Me)_{0.1}O₂ with Me= La, Zr, Hf, Nb and in co-doped Ce_{0.9}La_{0.05}Nb_{0.05}O₂. *In-situ* Raman spectroscopy was utilized to study the chemical reduction of doped-ceria materials under H₂ atmosphere up to 900 °C and the redox cycling under alternating reducing H₂ and oxidizing CO₂ atmospheres at a constant temperature of 800 °C.

Results revealed that the peak corresponding to the triply degenerate F_{2g} stretching mode of the cation and oxygen ions in the cubic fluorite structure of ceria shifts to lower frequencies and decreases in intensity during reduction; these changes correspond to chemical expansion with the reduction of the cation and an increase in the oxygen vacancy concentration. Additional vacancy bands also appear at different positions depending on the dopant choice and indicate how each dopant cation facilitates the formation of oxygen vacancies

Raman spectroscopy confirms that catalytic oxygen vacancy concentration determines the fuel yield of this process: samples with the highest fuel yield also had the largest shift of the peak corresponding to the triply degenerate F_{2g} when heated, suggesting the highest oxygen vacancy concentration and thus the highest oxygen storage capacity. This model experiment not only provides crucial preliminary results for understanding the mechanisms of oxygen vacancy formation in doped ceria catalysts but also provides an experimental template for future investigation of reaction mechanisms of other electrochemical materials. By utilizing Raman spectroscopy to understand the redox mechanisms of various materials, as was done in this experiment, materials scientists can optimize doping to engineer the redox performance of materials for a variety of applications.

[1] M. Kubicek, et al., *Journal of Materials Chemistry A*, vol. 5, no. 24, 2017.

[2] C. Muhich, et al. *Acta Materialia*, pp. 728-737, 2018.

1:45 PM CM03.07.02

***Operando* Characterization of Charge Extraction Profiles in Semiconductor Photoelectrodes with Nanoscale Resolution** Gideon Segev¹, Chang-Ming Jiang^{1,2}, Gregory Zaborski¹, Jason K. Cooper¹, Francesca Maria Toma¹ and Ian D. Sharp^{1,2}; ¹Lawrence Berkeley National Laboratory, Berkeley, California, United States; ²Walter Schottky Institut, Technische Universität München, Garching, Germany.

Detailed understanding of the opto-electronic properties of semiconductors and the driving forces and loss mechanisms that limit device performance is essential to the development of high efficiency solar energy conversion and storage systems. However, many photovoltaic and photoelectrochemical

systems are difficult to model and only few experimental methods are available for direct characterization of dominant loss processes under relevant operating conditions. To this end, empirical extraction of the spatial collection efficiency (SCE) is an operando, analytical tool to study new materials, and devices. Defined as the fraction of charge carriers that are photogenerated at a given location that contribute to the measured current, the SCE provides a functional depth profile of the active regions in the device. By combining incident photons to current efficiency (IPCE) measurements with optical modeling, we have extracted SCE cross-sectional profiles of several materials and photoelectrochemical cells. Thus, SCE extraction provides an in depth understanding of the driving forces and limiting mechanisms in new materials with relatively simple apparatus. For example, analyzing the SCE at different operating potentials while performing different chemical reactions allows distinguishing between bulk and surface losses. By focusing on the SCE at the surface, we were able to discern between surface losses attributed to slow reaction kinetics and fast surface recombination processes through charged band states. In this contribution, we analyze the transport properties of four different phases of copper vanadate photoanodes with a wide range of copper vanadium ratios. The spatial collection efficiency analysis is used to extract the potential dependent surface reactivity and collection length. Phases with a high copper content show a relatively high collection length yet suffer from high losses induced by losses induced by D-D transitions.

2:00 PM CM03.07.03

The Dynamics of Bubble Evolution on Structured Photoelectrochemical Interfaces Zebulon G. Schichtl, Hamed Mehrabi, James M. Lowe and Robert H. Coridan; University of Arkansas, Fayetteville, Arkansas, United States.

The dynamical behavior of product bubbles can limit the energy-conversion efficiency for electrodes performing gas-evolving reactions, such as hydrogen or oxygen evolution during water splitting. Bubbles can block or restrict the activity of catalytically-active areas and reduce light absorption due to undesired light reflection. While this problem is ubiquitous for applications like water splitting, the understanding of the collective dynamics of bubbles evolving at electrodes is lacking. Here, we explore these issues by measuring the high-speed dynamics of bubbles evolved from electrode interfaces. We describe the use of high-speed x-ray and optical imaging to study *in operando* gas-evolving electrodes under conditions relevant solar fuels applications. Imaging the high-speed dynamics of electrolytic bubble evolution allows us to measure the effects of electrostatic surface interactions, spatial organization of catalysts, and the mechanical interactions between evolving bubbles. Through high-speed imaging, we are able to map the local reaction kinetics by tracking bubble transport at the interface to better understand the collective behavior of evolving bubbles. Finally, we will discuss strategies to use rational hierarchical structuring of the electrocatalysts to improve catalytic performance.

2:15 PM CM03.07.04

Transient Absorption and Theoretical Studies of the Effect of Nitridation Time on Carrier Dynamics Of Ta₃N₅ Photoelectrodes for Overall Water Splitting Kazuhiko T. Seki¹, Dharmapura H. K. Murthy¹, Yohichi Suzuki^{1,5}, Hiroyuki Matsuzaki¹, Akihiro Furube², Zheng Wang³, Yasunobu Inoue³, Takashi Hisatomi⁴, Qian Wang³, Tsuyoshi Takata⁴, Shanshan Chen³ and Kazunari Domen³; ¹AIST, Tsukuba, Japan; ²Tokushima University, Tokushima, Japan; ³Tokyo university, Tokyo, Japan; ⁴Shinshu university, Matsumoto, Japan; ⁵Keio university, Kanagawa, Japan.

Photoelectrochemical (PEC) water splitting is a promising means for converting solar energy into chemical fuels. Decomposition of water into both H₂ and O₂ by a photocatalysts could be the simplest and efficient approach to scaling up fuel production from water. For decomposition of water, standard Gibbs free energy change of 1.23 eV is required. Therefore, a semiconductor with an energy band gap exceeding 1.23 eV, corresponding to a wavelength of 1008 nm, has the potential to decompose water by light absorption. Though semiconductors with smaller band gaps are suited for efficient use of solar energy, there are still limited number of visible-light responsive photocatalysts capable of splitting water into hydrogen and oxygen. Recently, Ta₃N₅ nanorods single crystals combined with Rh/Cr₂O₃ cocatalyst have been shown to split water into hydrogen and oxygen under visible light and simulated sunlight by Domen group. It was a remarkable achievement considering that the Ta₃N₅ photocatalyst had not yet accomplished overall water splitting despite its superior visible-light absorption.

In this paper, we used transient absorption spectroscopy (TAS) to study the origin of the overall water splitting activity of Ta₃N₅ nanorod single crystals. We show the correlation between the density of mid-gap defect states and the time of NH₃ nitridation process. The results were further investigated theoretically to estimate various parameters controlling the overall water splitting reaction by the one-step excitation. The effect of cocatalyst on the carrier dynamics in Ta₃N₅ nanorods single crystals was also studied for the Ta₃N₅ nanorod with different nitridation times. Our findings suggest the correlation between the overall water splitting activity of the Ta₃N₅ nanorod single crystals and the change in defect states by different nitridation times.

2:30 PM CM03.07.05

Disentangling the Role of Surface Chemical Interactions on Interfacial Charge Transport at BiVO₄ Photoanodes Johanna Eichhorn², Christoph Kastl¹, Adam Schwartzberg¹, Ian D. Sharp³ and Francesca Maria Toma²; ¹The Molecular Foundry, Lawrence Berkeley National Laboratory, Berkeley, California, United States; ²Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California, United States; ³Walter Schottky Institut and Physik Department, Technische Universität München, Munich, Germany.

Photoelectrochemical (PEC) water splitting is a promising approach to provide carbon neutral power and renewable fuels. The chemical transformation of water into oxygen and hydrogen takes place at the surface of catalysts and photoactive materials. Consequently, the activity, efficiency, and reaction pathway are critically controlled by the material surface properties. Under PEC operating conditions, surface properties strongly depend on the surrounding environment, and they may be altered in the course of the reaction. Thereby, absorption of molecules can modify the chemistry at the surface, for example by influencing the kinetics of reactants, products, or reaction intermediates, but they can also directly impact the electronic transport properties of the photoactive material by effectively acting as surface trap states. In this context, improved understanding of these complex surface interactions will aid the development of highly efficient light absorbers as well as the integration of effective passivation and catalyst layers for these materials.

In this work, we elucidate the influence of chemical interactions of adsorbed oxygen and water on charge transport and interfacial charge transfer of photogenerated charge carriers in polycrystalline BiVO₄ thin films – a promising material for solar water splitting. The charge transfer between adsorbates and BiVO₄ is monitored by *in situ* Kelvin probe measurements under dry nitrogen, humid nitrogen, and oxygen environments at atmospheric pressure. To gain complementary insight into the relationship between surface interactions and interfacial charge transport characteristics, we employ photoconductive AFM under the respective *in situ* conditions. By combining these complementary techniques, we demonstrate that adsorbed oxygen acts as a surface trap state for electrons, which enhances the built-in potential and depletes the BiVO₄ layer, resulting in an increase of the measured surface photovoltage. Furthermore, we have recently demonstrated that the low intrinsic bulk conductivity of BiVO₄ limits the electron transport through the film, and that the transport mechanism can be attributed to space charge limited current (SCLC) in the presence of trap states.[1] By analyzing the SCLC, we estimate that the contribution of surface adsorbed oxygen to the total number of shallow traps is as large as 40%. For humid environments, our results are consistent with the adsorption of water as an oriented dipole layer, which does not induce a surface charge transfer but partially inhibits the adsorption of oxygen at the surface. Disentangling the individual effects of oxygen and water on surface band alignment and charge carrier trapping underpins the importance of trap state passivation for efficient transport of photogenerated charge carriers in BiVO₄.

[1] Eichhorn *et al.* Nanoscale imaging of charge carrier transport in water splitting photoanodes, *Nat. Commun.* (2018).

2:45 PM CM03.07.06

Photoelectrochemical Scanning Droplet Cell Microscopy on Fe, Ni, Co Doped Tungsten Oxide Material Libraries Achim Walter Hasse^{1, 2, 3}, Junseob Lee^{3, 1}, Cezarina C. Mardare^{2, 1}, Andrei I. Mardare^{1, 3} and Jan P. Kollender¹; ¹Johannes Kepler Univ, Linz, Austria; ²CD-Lab COMBOX, Linz, Austria; ³CEST Competence Center for Electrochemical Surface Science, Linz, Austria.

A highly versatile method is introduced that combines microelectrochemistry, photoexcitation and downstream electrolyte analysis to a single method. The simultaneous in-situ use of all methods provides a comprehensive set of information for photoelectrochemical reactions. A 3D printed measuring head with flow guide is equipped with reference and counter electrodes and the electrolyte is continuously pumped down to an inductively coupled plasma optical emission spectrometer. Illumination of the wetted electrode spot is realised through a multi-mode optical fibre connected to a set of laser diodes being chopped for dark and illumination conditions. A state of the art physical vapour deposition system with thermal coevaporator, multi gun cosputtering system, electron deposition system and large travel range energy dispersive x-ray system is employed to fabricate lateral composition gradients of tungsten oxide with iron group metals iron, nickel and cobalt. Subsequent oxidation yields mixed oxide libraries which are characterised by scanning electron microscopy and scanning x-ray diffraction. In an attempt to quantify the performance of various compositions of mixed oxides the photoelectrochemical behaviour of each composition was studied using various illumination wavelengths and polarisation potentials. Wavelengths corresponding to energies lower than the bandgap resulted in very minor effects. Illumination with sufficient photon energy on the other showed clear increase in the photocurrent as the inherent comparison with dark current showed. Variation of the electrochemical potential compensated for the energy difference between bandgap and photostimulation. Electrochemical impedance spectroscopy under illumination was used to provide Mott Schottky plots for both, the determination of the flat band potential and the charge carrier concentration. The highest photocurrent was found for distinguished concentrations of the iron group metal, demonstrating that this combinatorial approach is very useful in the search for high performance water splitting photoelectrodes.

3:00 PM BREAK

SESSION CM03.08: Electrocatalysis
Session Chairs: Ethan Crumlin and Matthew McDowell
Tuesday Afternoon, November 27, 2018
Hynes, Level 3, Room 300

3:30 PM *CM03.08.01

Probing Electrochemical Reactions Under *Operando* Condition Bin Liu; Nanyang Technological University, Singapore, Singapore.

Semiconductor-based nanomaterials have been widely studied as promising electrocatalysts for energy conversion and storage. Understanding the reaction pathways and active sites on electrocatalysts are of critical importance for the development of highly active electrocatalysts made of earth abundant elements. In this talk, I will give a detailed summary about our approach using various *in-situ* and *ex-situ* techniques including X-ray absorption, X-ray diffraction, X-ray photoemission spectroscopy, electrochemical impedance spectroscopy, Raman spectroscopy, etc to study electrochemical reactions.

4:00 PM CM03.08.02

Probing the Promotion of CO Reduction at the Cu/Electrolyte Interface Using a Combined *In Situ* IR Spectroscopy and Online Electrochemical Mass Spectrometry Approach Matthias Waagele; Boston College, Chestnut Hill, Massachusetts, United States.

One of the grand challenges in electrocatalysis is to understand how the properties of a given electrochemical interface give rise to its catalytic reactivity. These interfacial properties are jointly engendered by solid electrode and liquid electrolyte and evolve under operating conditions. The chemical complexity and dynamic nature of the electrocatalytic interface pose formidable experimental challenges for the establishment of property-activity relationships. Herein, we aim to establish such relationships by simultaneously probing the electrocatalytic interface with surface-selective infrared (IR) spectroscopy and online electrochemical mass-spectrometry (OLEMS) under operating conditions.

Specifically, we focus on the electroreduction of surface-adsorbed CO to hydrocarbons on Cu electrodes. While it has previously been shown that cations of the supporting electrolyte can profoundly affect the catalytic selectivity and activity of this electrochemical interface, the physical origins of these cation effects are still poorly understood. In this talk, we will discuss the relative influence of purely electrostatic and specific chemical effects on the promotion of CO reduction.

For the first time, we have found that the CO coverage on the electrode is profoundly dependent on the identity of alkali cations in the supporting electrolyte. Specifically, in the presence of Cs⁺, a dramatic drop of the CO coverage to almost zero is observed at reduction potentials around -1 V vs. RHE, while only a small dip is observed in Li⁺-containing electrolyte. Time-resolved vibrational spectroscopy of the C≡O stretch band reveals that the reduction kinetics of CO is faster by approximately one order of magnitude in the presence of Cs⁺ compared to Li⁺-containing electrolyte. We have further found marked red-shifts of the peak frequencies of the C≡O stretch band of atop-bound CO in the presence of either of the two larger cations (K⁺ and Cs⁺) relative to the peak frequency observed in Li⁺-containing electrolyte, evidence of the electrostatic stabilization of CO on the surface by the highly localized electric fields generated by the larger cations, which have a relatively higher tendency to reside in the electrochemical double layer.

While recent theoretical work disagrees on the existence of specifically adsorbed cations on the copper electrode at potentials relevant to CO₂ reduction, our spectroscopic data suggest that the larger cations specifically adsorb on the polycrystalline copper electrode and induce the reconstruction of the surface.

We will further discuss how CO coverage and interfacial electric field strength correlate with the onset-potentials for ethylene and methane production as concurrently monitored by OLEMS.

4:15 PM CM03.08.03

Revealing CO₂ Adsorption Tunability on Metal Catalyst Surfaces Yifan Ye¹, Hao Yang², Jin Qian², Junko Yano¹, William Goddard² and Ethan J. Crumlin¹; ¹Lawrence Berkeley National Lab, Berkeley, California, United States; ²California Institute of Technology, Pasadena, California, United States.

A national priority is to convert CO₂ into high-value chemical products such as liquid fuels and synthesis gas. Because current electrocatalysts are not

adequate, we aim to develop improved catalysts by obtaining a detailed understanding of the initial steps of CO₂ electroreduction on catalyst surfaces. Thus we exposed Ag surfaces to CO₂ adsorption both alone and in the presence of H₂O at 298 K and modest gas pressure while we probed the electronic structures of the catalyst surfaces and reaction products. We monitored the surface adsorption and reaction using ambient pressure X-ray photoelectron spectroscopy (APXPS), the results of which we compared with density functional theory (DFT) to provide definitive interpretations. We find that *l*- and *b*-CO₂ are not stable on the pure Ag (111) surface, but rather *g*-CO₂ reacts with O on Ag surface to form a carbonic acid like O=CO₂^{δ-}-like species. Adding H₂O and CO₂ then leads to [H₂O--O=CO₂^{δ-}--H₂O] and [H₂O--*b*-CO₂--H₂O] clusters on the surface. The [H₂O--*b*-CO₂--H₂O] in bulk water leads to CO production. [H₂O--O=CO₂^{δ-}--H₂O] requires a surface O_{ads} so that it may not be stable under negative potentials, but maybe it could play a role under modified conditions. Our studies establish a comprehensive picture of how the interaction between adsorbate and catalyst is altered by tuning the charge transfer between them through changing the adsorption sites and configuration and by introducing surface co-dosing adsorbates. This behavior of CO₂ and H₂O on Ag contrasts dramatically from the results on Cu providing a comprehensive understanding behind the remarkable differences in the catalytic performance of Cu vs. Ag that be useful for tuning CO₂ adsorption behaviors in designing advanced electro-catalysts to facilitate selective product formations.

4:30 PM CM03.08.04

Differential Electrochemical Mass Spectrometry for Electrocatalysis—Au-Based Systems for CO₂ Reduction Case Study Daniele Perego, Juan Herranz, Marie Porto and Thomas J. Schmidt; Laboratory for Electrochemistry, Paul Scherrer Institut, Villigen, Switzerland.

Carbon dioxide is one of the major contributors to global warming and the possibility of recycling this greenhouse gas is gaining attention within the scientific community. The electrochemical reduction of CO₂ (CO₂RR) is an attractive way to utilize this greenhouse gas by converting it into a broad range of useful carbon neutral fuels using renewable energy sources (i.e. wind, solar, geothermal). That would allow not only to store excess energy, but also to eventually close the global carbon cycle. Nevertheless, on top of the high overpotential required to drive this reaction, the CO₂RR suffers from a poor yield/selectivity towards hydrocarbons. Improvements in this scenario require a better understanding of the fundamental reactions on various metal surfaces, along with the development of analytical tools that allow for the quantification of the reaction products. We have designed and built a differential electrochemical mass spectrometry (DEMS) setup consisting of an electrochemical flow cell coupled to an MS, which demonstrated to be an excellent and versatile choice for the *operando* quantification of the volatile species produced upon electrocatalysis reactions. Mass Spectrometry (MS) is a widely applied technique in catalysis research for the quantitative detection of reactants and products with high precision. In many cases, pre-separation of the gas mixture is necessary, because of interferences between different gases that contribute to the same mass-to-charge (m/q) ratios and, thus, to the same MS peaks. However, combining MS with a pre-separation technique not only makes the overall system more complex, but also prevents *operando* detection of gas. To overcome such limitations, our DEMS system is based on a new MS calibration approach using several different gas mixtures that enables unambiguous and quantitative distinction of CO, N₂, and CO₂ via measurement of the MS peaks at (m/q) = 44, 28, and 14. As an example of the possible applications offered by a calibrated DEMS setup, herein we present our results upon studying the CO₂RR on a polycrystalline Au electrode and high-surface area Au aerogel. Moreover other applications in Oxygen Evolution Reactions (OER) and Vanadium Redox Flow Batteries (VRB) will be presented showing the versatility of the developed DEMS setup. Furthermore new cell designs will be presented and discussed.

4:45 PM CM03.08.05

Multimodal *Operando* X-ray Characterization of Electrocatalytic Interfaces for Solar Fuels Production Maryam Farmand¹, Alan Landers², Christopher Hahn³ and Walter Drisdell¹; ¹Lawrence Berkeley National Laboratory, Berkeley, California, United States; ²Stanford University, Palo Alto, California, United States; ³SLAC National Accelerator Laboratory, Menlo Park, California, United States.

The primary challenge in electrochemical CO₂ reduction lies in tuning the catalytic selectivity for desired solar fuels products. Molecular-scale knowledge of the catalytic mechanism for CO₂ reduction is required, ideally for systems with controlled morphology that can be directly compared to first principles calculations. Achieving this control is difficult, as CO₂ reduction competes with hydrogen evolution and only proceeds with appreciable efficiency at high current densities, and suffers from mass transport limitations due to low solubility of CO₂. I present a new electrochemical flow cell system designed collaboratively in the Joint Center for Artificial Photosynthesis (JCAP) at Lawrence Berkeley National Laboratory and SLAC National Accelerator Laboratory, which uses a fast liquid flow design to enable grazing incidence X-ray absorption spectroscopy (XAS) and X-ray diffraction (XRD) of a smooth planar catalyst surface (top 2–4 nm) during operation. These measurements characterize the chemical state, local electronic structure, and long-range atomic structure of the catalyst surface as a function of electrochemical conditions, including full catalytic chemistry at high current density. I demonstrate the surface sensitivity and electrochemical control of the technique, and present early data on model CO₂ reduction catalysts.

SESSION CM03.09: Poster Session I: In Situ Investigation of Electrochemical Materials

Session Chairs: Neil Dasgupta and Matthew McDowell

Tuesday Afternoon, November 27, 2018

8:00 PM - 10:00 PM

Hynes, Level 1, Hall B

CM03.09.01

The Electrochemical Study of the Interaction Between Bacterial Cytochromes and Iron Oxide Minerals Hanyu Wang, Alexander Johs, Jim Browning, Liyuan Liang and Alan Tennant; Oak Ridge National Lab, Oak Ridge, Tennessee, United States.

Microbial life has played an important role in the course of earth's entire developmental history. Due to the small size of microorganisms, the high surface area to volume ratio and incredible diversity of microbial metabolism, microbes are involved in many reactions driving the formation of geological structures. The electron transfer across the interfaces between microbes and minerals is a prime example of this interplay. Extracellular electron transport processes to solid electron acceptors, such as Fe and Mn oxide minerals and artificial electrodes, represents a central driving force for geochemical mineral cycling and bioelectrical systems. The extracellular electron transfer by dissimilatory metal-reducing bacteria (DMRB), such as the Gram-negative bacterium *Shewanella oneidensis* MR-1, involves a series of multiheme cytochromes. These mostly membrane-associated redox proteins shuttle electrons from the inner membrane across the periplasmic space and through the outer membrane to a terminal electron acceptor [e.g. Fe(III)]. Exploring electron transfer between redox active proteins and earth mineral oxides presents an opportunity for this post-genomic era. The molecular-scale microbiological-mineral interactions are central to understanding electron transfer mechanisms and microbial ecosystem reactions in subsurface environments. We carried out electrochemical study to understand the electron transfer from redox active proteins to minerals surfaces by investigating interactions of horse heart cytochrome *c* (cyt *c*) with hematite nanowire-arrayed electrodes. Using this model system, specific interactions of cyt *c* with hematite as a function of electrical potential and pH were examined. Direct electron transfer between cyt *c* and hematite was observed, and the apparent adsorption-induced

conformation change of cytochrome c was proved. Moreover, the role of electron shuttling compound on electron transfer was studied with the addition of exogenous electron shuttle anthraquinone-2,6-disulfonate (AQDS). To our knowledge, this is the first report on rate constants of electron transfer between cytochrome c and hematite nanowire-arrayed surface in absence and in presence of AQDS in the system. The investigation of this system is fundamental to understanding of how microbial cells function with biological and environmental system, as well as understanding of complex interactions and chemical transformations at cell-mineral interfaces.

CM03.09.02

Investigation of the Valence Variation of Ruthenium Oxide Nanosheet Between the Low and High Potential Regions Using *In Situ* XAFS Takahiro Saida, Fumiaki Sato and Takahiro Maruyama; Meijo Univ, Nagoya, Japan.

Ruthenium oxide nanosheet (RuO₂ns) which is one of the two-dimensional materials is the prospect as the electrode material of high power electrochemical capacitor because of shows to high pseudo-capacitance and long service life. RuO₂ns is possible to stack easily onto the substrate and its number of layers is controlled from one molecule layer. Therefore, RuO₂ns is expected to the application for the nano- or micro super-capacitor needing high energy density than its raw material cost. The pseudo-capacitance of ruthenium oxide is mainly catered by the redox peaks. It has been known that the redox peaks of common ruthenium dioxide are produced by the proton adsorption on the surface involving valence variation of Ru atom in the oxide. On the other hand, the charge storage mechanism of RuO₂ns has been unclear, yet. One reason for this is thought that the adsorption site on RuO₂ns surface and the adsorption species were not decided. In addition, the valence variation between the low and high potential regions of Ru atom in RuO₂ns seems to larger than that of common ruthenium dioxide. Low valence state is probably introducing the low electron conductivity site. As a result, the rate dependence of RuO₂ns was drastically decaying. Now, we speculate that this valence variation is depending on the number of RuO₂ns layers. Because this valence variation was stronger in layered structure as the precursor of RuO₂ns rather than the nanosheets morphology. In this study, the variation of electron conductivity and the valence of ruthenium in a controlled number of the RuO₂ns layers was investigated by the electrochemical impedance spectroscopy and the in-situ XAFS method.

RuO₂ns was synthesized by following the previous literature. Controlling of the RuO₂ns thickness was conducted by the layer by layer method using polycations solution and RuO₂ns colloid solution. A glassy carbon plate was employed as the substrate and the current collector. In-situ XAFS measurement was conducted at BL55S1 in Aichi Synchrotron Radiation Center. X-rays were monochromatized by a Si(333) double-crystal monochromator. XAFS spectra were recorded by the 19-element Ge solid-state detector. An electrochemical cell for in-situ XAFS was based on typical three-electrode cell, which has a carbon fiber counter-electrode, an Ag/AgCl electrode as the reference, and 0.5 M H₂SO₄ as the electrolyte. XAFS and electrochemical measurement were conducted at room temperature.

The difference of electric double layer charge between low and high potential regions was expanding with increasing the number of RuO₂ns layers. Results of in-situ XAFS showed that the ruthenium valence was changed by the applied potential and decreased in the low potential region. This phenomenon suggests that the interlayer resistance is increasing with increasing the number of RuO₂ns stacking layer. This means that the RuO₂ns monolayer should be used if the performance of RuO₂ns needs to play out.

CM03.09.03

Electrochemical Performance of Electron Withdrawing Group Substituted Benzoquinone and Benzoquinone-Functionalized Poly(3,4-ethylenedioxythiophene) Conducting Redox Polymer Huan Wang, Rikard Emanuelsson, Martin Sjödin and Maria Strømme; Uppsala University, Uppsala, Sweden.

Conducting redox polymers have been investigated massively as an efficient cathode material. Herein we synthesize a series of quinone substituted PEDOT conducting redox polymers and investigate the effect of electron withdrawing substitutions on the redox potential of quinone in the PEDOT backbone in two electrolyte 0.1M LiClO₄/MeCN. Electron withdrawing substitutions leads to an increase of the redox potential of quinone in LiClO₄/MeCN. The conductivity of PEDOT backbone is hindered by the lithiated reduced quinone. In-situ UV-vis and EQCM is used to probe the exact PEDOT doping onset potential, confirming that conductivity of quinone is hindered by lithiated reduced quinone. In situ EQCM proves that mass change in the PEDOT doping region involves cation repulsion and dopants anion uptake.

CM03.09.04

Effect of Coating on Lithiation in LiMn₂O₄ Kimberly Bassett¹, Robert Warburton², Siddharth Desphande², Tim Fister³, Kim Ta¹, Jennifer Esbenshade¹, Kamila Wiaderek³, Karena W. Chapman³, Jeffrey Greeley² and Andrew Gewirth¹; ¹University of Illinois at Urbana-Champaign, Urbana, Illinois, United States; ²Purdue University, West Lafayette, Indiana, United States; ³Argonne National Laboratory, Lemont, Illinois, United States.

We utilize in-operando powder X-ray diffraction (XRD) coupled with Rietveld analysis and density functional theory (DFT) calculations to describe how a Au coating affects the degree of lithiation available in bulk LiMn₂O₄ (LMO) and to explore the electronic interactions between the active material and its coating.

Lithium-ion batteries enable the portable electronics industry and appear increasingly in electric and hybrid vehicles. However, capacity fade in Li-ion cathodes remains a barrier between current technologies and longer-lasting devices and vehicles. LMO is a cathode active material that experiences limited life-times due to (1) a Jahn-Teller distortion which incites the formation of the tetragonal phase below 3 V vs Li/Li⁺, (2) Mn²⁺ dissolution into the electrolyte, and (3) electrolyte degradation at high potentials. Many approaches have been developed to protect LMO from these mechanisms, such as bulk or surface doping and deposition of protective coatings on the electrode surface.

Previously we deposited a Au coating via electroless deposition onto LMO.[1] The Au-coated LMO exhibited higher capacity after prolonged cycling likely due to a decrease in Mn dissolution. However, the effect of the coating on the initial capacity of LMO is unclear.

XRD results show that the Au-coated LMO exhibits smaller lattice parameters than uncoated LMO at low voltages (3.5 V vs Li/Li⁺) at which lithiation should be complete. The smaller lattice parameter suggests less Li⁺ has intercalated into Au-coated LMO compared to uncoated LMO. Integration of the cyclic voltammograms further supports this observation because Au-coated LMO passes less charge in comparison to uncoated LMO. DFT calculations suggest that Au coatings in contact with the LMO surface make a partially delithiated surface more thermodynamically favorable, even at potentials where fully lithiated domains are expected. Chemical bonding analysis shows enhanced hybridization between Au and LMO at partially delithiated surfaces, including strong Au-O bonding character below the Fermi level. The partially oxidized Au leads to less electron density available to complete lithiation.

[1] Esbenshade, J. L.; Fox, M. D.; Gewirth, A. A. LiMn₂O₄@Au Particles as Cathodes for Li-Ion Batteries. *J. Electrochem. Soc.* 2014, 162, A26–A29.

CM03.09.06

***In Situ* Optical Spectroscopy During Electrochemical Coloration of WO₃ Thin Films** Simon Burkhardt^{1,2}, Jan Luka Dornseifer^{1,2}, Alexander Günter Strack^{1,2}, Matthias T. Elm^{1,2,4}, Bernhard Lani-Wayda³ and Peter J. Klar^{1,2}; ¹Institute of Experimental Physics I, Justus Liebig University Giessen, Giessen,

Germany; ²Center for Materials Research (LaMa), Justus Liebig University Giessen, Giessen, Germany; ³Mathematical Institute, Justus Liebig University Giessen, Giessen, Germany; ⁴Institute of Physical Chemistry, Justus Liebig University Giessen, Giessen, Germany.

Various applications for tungsten trioxide (WO₃) thin films can be anticipated. Key applications include the employment of such films in electrochromic devices or lithium-ion batteries. For example, tungsten trioxide based “Smart Windows” already have been launched commercially. Nevertheless, optimization is still desirable in order to improve decisive product properties or to substitute critical materials such as tungsten itself. In particular, the former requires a very deep understanding of the electrochemical and optical properties of WO₃ thin films under operating conditions. Furthermore, a correlation of properties and morphology needs to be established as the film morphology strongly affects charge transfer, charge transport, and coloration dynamics. To simultaneously investigate electrochemical and optical properties, a specially designed electrochemical cell has been used^[1]. It enables us to perform in-situ optical experiments during the application of electrochemical methods. Results from spatially and temporally resolved transmission spectroscopy during potentiostatic coloration of amorphous and polycrystalline WO₃ thin films reveal a significant impact of the thin film morphology on the concentration dependent lateral diffusion of protons. The impact of morphology on results from in situ transmission spectroscopy and in-situ Raman spectroscopy during electrochemical impedance spectroscopy is also investigated.

[1] Simon Burkhardt, Matthias T. Elm, Bernhard Lani-Wayda, and Peter J. Klar, *Adv. Mater. Interfaces* **5**, 1701587 (2018).

CM03.09.07

A Study of Direct Methane Oxidation at Ceria/Gas Electrochemical Interface Yoonseok Choi¹, JeongDo Yoo¹, Han Gil Seo¹, Hyun You Kim² and WooChul Jung¹; ¹MSE, KAIST, Daejeon, Korea (the Republic of); ²MSE, Chungnam National University, Daejeon, Korea (the Republic of).

Direct-methane-fueled solid oxide fuel cells has received great attention for near-term realization of the high-efficiency energy conversion advantages even in the absence of a hydrogen delivery infrastructure. In particular, essentially all of the successful demonstrations in the related studies included ceria, either doped or undoped, as a component. However, limited understanding of the electrochemical oxidation of methane on ceria surface hinders implementing the electrode performance comparable to hydrogen fuels. Therefore, the aim of this study is to identify the electrochemical oxidation pathways of methane (CH₄) on ceria surface through combined theoretical and experimental analyses. The identification of the predominant species on ceria surface coupled to the mixed valence of Ce³⁺ and Ce⁴⁺ can be a key to clarify the reaction mechanism. Here, we propose a real-time analysis of surface adsorbates and lattice ions during the methane electrooxidation using ambient pressure X-ray photoelectron spectroscopy. We combine the AP-XPS results with AC impedance spectroscopy (ACIS) and density functional theory (DFT) calculations for atomic-level mechanisms to understand the overall processes.

CM03.09.08

Multi-Dimensional Electrochemical Characterization at Sub-100 nm Length Scale Omur E. Dagdeviren, Tyler Enright, Aaron Mascaro, Yoichi Miyahara and Peter Grutter; McGill University, Montreal, Quebec, Canada.

Simultaneous characterization of surface structure and local electrochemical properties is essential to establish correlations between mechanical and electrochemical material properties. In this work, we show that multi-dimensional electrochemical material characterization at sub-100 nm length scales can be routinely achieved by combining atomic force microscopy (AFM) and scanning electrochemical microscopy (SECM). We use an amplitude modulation based AFM technique to modulate the distance between the scanned probe and the substrate [1]. Using a quartz tuning fork as our oscillator integrated with a pulled pipette allows the robust operation at small oscillation amplitudes [2, 3]. The pipette is filled with electrolyte and a back electrode inserted into the pipette allows for electrochemical measurements. We exhibit the robustness of combined electrochemical measurements on different surfaces and along interfaces. Moreover, our experiments elucidate the variation of local electrochemical properties of surfaces previously assumed to be pristine. We are also able to resolve electrochemical properties across grain boundaries due to the spatial resolution afforded by our operation architecture. Most importantly, our technique enables characterization of electrochemical properties across conducting/non-conducting interfaces. Also, our technique allows for the simultaneous measurement of local electrochemical properties and topography as a function of time, which opens a new pathway for corrosion studies of materials at nanometer length scale. All in all, we demonstrate a novel approach that facilitates robust operation of a scanning electrochemical microscope with AFM feedback while revealing electrochemical properties with sub-100 nm spatial resolution as a function of time at a selected potential landscape.

[1] O.E. Dagdeviren *et al.*, *Nanotechnology* **27**, 065703 (2016).

[2] O.E. Dagdeviren *et al.*, *Measurement Science and Technology* **28**, 015102 (2017).

[3] O.E. Dagdeviren *et al.*, *Beilstein Journal of Nanotechnology* **8**, 657-666 (2017).

CM03.09.09

Why Does Oxide-Derived Silver Work so Well as an Electrocatalyst for CO₂ Reduction? An EXAFS Study Nienke Firet¹, Marijn Blommaert¹, Thomas Burdyny¹, Anirudh Venugopal¹, Alessandro Longo² and Wilson Smith¹; ¹Delft University of Technology, Delft, Netherlands; ²European Synchrotron Radiation Facility, Grenoble, France.

To be able to fully take advantage of the current rise in renewable electricity production, we have to find means to convert the electricity in fuels for both mobile (e.g. automotive and airplane) and storage applications. With electrocatalysis, we can directly use renewable electricity to convert carbon dioxide and water into valuable products such as carbon monoxide, hydrogen, ethanol, and methane. One of the main bottlenecks for this technology is to find suitable electrodes that can act as efficient, stable and selective catalysts in the electrochemical reduction of CO₂.

Due to the vast possibilities in choice for electrocatalyst, we use in operando techniques such as extended X-ray absorption fine-structure spectroscopy (EXAFS) to study the difference between highly active and less active catalysts, to see if any electronic, structural or compositional changes may promote the enhanced activity. In particular, we studied the difference between a pure silver film and oxide-derived silver, a nanostructured catalyst with improved CO₂ reduction performance. We found that the presence of trace amounts of oxygen in the oxide-derived silver improves the reactivity of the silver. We found a direct correlation between the faradaic efficiency (or selectivity) of carbon monoxide and the amount of oxygen present in these catalysts. The faradaic efficiency relation does not scale with electrochemical surface area, ruling out other explanations for the enhanced selectivity that are related to mass transfer limitations. Earlier studies based on X-ray photoelectron spectroscopy (XPS) were not able to identify this oxygen, most likely because in ultra-high vacuum conditions, the silver self-reduces to Ag⁰. This in operando EXAFS study shows how vital the participation of in situ and in operando techniques is to properly understand electrochemical systems.

CM03.09.10

In Situ XANES and PDF Analysis of Electrochemical Cycling of Defective δ-MnO₂ Nanosheet Electrodes Madeleine N. Flint, Peng Gao, Robert Koch, Alec Ladonis and Scott Misture; Kazuo Inamori School of Engineering, Alfred University, Alfred, New York, United States.

The roles of defects in electrochemical charge storage in 2-D oxides remain largely unexplored. MnO₂ nanosheets exhibit an interesting defect, where reduction of Mn⁴⁺ causes displacement of the Mn³⁺ out of the plane of the nanosheet, forming a “surface Frenkel” defect. The defect content dramatically impacts the capacitance, where defects improve charge storage by factors of 2 or even 3 times. *In-situ* XANES data showed an increase in Mn³⁺ content with increasing charge state (13% for a sample with 20% cation defects, and 17% for a sample with 27% cation defects), confirming that the Faradaic redox reaction is the main charge storage mechanism. Comparing XANES and CV loop calculations indicates that the change in Mn oxidation state upon charging is a function of the overall defect content, with higher defect content yielding proportionally less Mn reduction to the trivalent state. This result suggests that the Mn vacancies serve as new sites for K⁺ intercalation without changing the average Mn oxidation state. The XANES data corresponds well to our synchrotron X-ray PDF study, which shows a reversible expansion of ~0.5 to 1% of the in-plane lattice spacing upon charging.

CM03.09.11

High-Temperature Thin-Film Calorimetry Hendrik Wulfmeier, Alexander Omelcenko and Holger Fritze; Clausthal Univ of Technology, Goslar, Germany.

Thermodynamic properties of thin films may differ significantly from bulk counterparts due to e.g. increased impact of surface energy or grain boundary densities. As a consequence, sophisticated approaches to determine phase transformation temperatures and enthalpies of thin films and thin-film systems are indispensable. Moreover, numerous film deposition processes include high-temperature steps which require the applicability of calorimetry at high temperatures. A topical example is the deposition of active materials for thin-film batteries which is carried out at temperatures of up to 1000 °C [1]. The thin-film calorimeter (TFC) presented here takes advantage of the extraordinarily high temperature sensitivity of piezoelectric resonators which are simultaneously used as planar temperature sensors and substrates for the films of interest. Operation temperatures up to at least 1000 °C are ensured by applying piezoelectric crystals of the langasite family. Generation or consumption of heat in the deposited films induces changes in the otherwise undisturbed resonance frequency which is evaluated and converted in related enthalpies of phase transformations.

A detailed analysis of the heat transport is given as it is necessary for the accurate determination of enthalpies. To generate well defined amounts of heat, resistive heating by platinum structures is applied. The latter replace the films of interest for calibration purposes under different conditions including varying total pressure and gas composition in the furnace of the TFC system. Further, variation of length and intensity of the heat pulses is done to simulate different characteristics of phase transformations. A key result is that phase transformations that occur within less than 0.2 s can be regarded as adiabatic. Further, the detectable amount of heat is as low as about 1 mJ. Finally, improvements of the TFC system are done by application of free-standing piezoelectric resonators which show increased thermal insulation and, thereby, improved sensitivity.

Materials investigation is done on the one hand by focusing on well known systems such as tin films to confirm the functionality of the TFC system. On the other hand, promising materials for thin-film batteries are investigated. One example is Li(Ni_xMn_yCo_z)O₂ (NMC, x+y+z=1) where the number of phase transformations between room temperature and 850 °C depends on the atmosphere applied. Temperatures and enthalpies of the phase transformations are extracted. Obviously, the presence of air suppresses the Jahn-Teller effect and, thereby, a phase transformation at high temperatures. Aluminum doping increases the stability of NMC which becomes evident from increased phase transformation temperatures.

[1] T. Ohzuku et al., Chemistry Letters 30 (2001) 744-745.

CM03.09.12

The Effect of Illumination on the Geometric Structure of Water Molecules on GaN(0001) Surface Masahiro Sato¹, Yuki Imazeki², Katsushi Fujii³, Yoshiaki Nakano^{2,4} and Masakazu Sugiyama¹; ¹Research Center for Advanced Science and Technology, The University of Tokyo, Tokyo, Japan; ²Department of Electrical Engineering and Information Systems, The University of Tokyo, Tokyo, Japan; ³RIKEN, Tokyo, Japan; ⁴Global Solar Plus Initiative, The University of Tokyo, Tokyo, Japan.

First principles calculation has become a powerful tool for materials design in many fields [1]. However, theoretical design of photocatalysts has met with limited success, due to the lack of adequate modeling criteria; although photogenerated carriers accumulate at the semiconductor surface under continuous illumination, the effect of “semiconductor surface charging” on the photocatalytic activities have not been studied in detail. Thus, in our previous work, in order to handle the charged surface, we used the effective screening medium method, [2] in conjunction with density functional theory (DFT) calculations. We have modeled H atom adsorption on GaN surface and showed that the apparent adsorption energy decreases with decreasing surface electron density. In this contribution, we study in more detail the effect of illumination on the geometric structure of water molecules on GaN surface by both DFT calculations and infrared absorption spectroscopy.

The effect of UV illumination was modeled by adding excess holes to the GaN surface. The computational results show that both H atoms and -OH adsorbed on the GaN(0001) surface prefer the on-top site. Interestingly, when excess holes accumulate on the surface at low surface coverage, the hollow site becomes the most stable site for -OH even at moderate surface charge density around 10 μF/cm². On the other hand, in the case of H atoms, the on-top site remains the most stable site. At higher surface coverage (~ 1 ML), as the surface electron density decreases, the number of H atoms and -OH adsorbed on the surface decreases, i.e., the number of water molecules in the intact form increases. The number of dissociated water molecules roughly follows the “extended electron counting rule”; the maximum number of H atoms and -OH on a single Ga atom is around 3/4 - *n*, where *n* is the number of excess holes per Ga atom. In addition to the change of the geometric structure of the water wetting layer, a significant change in the O-H stretching frequency of the -OH on Ga atom is observed. The O-H stretching frequency shifts downwards as the surface electron density decrease, at the rate of - 2 cm⁻¹/(μC/cm²). Transmission and ATR-FT(N)IR experiments are conducted to confirm this frequency shift. Although quantitative measurement of the O-H stretching frequency shift is difficult due to the strong absorption of bulk water, in line with the computational results, the red shift of the O-H stretching frequency upon UV illumination is observed. Considering the fact that water splitting involves bond cleavage, these results, which demonstrates that bond strengths change according to surface charging, indicate that surface charging has a large effect on photocatalytic reactions and should be taken into account when modeling the semiconductor/electrolyte interface.

[1] S. Charkraborty et al., ACS Energy Lett. 2017, 2, 837

[2] M. Otani and O. Sugino, Phys. Rev. B 2006, 73, 115407

CM03.09.13

Charge Transfer Dynamical Processes at Graphene-Transition Metal Oxides/Electrolyte Interface—Insights from *In Situ* Raman Spectro-Electrochemistry Sanju Gupta and Sara B. Carrizosa; Western Kentucky University, Bowling Green, Kentucky, United States.

Hybrids consisting of supercapacitive functionalized graphene (graphene oxide; GO reduced graphene oxide; rGO multilayer graphene; MLG, electrochemically reduced GO; ErGO) and three-dimensional graphene scaffold (rGO_{HT}; hydrothermally prepared) decorated with cobalt nanoparticles (CoNP), nanostructured cobalt (CoO and Co₃O₄) and manganese (MnO₂) oxide polymorphs, assembled electrochemically facilitate chemically bridged interfaces with tunable properties. Since Raman spectroscopy can capture variations in structural and chemical bonding, Raman spectro-electrochemistry in operando *i.e.* under electrochemical environment with applied bias is employed to 1) probe graphene/metal bonding and dynamic processes, 2) monitor the spectral changes with successive redox interfacial reactions, and 3) quantify the associated parameters including type and fraction of charge transfer. The

transverse optical (TO) and longitudinal optical (LO) phonons above 500 cm^{-1} belonging to Co_3O_4 , CoO , MnO_2 and carbon-carbon bonding occurring at 1340 cm^{-1} , 1590 cm^{-1} and 2670 cm^{-1} belonging to D, G, and 2D bands, respectively, are analyzed with applied potential. Consistent variation in Raman band position and intensity ratio reveal structural modification, combined charge transfer due to localized orbital re-hybridization and mechanical strain, all resulting in finely tuned electronic properties. Moreover, the heterogeneous basal and edge plane sites of graphene nanosheets in conjunction with transition metal oxide 'hybrids' reinforce efficient surface/interfacial electron transfer and available electronic density of states near Fermi level for enhanced performance. We estimated the extent and nature (*n*- or *p*-) of charge transfer complemented with Density Functional Theory calculations affected by hydration and demonstrate the synergistic coupling between graphene nanosheets and nanoscale cobalt (and manganese) oxides for applied electrochemical applications.

CM03.09.14

Replicating Bulk Electrochemistry in Multimodal Liquid Cell Microscopy [Khim Karki](#)¹, Julio A. Rodriguez Manzo¹, Daan H. Alsem¹, J. Tyler Mefford², Jungjin Park², William Chueh² and Norman Salmon¹; ¹Hummingbird Scientific, Lacey, Washington, United States; ²Department of Materials Science and Engineering, Stanford University, Stanford, California, United States.

Liquid electroanalytical measurements performed inside the transmission electron microscopy (TEM) and synchrotron X-ray microscopy (XRM) are becoming more common and are used to study a wide range of electrochemical reaction-systems at the nanoscale. This approach has already started to produce new insights on the dynamics and structural changes during processes as lithium ion insertion/extraction, dendrite formation, metal nucleation, and metal corrosion. Despite the power of this approach, the challenges associated with replicating bulk-scale electrochemistry data in the environmental cell microscopy platform are well-known. First, the hardware components are not best optimized to perform in the reduced scale environment. Second, the chips configurations such as sizes and aspect ratios of different electrodes suitable for various electroanalytical measurements are poorly designed. Here, we present an *operando* liquid cell TEM/XRM microscopy platform that enables true electroanalytical measurements using some model compounds, mimicking bulk behavior.

The studies presented here are performed using electrochemical cells, which consist of two microfabricated chips sandwiched with electron transparent SiN_x membranes for viewing in TEM/XRM. Using a new developed hardware system with a specialized configuration of working, counter and reference electrode, we performed cyclic voltammetry studies in 0.1M CuSO_4 and $20\text{ mM K}_3\text{Fe}(\text{CN})_6/20\text{ mM K}_4\text{Fe}(\text{CN})_6$ in 0.1M KCl solutions. In the former case the copper deposition and stripping occurs at the working electrode at distinct redox peaks and the result mimics the bulk electrochemical cells with large electrode areas and larger volume of electrolyte solution. In the latter case, the redox reaction of $20\text{ mM ferrocyanide}/20\text{ mM ferricyanide}$ in 0.1M KCl at different voltage scans show reversible electrode reaction during both the forward and reverse scans, elucidating bulk behavior. We will also present results where we apply this result to energy systems. These results and methodologies demonstrate that minimizing artefacts as well as optimizing the hardware for small volume and limited diffusion cell geometries allow mimicking the bulk data, which can be further implemented in the quantitative measurements of broader electrochemical systems.

SESSION CM03.10: Battery Materials Properties
Session Chairs: Matthew McDowell and Jagjit Nanda
Wednesday Morning, November 28, 2018
Hynes, Level 3, Room 300

8:00 AM CM03.10.01

In Situ Observation of Magnetic Changes During Electrochemical Reactions of FeOx/Fe Nanostructures [Jonas Zehner](#), Kenny Duschek, Ivan Soldatov, Nicolas Perez, Andreas Petr, Sebastian Faehler, Rudolf Schaefer, Kornelius Nielsch and Karin Leistner; IFW Dresden, Dresden, Germany.

Electrochemical concepts were recently identified as a novel route for low power voltage control of interfacial magnetism [1]. For this, electrolyte-gated structures are utilized, in which changes of magnetism can occur via capacitive and/or redox effects. Up to now, however, the underlying mechanisms at the electrode/electrolyte interface that are triggered by the applied voltage are often controversial. Solid state-, gel- and liquid electrolytes can all be utilized [1–4]. Liquid electrolytes offer a high ionic mobility and, due to electric double layer charging, an enhanced electric field at the interface. Therefore, they are favorable for achieving room-temperature effects at low voltage [4].

We present large electrochemically induced changes within several nanometers of FeOx/Fe films at room temperature utilizing a liquid alkaline electrolyte. In situ anomalous Hall effect and in situ ferromagnetic resonance demonstrate that large changes in magnetization can be achieved when applying merely 1 V. With those magnetic methods, integral magnetic changes are probed. Kerr microscopy is a powerful tool to probe and visualize the magnetic microstructure, but has not been applied during electrochemical operations yet. We designed an electrochemical cell for a Kerr microscope which allowed us, for the first time, to resolve the local impact of electrochemical redox reactions on the magnetic domain characteristics. Significant changes of the magnetic domains and the magnetization curve are observed in FeO_x/Fe thin films. Changes of Fe metal thickness as well as the oxide transformation are discussed as possible key factors for the occurring phenomena.

[1] C. Song, B. Cui, F. Li, X. Zhou, F. Pan: Recent progress in voltage control of magnetism: Materials, mechanisms, and performance, *Progress in Materials Science* **87**, 33–82, 2017
DOI: 10.1016/j.pmatsci.2017.02.002

[2] K. Leistner, J. Wunderwald, N. Lange, S. Oswald, M. Richter, H. Zhang, L. Schultz, S. Fähler: Electric-field control of magnetism by reversible surface reduction and oxidation reactions, *Physical Review B* **87**, 224411, 2013
DOI: 10.1103/PhysRevB.87.224411

[3] U. Bauer, L. Yao, A. J. Tan, P. Agrawal, S. Emori, H. L. Tuller, S. van Dijken, G.S.D. Beach: Magneto-ionic control of interfacial magnetism, *Nature Materials* **14**, 174–181, 2015
DOI: 10.1038/nmat4134

[4] K. Duschek, D. Pohl, S. Fähler, K. Nielsch, K. Leistner: Research Update: Magnetoionic control of magnetization and anisotropy in layered oxide/metal heterostructures, *APL Materials* **4**, 032301, 2016

[5] K. Duschek et al. submitted

8:15 AM CM03.10.02

Thermal Conductivity Changes of TiO₂, V₂O₅, NiO, Fe₂O₃ and Sb During Electrochemical Cycling with Li⁺ Ions Jungwoo Shin¹, Sanghyeon kim¹, HoonKee Park², Ho Won Jang², David G. Cahill¹ and Paul V. Braun¹; ¹University of Illinois at Urbana-Champaign, Urbana, Illinois, United States; ²Materials Science and Engineering, Seoul National University, Seoul, Korea (the Republic of).

We study thermal and mechanical properties of five Li-ion electrode materials using *in situ* time-domain thermoreflectance (TDTR) and picosecond acoustics during charge/discharge cycles with Li⁺ ions. The conversion NiO and Fe₂O₃ electrodes show irreversible thermal conductivity and mechanical modulus loss of up to 80% and 40% after the first cycle. The intercalating V₂O₅ and TiO₂ electrodes exhibit reversible thermal conductivity switching as a function of Li⁺ ion contents without the irreversible thermal conductivity and mechanical modulus loss. The alloying Sb electrode shows thermal conductivity switching but the switching contrast gradually decreases with cycling. We attribute these large differences in the thermal and mechanical switching properties to the existence of Li-ion pathways in the crystal structure of electrode materials. While the irreversible thermal conductivity and mechanical modulus loss of conversion electrode materials are caused by the lattice disordering and loss of crystal structure of electrodes by Li⁺ ion penetration, the Li⁺ ion pathway and the crystal structures of the intercalating electrodes are maintained during cycling. This study emphasizes the role of Li⁺ ion pathways of the electrode materials and their thermal and mechanical properties during cycling with Li⁺ ions.

8:30 AM CM03.10.03

Operando Probing of Phase Transformation in Li_xTiO₂ Using Electronic Conductivity and Its Applications in Neuromorphic Computing Yiyang Li, Elliot J. Fuller, Yuping He, Sapan Agarwal and A. A. Talin; Sandia National Laboratories, Livermore, California, United States.

Electrochemical ion insertion yield phase transformations in many transition metal oxides, and such materials are used as electrodes in lithium-ion batteries. Based on nucleation theory, phase transformation initiates from a supersaturation of ions. This metastable or unstable ion concentration in the miscibility gap begins nucleation and growth. While this behavior is accepted from nucleation theory, it is very difficult to quantify and observe in electrochemical insertion materials because *operando* techniques typically do not possess the sufficient temporal resolution (< 1 sec) and sensitivity to both the ion concentration and the crystal phase to capture the supersaturation and subsequent phase transformation process.

Operando measurement of electronic conductivity possess high temporal resolution (up to megahertz) and is extremely sensitive to small changes in conductivity that correspond to differences in ion concentration or crystal phase. We use lithium insertion into a TiO₂ thin film as a model system to measure the changes in electronic conductivity as a function of ion concentration and phase separation. TiO₂ transforms from a lithium-poor anatase phase to a lithium-rich titanate phase upon lithium insertion. Lithium insertion into either solid solution anatase or solid solution titanate increases the electronic conductivity by reducing Ti⁴⁺ to Ti³⁺. On the other hand, the titanate phase has a lower conductivity than anatase; therefore, during the anatase-to-titanate phase transformation, the electronic conductivity drops despite an overall increase in the lithium concentration. We further confirm this relationship between doping, phase transformation, and conductivity using *operando* Raman spectroscopy.

Because lithium doping and the anatase-to-titanate phase transformation have opposite contributions to the electronic conductivity, we are able to temporally distinguish between the two behaviors. In particular, we note that the electronic conductivity momentarily rises a few seconds after lithium is inserted, corresponding to the supersaturation of lithium dopants. Over the course of several minutes, the conductivity drops because of some conversion of anatase to titanate and the restoration of each phase back to their equilibrium lithium concentrations. This *operando* electronic conductivity measurement is able to directly capture this nucleation and growth process and shows that lithium diffusion and doping is much faster than the phase transformation in Li_xTiO₂. We demonstrate how lithium insertion in the solid solution anatase can be used as a non-volatile redox transistor for neuromorphic computing. More broadly, we demonstrate an *operando* method to probe supersaturation, nucleation, and growth with extremely high sensitivity and temporal resolution.

SESSION CM03.11: Batteries II
Session Chairs: Matthew McDowell and Jagjit Nanda
Wednesday Morning, November 28, 2018
Hynes, Level 3, Room 300

8:45 AM CM03.11.01

Combined TXM/Acoustic Study of Sudden Pouch Cell Expansion Daniel Steingart and Clement Bommier; Princeton University, Princeton, New Jersey, United States.

Gas formation during lithium ion battery cycling can be both subtle and dramatic. In some cases it is a slow degradation of the electrolyte solvent during cycling due to impurities, over charge, over discharge, or a cumulative combination of all three. In other cases it can be sudden and dramatic expansion due to auto-catalytic cathode decomposition, SEI decomposition, or again, a combination of these and other factors.

In this study we combine electrochemical acoustic signal interpretations with *in operando* transmission x-ray microscopy to determine the sequences and rates associated with various gassing modes in lithium ion pouch cells.

9:00 AM CM03.11.02

Simultaneous Operando Measurements of the Local Temperature, State of Charge and Strain Inside a Commercial Lithium-Ion Battery Pouch Cell Stephen J. Harris¹, Zhili Feng² and Yang Ren³; ¹Lawrence Berkeley National Laboratory, Berkeley, California, United States; ²Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States; ³APS, Argonne National Laboratory, Argonne, Illinois, United States.

A high energy X-ray diffraction technique is employed in a new way to make *operando* through-thickness measurements inside a large format commercial Li-ion pouch cell. The technique, which has a sub-mm in-plane spatial resolution, simultaneously determines the local temperature, the local state of charge of each electrode separately (as opposed to the global average state of charge determined electrochemically), and the local in-plane elastic strain in each current collector, all without embedding any intrusive sensors that could alter battery behavior. As both thermal strain and mechanical strain develop during

the charge-discharge cycling of the pouch cell, a novel approach developed herein makes it possible to separate them, allowing for measurement of the local temperature inside the battery. The operando experiment reveals that the temperature inside the cell is substantially higher than the external temperature. We propose that mechanical strain is due primarily to load transfer from the electrode to the current collector during lithiation, allowing determination of the local binder adhesion to its current collector. Detailed local SOC mapping illustrates non-uniform degradation of the battery pouch cell. The possibility for 3D measurements is proposed. We believe that this new approach can provide critically needed data for validation of detailed models of processes inside commercial pouch cells.

9:15 AM CM03.11.03

Interrogating Electrolyte Decomposition Reactions in Advanced Batteries with Collector-Generator Measurements and Molecular Probes Maureen Tang, Oliver Harris and Sophia Lee; Drexel University, Philadelphia, Pennsylvania, United States.

One of the most serious lifetime problems for established Li-ion and emerging “Beyond-Li” batteries is electrolyte degradation from unwanted side reactions. Electrolyte reduction into insoluble products causes formation and growth of the solid electrolyte interphase (SEI) and has been well-studied. However, both oxidation and reduction can also result in soluble gaseous or liquid products, which then can migrate to the opposite electrode and contribute to electrochemical activity. Such inter-electrode ‘communication’ reactions may be detrimental to battery lifetime; for example, dissolution of transition metals from the cathode and their deposition at the anode is known to accelerate capacity fade [1]. However, communication can also be beneficial when harmful products generated from the cathode are consumed by reduction at the anode [2]. Controlling chemical communication between electrodes for improved battery lifetime requires better understanding of the chemical reactions that generate soluble products. Electrochemical methods are particularly advantageous because they can directly assess the redox activity of reaction products. In particular, four-electrode generator-collector measurements such as the rotating ring-disk electrode (RRDE) are commonly used to quantify reaction selectivity in fuel cell catalysis. Despite their utility, these methods are seldom applied to nonaqueous battery research. In this work, we apply generator-collector measurements and other electroanalytical techniques in order to understand how chemical communication between electrodes affects cell lifetime. In one application of our approach, the RRDE is used to probe mechanisms of transition metal incorporation into the SEI and their effect on through-film electron transport [3]. By using convection to control electrode cross-talk, we observe the presence of Mn contaminants from an upstream cathode at the downstream anode. Electrochemically interrogating the SEI with functionalized ferrocene mediators demonstrates that the through-film mediator reduction is much more sensitive to mediator functional group than size, indicating preferential partitioning into the organic SEI layer. Continuum-scale models to interpret the voltammetry show that incorporation of dissolved transition metals increases both the density and the activity of active sites within the SEI. We conclude that the inner, inorganic layer is responsible for preventing charge transfer through the SEI while the outer, organic layer is minimally important. Our model reconciles contradictory observations from the literature and identifies the most important components of a functional battery interface. Future work will discuss this mechanism in greater detail as well as our development of improved methods for studying these and related reactions.

[1] Gilbert et al, J. Electrochem. Soc. 164, A389, 2017.

[2] Xiong et al. J. Electrochem. Soc. 163, 546, 2016.

[3] O. C. Harris, M.H. Tang, *under review*, 2018.

9:30 AM *CM03.11.04

Using *In Situ* and *Operando* Methods to Characterize Phase Changes in Charged Lithium Nickel Cobalt Aluminum Oxide Cathode Materials Eric A. Stach^{1,2}, Sooyeon Hwang³, Khim Karki², Seung Min Kim⁴, Seongmin Bak⁷, Dongdong Xiao⁵, Noah Glachman¹, Wonyoung Chang⁸, Kyung Yoon Chung⁸, Guangwen Zhou⁵, M. Stanley Whittingham⁶, Xiao-Qing D. Yang⁷ and Y. Shirley Meng⁹; ¹Department of Materials Science and Engineering, University of Pennsylvania, Philadelphia, Pennsylvania, United States; ²Hummingbird Scientific, Lacey, Washington, United States; ³Center for Functional Nanomaterials, Brookhaven National Laboratory, Upton, New York, United States; ⁴Carbon Composite Materials Research Center, Korea Advanced Institute of Science and Technology, Jeonbuk, Korea (the Republic of); ⁵Department of Mechanical Engineering, Binghamton University, The State University of New York, Binghamton, New York, United States; ⁶Department of Chemistry, Binghamton University, The State University of New York, Binghamton, New York, United States; ⁷Department of Chemistry, Brookhaven National Laboratory, Upton, New York, United States; ⁸Center for Energy Convergence Research, Korea Advanced Institute of Science and Technology, Seoul, Korea (the Republic of); ⁹Department of Materials Science and Engineering, University of California, San Diego, San Diego, California, United States.

Lithium nickel cobalt aluminum oxide cathode materials ($\text{Li}_x\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_3$ – “NCA”) are seeing increasing use in demanding energy storage applications due to their high energy storage capacity. However, these materials can experience undesirable thermal runaway in real life applications, leading to catastrophic failures. In this presentation, I will review our work investigating the atomic scale changes that occur in NCA during thermal excursions. These studies will mostly focus on the use of in-situ transmission electron microscopy (TEM) but will include information gleaned from complementary probes such as in-situ x-ray diffraction and x-ray absorption. We have used these approaches to understand how thermal excursions can lead to bulk oxygen loss from the structure, how this oxygen loss is correlated with the movement of the transition metal ions, and how these movements lead to a series of structural changes from the spinel structure to the ‘disordered spinel’ structure to the rock-salt structure on the surface of the particles. Environmental TEM also allows us to explore how we can tune the surface activity, leading to the suppression of both oxygen loss and the initiation of the phase transitions. Finally, we will show how operando TEM approaches using electrochemical liquid-cell methods can lead to further insights into the relationship between lithium extraction and surface structural changes.

10:00 AM BREAK

SESSION CM03.12: Solid-State Electrolytes II
Session Chairs: Matthew McDowell and Jagjit Nanda
Wednesday Morning, November 28, 2018
Hynes, Level 3, Room 300

10:30 AM *CM03.12.01

Probing Interfacial Charge Transfer Limitations of Sulfide Solid Electrolytes for All Solid-State Battery Applications Y. Shirley Meng^{1,2}; ¹University of California, San Diego, La Jolla, California, United States; ²Sustainable Power and Energy Center (SPEC), La Jolla, California, United States.

All-solid-state battery (ASSB) technology has its unique capabilities, among them the potential ability to enable the Li metal anode, operate at high

voltage, along with improved safety. Among the known solid electrolytes, sulfides have shown promise due to facile battery fabrication, demonstrated high ionic conductivity, and ductility. Even though current sulfide electrolytes enable room temperature ASSB operation, their performance is still limited in terms of energy efficiency, power density and the issue of dendritic growth of lithium at high current densities. All of those problems are closely related with solid-solid interfaces that arise in an ASSB. In this talk, we discuss and highlight the importance of probing and understanding interfacial phenomena with some of the advanced diagnosis techniques. Controlling and optimizing interfacial phenomena are crucial to overcome the performance obstacles to creating practical ASSB devices.

11:00 AM CM03.12.02

Operando XPS and In Situ SAM Measurements of Solid Electrolyte Interphase Formation at Lithium/Solid Electrolyte Interfaces Kevin N. Wood³, Andrew L. Davis², K. X. Steirer¹, Shriram Santhanagopalan³, Chunmei Ban³, Sehee Lee⁴, Neil P. Dasgupta² and Glenn Teeter³; ¹Colorado School of Mines, Golden, Colorado, United States; ²University of Michigan–Ann Arbor, Ann Arbor, Michigan, United States; ³National Renewable Energy Laboratory, Golden, Colorado, United States; ⁴University of Colorado Boulder, Boulder, Colorado, United States.

Solid electrolytes such as $\text{Li}_7\text{P}_3\text{S}_{11}$ (LPS), $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ (LGPS), and related materials show great promise for battery applications, with the potential to enable lithium-metal anodes and improve safety relative to conventional liquid electrolytes. On the other hand, many solid electrolytes are unstable against metallic lithium, and little is known about the chemical evolution of the solid electrolyte interphase (SEI) during cycling. The lack of detailed knowledge about SEI formation and evolution hinders the rational design of novel solid electrolytes with superior ionic conductivity, coupled with passivating SEI layers that facilitate interfacial charge transfer. Here we report on recent efforts to develop and apply novel *operando* X-ray photoelectron spectroscopy (opXPS) techniques that enable compositional and chemical-state analysis of battery interfaces during cycling. OpXPS measurements are implemented via the ‘virtual electrode’ approach, in which electrons are supplied to or extracted from an exposed interface using either an electron gun or ultraviolet light source, eliminating the need for a physical electrode and current collector. This approach enables real-time, *in situ* XPS measurements of an electrode/electrolyte interface under electrochemical operating conditions. Initial opXPS measurements probed the formation and evolution of the SEI between LPS and metallic lithium and documented chemically resolved overpotential losses associated with specific SEI phases during electrochemical cycling.¹ These results are compared with experiments LGPS, and recent extensions of the virtual-electrode approach, including opXPS measurements on full cells, real-time *in-situ* scanning Auger microscopy (SAM) results, and the use of a low-energy Li^+ ion gun to drive interfacial electrochemistry, are also described.

11:15 AM CM03.12.03

Lithium-Electrolyte Interface Characterization in All-Solid Batteries with Operando Electron and X-Ray Microscopies Natalie Seitzman¹, Harvey Guthrey², Johanna N. Weker⁴, Heather A. Platt³, Mowafak Al-Jassim² and Svitlana Pylypenko¹; ¹Colorado School of Mines, Golden, Colorado, United States; ²National Renewable Energy Laboratory, Golden, Colorado, United States; ³Solid Power, Inc., Louisville, Colorado, United States; ⁴SLAC National Accelerator Laboratory, Menlo Park, California, United States.

All-solid batteries offer increased theoretical capacity and wider voltage windows over traditional lithium-ion systems. Additionally, replacing flammable liquid electrolytes with a solid material provides a significant safety improvement, making solid electrolytes particularly attractive for electric vehicle applications. Lithium dendrite propagation at electrolyte surfaces, a micro- to nano-scale phenomenon, can be severely detrimental to battery lifetime. A greater understanding of fundamental processes at the lithium anode-electrolyte interface is therefore critical for the success of solid-state lithium battery technologies.

Characterization of this interface comes with challenges, which include the extreme reactivity of lithium metal, narrowing the scope of experiments that can be conducted with conventional laboratory techniques, such as scanning electron microscopy (SEM). In this work, we developed *operando* SEM to provide high-resolution visualization of $\beta\text{-Li}_3\text{PS}_4$ electrolyte and lithium metal electrode surfaces during cycling, and windowless EDS enabled identification of resultant lithium dendrites within the electrolyte. However, the near-surface nature of SEM and the reactivity of lithium ions to the electron beam complicate the analogy between laboratory experiments and practical batteries. Integration of surface observations from SEM with x-ray tomography experiments-in which a battery or symmetric cell can be analyzed whole-was used to increase the reliability of SEM data and to probe all anode-electrolyte interfaces at both the micro- and nano-scale.

At the micro-scale, *operando* X-ray computed tomography revealed the same pattern of lithium migration with applied current in a sample that is more reflective of a realistic battery. Further, X-ray transmission microscopy (TXM) was utilized due to improved spatial resolution allowing the study of nano-scale features, with resolution closer to that of SEM but without reactivity of the sample to the beam. Our approach, combining SEM and X-ray *operando* studies, revealed lithium growth through cracks and pores in the $\beta\text{-Li}_3\text{PS}_4$ ceramic material and demonstrated the influence of inhomogeneities in the lithium anode on dendrite growth at the electrode-electrolyte interface.

11:30 AM *CM03.12.04

Elucidating Ion Transport and Charge Transfer Behavior at Solid-Solid Interfaces via STEM Miaofang Chi; Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States.

Understanding transport behavior in solid-solid heterogeneous interfaces represents one of the most challenging problems in electrochemical systems. Sluggish ion transport and cycling instability are frequently observed at interfaces and the exact origins are unclear. These interfaces are composed of two materials with dissimilar lattice structures, distinctive chemical potentials, and can experience different responses to external stimuli. Multiple interfacial phenomena are often involved, including electrochemical and chemical reactions, elemental inter-diffusion, phase transformation, mechanical integrity, and interfacial space charge. These phenomena are spatially confined and are often correlated, complicating the mass and charge transfer behavior at interfaces and imposing challenges in their characterization. Scanning transmission electron microscopy (STEM) represents an ideal platform for studying interfacial behavior owing to its unprecedented spatial resolution. Recent new developments in STEM-based *in situ* and functional imaging is creating new opportunities to elucidate interfacial charge transfer behavior not previously feasible. This talk will highlight our recent studies conducted to probe the stability of solid-solid electrochemical interfaces using atomic-resolution *in situ* STEM and electron energy loss spectroscopy (EELS). Two systems, LIPON-Li and LLZO-Li will be compared and discussed. Observations show that while both LIPON and LLZO form a passivation layer when contacted with Li metal, their formation mechanism and equilibrium thicknesses differ significantly. Further, different responses are detected between the grain bulk and grain boundary when contacted with Li metal under an external bias; LLZO grains tend to be stable under a high external bias while grain boundaries are more prone to chemically react with Li. These results provide valuable insight toward the design of stable and conductive interfaces in Li metal batteries. This presentation will also focus on the application of new STEM-based techniques as applied to battery research, and will emphasize recent developments in 4-D STEM-based differential phase contrast imaging and EELS-based vibration spectroscopy.

Acknowledgement

Research sponsored by the Materials Sciences and Engineering Division, Office of Basic Energy Sciences, U.S. Department of Energy (DOE). Microscopy performed as part of a user project at Oak Ridge National Laboratory’s Center for Nanophase Materials Sciences (CNMS), which is a U.S. DOE Office of

SESSION CM03.13: Battery Interfaces and Ion Insertion

Session Chairs: Miaofang Chi and Stephen Harris

Wednesday Afternoon, November 28, 2018

Hynes, Level 3, Room 300

1:30 PM *CM03.13.01

X-Ray and Optical Spectroscopy and Imaging of the Electrode/Electrolyte Interface on Intermetallic Anodes [Robert Kostecki](#), Philip N. Ross, Hans Bechtel, Jinghua Guo, Liang Zhang, Atetegeb Haregewoin and Ivana Hasa; Lawrence Berkeley National Lab, Berkeley, California, United States.

Intermetallic anodes e.g., Si, Sn, Sb have received significant attention as a viable alternative to graphitic carbon as the negative electrode in lithium-ion batteries due to its high capacity and availability. These electrodes can theoretically store charge nearly an order of magnitude higher than graphite. However, several problems have been identified that limit its utility including large crystallographic expansion upon lithiation, which translates to particle cracking, particle isolation, and electrode delamination issues, as well as electrolyte side reactions, which affect electrochemical performance and lifetime of these electrodes in battery cells.

The key problems that have hindered practical application of intermetallic anodes in commercial Li-ion batteries are: (i) the large volume changes during cycling, which results in cracking and decrepitation of the active material, and loss of electronic connectivity and mechanical integrity in the composite electrode, (ii) inherent non-passivating behavior of silicon in organic electrolytes, which results in large irreversible capacity loss and gradual electrolyte consumption during the electrode operation. However, despite extensive research in the past four decades, the intrinsic behavior and the corresponding barriers to implementation of silicon anodes have in Li-ion systems have not been fully understood and remedied.

This study involves diagnostic evaluations of silicon composite electrodes as well as studies of the properties of the individual components and their interfaces. Unraveling the basic function and operation of the SEI layer on Si, Sn, Sb and their binary and ternary alloys with transition metals at the length-scale that corresponds to its basic building blocks is the primary focus of this work. Surface characterization techniques such as FTIR, Raman, x-ray and NMR spectroscopy and microscopy have provided valuable information regarding the SEI chemical composition and structure at a micrometer scale. In this research effort we leverage the use of model experimental systems and novel characterization techniques to investigate and evaluate intrinsic properties of individual components such as additives and advanced binders and their effects on the composite silicon anode electrochemical performance. For instance, using far- and near-field IR spectroscopy, AFM imaging and LIBS depth-profiling, we correlate the changes of passivating properties of model electrodes in the presence of electrolyte additives, multifunctional binders, and residual contaminants. This study also demonstrates a unique ability of the synchrotron infrared nanospectroscopy to probe individual chemical building blocks at electrochemical interfaces at the spatial resolution of ca. 20 nm with an exceptional surface sensitivity, chemical selectivity and specificity.

2:00 PM *CM03.13.02

Understanding the Many Length Scales of Ion Insertion Solids [William Chueh](#); Materials Science and Engineering, Stanford University, Stanford, California, United States.

The availability of low-cost but intermittent renewable electricity (e.g., derived from solar and wind) underscores the grand challenge to store and dispatch energy so that it is available when and where it is needed. Redox-active materials promise the efficient transformation between electrical and chemical energy and are at the heart of carbon-neutral energy cycles. Understanding design rules that govern materials chemistry and architecture holds the key toward rationally optimizing technologies such as lithium-ion batteries and solid oxide fuel cells. Electrochemical reactions involved in these technologies span diverse length and time scales, ranging from Ångströms to meters and from picoseconds to years. As such, establishing a unified, predictive framework has been a challenge. The central question that motivates our research is, “can we understand and engineer redox reactions at the levels of electrons, ions, molecules, particles and devices using a bottom-up approach?” In this talk, I will discuss how we integrate synthesis, fabrication, in-situ characterization, modeling and data analytics to understand molecular pathways and interfacial structure, and to bridge fundamentals to energy storage and conversion technologies by establishing new design rules.

2:30 PM BREAK

SESSION CM03.14: Batteries III

Session Chairs: Miaofang Chi and Stephen Harris

Wednesday Afternoon, November 28, 2018

Hynes, Level 3, Room 300

3:30 PM *CM03.14.01

Revealing Li-Ion Battery Processes Using Operando Neutron Depth Profiling and NMR Methods [Anne Co](#), Danny Liu, Jose Lorie Lopez, Daniel Lyons, Lei Cao and Philip Grandinetti; Department of Chemistry and Biochemistry, The Ohio State University, Columbus, Ohio, United States.

Rechargeable Li-ion batteries (LIBs) have been the predominant energy storage for a wide range of portable devices like cell phones, laptops and digital electronics. Non-destructive methods such as neutron depth profiling (NDP) and solid state NMR are ideal for probing Li complex formation, accumulation and transport within the battery material during charge/discharge. Currently, our work is focused on understanding the effect of an electrochemical event to the materials' storage properties using NDP and NMR techniques *in operando*. Specifically we report our recent work on the preferential Li nucleation, Li trapping, Li transport in intermetallic materials like Li_xSn_y , Li_xSi_y and Li_xAl_y and evidence of formation and accumulation of a LiSn metastable phase that is correlated to capacity fade.

4:00 PM CM03.14.02

Operando and Three-Dimensional Visualization of Ion Depletion and Lithium Growth by Stimulated Raman Scattering Microscopy Qian Cheng, Lu Wei, Wei Min and Yuan Yang; Columbia University, New York, New York, United States.

Visualization of ion transport in electrolyte provides fundamental understandings of electrolyte dynamics and electrolyte-electrode interaction, shedding light on material designs to enhance device performance, such as batteries and fuel cells. However, this task is extremely challenging for existing techniques due to their inability to capture the low ionic concentration (<1 M) and the fast dynamics (1-10 s) of the electrolyte. Here we show that an emerging Stimulated Raman Scattering (SRS) microscopy offers the required spatial (sub-micrometer optical resolution), temporal (faster than 1 s per frame) and chemical (around mM) sensitivities to address this challenge. In Raman, $[\text{Li}^+]$ can be probed by either Li^+ -solvent interaction, or vibrational mode in the anion which has the same concentration as Li^+ due to electroneutrality. Utilizing this technique, we examined and provided evidence for a long-lasting question: How does Li^+ concentration correlate with and contribute to the uneven deposition of lithium metal? A three-stage lithium deposition process is uncovered, each corresponding to no-depletion, partial-depletion and full-depletion regime of Li^+ , respectively. Further analysis reveals a previously uncharacterized spatial heterogeneity of Li^+ concentration near lithium surface, and a positive feedback mechanism between the inhomogeneous growth of lithium and the local ionic concentration or flux. Finally, we demonstrate that Li_3PO_4 -based artificial solid electrolyte interface (SEI) is effective in homogenizing Li^+ concentration near lithium surface and suppressing the dangerous dendritic growth of lithium, which provides new insights into battery safety. This study shows that SRS microscopy is a powerful technique for imaging ion transport and will open various applications in materials and energy fields.

4:15 PM CM03.14.03

Solvent Dynamics at Electrode Interfaces—Analysis of SEI Formation Pathways and Electric Fields Using Vibrational Spectroscopy Jarred Olson, Patrik Johansson, David Castner and Cody Schlenker; University of Washington, Seattle, Washington, United States.

At an electrode interface, redox mechanisms associated with electrolyte solvent breakdown into components of the solid-electrolyte interphase (SEI) layer are often invoked to rationalize the cycling performance of battery materials. Mechanisms of SEI formation frequently include the release of gas, whose composition serves as an indicator of subsequent chemical structures comprising the SEI. Recently, our group monitored reduction of fluoroethylene carbonate (FEC) and ethylene carbonate (EC) electrolyte solvents on silicon nanoparticles using interface-sensitive vibrational sum frequency generation (SFG) spectroscopy in tandem with electrochemistry. We observe SFG signatures that suggest carbon monoxide (CO) evolution on nano-Si proceeds at distinct lithiation potentials for different electrolyte solvents. FEC appeared to preferentially follow a 2-electron reduction pathway regardless of the degree of lithiation (potential) of silicon. However, EC appeared to be more sensitive to the degree of Si lithiation, reducing to CO only at the highest lithiation state of Si. Upon prolonged reduction of EC, we additionally observe the formation of poly(EC), which is soluble in carbonate-based electrolytes and appears to form through the release of CO_2 . The results of this study validate previous computational descriptions of FEC and EC reduction, as well as provide insight on a failure mechanism EC-based electrolytes impart upon Si anodes.

The phenomena responsible for the aforementioned SEI-formation processes is the intense electric field magnitude at the electrode interface. Quantification of the local field at the electrode/electrolyte junction has remained an elusive endeavor due to the lack of a reference material that is calibrated against fields of known value. Vibrational Stark effect spectroscopy, a method historically used to characterize the strength of electric fields in enzyme active sites, commonly utilizes the C=O group as a calibrated field reporter. Thus, carbonate-based electrolyte solvents (all of which contain the C=O group) provide amendable conditions for operando characterization of electric fields confined within the electrochemical double layer. Recently, we calibrated the sensitivity of EC, FEC and diethyl carbonate (DEC) to electric fields, demonstrating that their responsivity to an arbitrary field follows a linear trend. Referencing results of the DEC/ LiCoO_2 junction as a model system, we estimate that the field localized within the electrochemical double layer is in the MV/cm range before electrochemical cycling is induced, providing a lower boundary of field strengths prior to electrochemical cycling. As the progress of high-voltage electrode storage materials advances, understanding interfacial fields may provide new avenues for improving electrolyte stability by tailoring the interface electrostatics.

4:30 PM CM03.14.04

Electrode-Electrolyte Reactivity Trends and Coatings Screening at Positive Electrodes in Li-Ion Batteries Livia Giordano¹, Pinar Karayaylali¹, Yang Yu¹, Yu Katayama^{1,4}, Soo Kim¹, Yirui Zhang¹, Neni Charles¹, Sokseih Mui¹, Filippo Maglia², Isaac Lund³ and Yang Shao-Horn¹; ¹Massachusetts Institute of Technology, Cambridge, Massachusetts, United States; ²BMW Group, München, Germany; ³BMW Group Technology Office USA, Mountain View, California, United States; ⁴Department of Applied Chemistry, Yamaguchi University, Ube, Japan.

Understanding the (electro)chemical reactions at the interface between the positive electrode and the organic electrolyte is crucial for the rational design of Li-ion batteries towards improved capacity retention and cycle life. Commonly used positive electrodes, such as layered intercalation oxides, exhibit different degrees of chemical reactivity with carbonate-based electrolytes [1, 2], yet a comprehensive understanding of the reaction mechanisms and the parameters governing the interfacial reactivity is still lacking. Here we employed density functional theory calculations to study the reaction mechanism and reactivity trends for organic solvents at the surface of oxides. We found that solvent dissociation is thermodynamically more favorable than electrophilic attack, nucleophilic attack and dissociation with oxygen extraction from the oxide surface on layered oxides. We showed that the dissociation is accompanied by an interfacial charge transfer, where the solvent molecule is oxidized and the transition metal oxide is reduced. Solvent dissociation became thermodynamically more favorable on oxide surfaces with transition metal ions from left to right in the periodic table or by increasing transition metal oxidation state in the oxides upon delithiation, where greater solvent dissociation was found as the oxide Fermi level was lowered into the oxide O 2p band [3]. Similar driving force was found for the dissociation of ethylene carbonate (EC), ethyl methyl carbonate (EMC) and diphenyl carbonate (DPC) additive [4]. The predicted trends can explain the reactivity and the interfacial compositions observed experimentally for LiCoO_2 , $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ (NMC) and Ni-rich NMC. These findings were used to identify a design principle for the screening of coating materials which can prevent the dissociation of organic carbonates.

[1] D. Aurbach *et al.*, *J. Electrochem. Soc.* 147, 1322 (2000).

[2] O. Borodin *et al.*, *Acc. Chem Res.* 50, 2886(2017).

[3] L. Giordano *et al.*, *J. Phys. Chem. Lett.* 8, 3881 (2017).

[4] M. Gauthier *et al.*, *J. Electrochem. Soc.* 165, A1377 (2018).

8:00 PM - 10:00 PM
Hynes, Level 1, Hall B

CM03.15.01

Development of a Method to Characterize Active Sites in Photocatalysis Using *In Situ* Transmission Electron Microscopy Noah Glachman¹, Noah Geller¹, Alexander Shea¹, Khim Karki², Daan H. Alsem², Julio A. Rodriguez Manzo², Norman Salmon², Deep M. Jariwala³ and Eric A. Stach^{1,4}; ¹Materials Science and Engineering, University of Pennsylvania, Philadelphia, Pennsylvania, United States; ²Hummingbird Scientific, Lacey, Washington, United States; ³Electrical and Systems Engineering, University of Pennsylvania, Philadelphia, Pennsylvania, United States; ⁴Nanoscale Characterization Facility, Philadelphia, Pennsylvania, United States.

Hydrogen gas has the potential to be a clean source of sustainable energy due to its high energy density. However, greenhouse gas emissions are still a major byproduct of current hydrogen production methods. Photoelectrochemistry provides a promising, environmentally friendly route to hydrogen production; however, the atomic scale mechanisms of the photocatalysts that facilitate the water splitting reaction are currently poorly understood. Further understanding of the chemical physics governing the active hydrogen evolution sites would allow for better design of photoelectrochemical devices and thus lead to improved reaction efficiencies. This will overcome one of the major barriers impeding this promising technology. We have developed a unique *in-situ* photoelectrochemistry transmission electron microscope (TEM) liquid cell sample holder which can be used to characterize these reactions in real time at nanometer length scales. In order to provide accurate, quantitative information, it is necessary to accurately deposit the photocatalyst of interest onto microfabricated electrodes. In this research, a precise sample deposition technique utilizing an inkjet printer has been developed along with stable suspensions of known photocatalysts, leading to site-specific deposition onto the electrode chips. These experiments will investigate the mechanisms by which selected photocatalysts induce water splitting and allow for the identification of defect features that serve as the active sites. Specifically, this experimental design allows for correlation between I-V characteristics and real time, high magnification imaging and spectroscopy, elucidating information about photocatalytic mechanisms at the nanoscale. The following photocatalysts used were chosen because the proposed mechanism for each exhibits a spatial dependence: plasmonically enhanced catalysis for Au nanoprisms and catalytically active edge sites for MoS₂ flakes. These experiments will lay the groundwork for the use of this novel experimental design to investigate a wide variety of photoelectrochemical systems using this *in-situ* approach.

CM03.15.02

***In Operando* Optical Microscopy and Vertex Delay Cyclic Voltammetry for Direct Observation of Lithium Dendrite Regimes** Noam Hart; NICE, Mountain View, California, United States.

Understanding the mechanisms of lithium dissolution/deposition has benefitted significantly from *in-operando* microscopy. Recent work has used optical microscopy to explore dendritic growth. Existing designs face lithium strips across from each other, with the optical instrument placed in the plane of the strips. This work presents a system that cycles lithium from the edge, rather than the face. By limiting electrochemical activity to an edge, (a) the entire electrochemical process on the electrode surface is within the optical instrument's depth of field, (b) tight control of current density can be achieved and (c) the removal of a native layer can be easily and reliably replicated, offering a high purity lithium surface unaffected by shelf-life. This system allows for unambiguous identification of which deposition/dissolution phenomena are occurring in the cell at different current densities and cycle life.

Optical observations are paired with cycling and cyclic voltammetry with vertex delays (CV). A simple $V=IZ$ relationship is used to convert current-controlled cycling and voltage-controlled CV, showing how directly these two regimes translate. CV is then used to explore a voltage controlled environment for the investigation. With CV a milder voltage environment can be imposed, reducing the reaction complexity and the cell can be observed via current response. This allows for a clear delineation of different reaction regimes, where kinetic, electronic and diffusion limitations are expressed clearly via current rate and regimes can run their course, independent of the requirements of cell cycling. Decoupling the reaction from a controlled current allows for more dramatic changes in the scale of the reactivity, as one regime takes over from another, with a current response that reflects their distinct bottlenecks. The optical cell allows different dendrite deposition/dissolution regimes to be unambiguously identified and studied, validating shifts between regimes and correlating them to the electrochemical response.

CM03.15.03

Asymmetric Dynamics of Ion Insertion/Extraction of Lithium Battery Electrodes by Electro-Autocatalyst and Electro-Autoinhibitor Jihyun Hong^{1,2}, Hongbo Zhao³, Jungjin Park^{1,4}, Kipil Lim^{1,2}, William Gent^{4,5}, Samanbir Kalirai^{1,4}, Michael F. Toney², William Chueh^{1,2} and Martin Bazant^{3,6}; ¹MSE, Stanford University, Stanford, California, United States; ²Stanford Synchrotron Radiation Lightsource, SLAC National Accelerator Laboratory, Menlo Park, California, United States; ³Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States; ⁴The Advanced Light Source, Lawrence Berkeley National Laboratory, Berkeley, California, United States; ⁵Department of Chemistry, Stanford University, Stanford, California, United States; ⁶Department of Mathematics, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

Reversible insertion and extraction of a guest ion into the host crystal is the fundamental reaction underpinning insertion electrochemistry and has been widely applied to store energy and tune catalysts. It has been considered that the ion extraction and insertion reactions are reversible and following near-equilibrium paths for charge and discharge of lithium ion batteries, respectively. However, recent studies have revealed that the dynamics of the ion insertion and extraction can be altered by current density (reaction rate) and reaction direction in a phase-separating compound, Li_{1-x}FePO₄, using operando characterization techniques such as X-ray diffraction (XRD) and X-ray microscopy. We recently demonstrated that the kinetics of the reactions at solid-liquid interface governs the uniformity of ion insertion/extraction reactions by electro-autocatalyst and autoinhibitory. Here, we first show the asymmetric dynamics of ion insertion and extraction of a model solid-solution compound, lithium transition metal oxides. Combining population dynamics theory, operando XRD and scanning transmission X-ray microscopy (STXM), we show that the non-constant reaction kinetics results in the heterogeneous delithiation and homogeneous lithiation, which eventually affects the fast-charging capability of lithium ion batteries.

CM03.15.04

Controlling Interfacial Properties of Solid-State Lithium Batteries Using Atomic Layer Deposition Kirit Joshi¹, Francisco Javier Quintero Cortes², John Lewis² and Matthew McDowell^{1,2}; ¹George W. Woodruff School of Mechanical Engineering, Georgia Institute of Technology, Atlanta, Georgia, United States; ²School of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, Georgia, United States.

Solid-state lithium batteries (SSLiBs) could enable improved safety and higher energy density compared to traditional lithium-ion batteries due to the use of metal anodes without dendrite growth. However, successful implementation of solid electrolytes within batteries is contingent upon controlling the chemical, mechanical, and electronic properties at solid electrolyte/electrode interfaces. SSLiB interfaces can exhibit poor wetting properties, leading to interfacial void spaces and high impedance. Furthermore, many solid electrolytes are chemically unstable in contact with electrodes. This project aims to stabilize traditionally unstable interfaces between lithium metal and ceramic electrolytes through the use of atomic layer deposition (ALD) of thin film

oxide protection layers. It is expected that these protection layers will improve wetting properties and prevent or slow detrimental anode-electrolyte interactions. A custom ALD instrument has been designed and constructed for this project. This fully-automated instrument allows for the deposition of ternary oxides with atomic precision. It features pneumatic control of valves, a custom LabVIEW Virtual Instrument interface, and real-time pressure feedback control. This instrument is ideal for coating nanometer-scale films on either bulk solid electrolyte pellets or on powder. The custom reactor is used to coat NASICON-type solid electrolytes, including $\text{Li}_{1+x}\text{Al}_x\text{Ti}_{2-x}(\text{PO}_4)_3$, with oxide thin films (Al_2O_3 , ZnO). These NASICON materials are shown to readily react in contact with Li metal. The effect of these ALD protection films on electrochemical behavior and lifetime are compared to that of uncoated materials to determine whether the ALD coating improves battery performance and stability. Ultrathin oxide layers are found to improve the stability of the solid electrolytes in contact with Li during galvanostatic cycling. In particular, the ALD layers are shown to substantially extend the time to failure during cycling and to alter degradation pathways within cells. In conjunction with other students, *ex situ* and *in situ* characterization is used to uncover the evolution of these layers during cycling. These results are important for the development of stabilized, high-conductivity solid electrolytes for solid-state batteries.

CM03.15.05

Enhancing *In Situ* Far-Infrared Spectroelectrochemistry Sensitivity with Gold Nanostructures Lucyano J. Macedo and Frank N. Crespilho; São Carlos Institute of Chemistry, University of São Paulo, São Carlos, Brazil.

Organometallic structures are fundamental building blocks in life, being crucial components of biological systems such as metalloproteins and far-infrared (FIR) spectroscopy plays a fundamental role in the identification and investigation of metal-ligand bond vibrational modes in these organometallic structures. Due to the possibility of investigating the influence of the redox state of the metal on the structural behavior, *in-situ* spectroelectrochemistry using this region of the electromagnet spectrum is applied; however, this analytical approach is limited due to the low sensitivity of optical components available to date even when synchrotron light is used as source of infrared radiation. To address this issue, we utilized the surface-enhanced infrared absorption (SEIRA) effect to promote more sensitivity in the spectroscopic analyses, using surfactant-free gold nanostructures in order to avoid the interference from organic matter. As probe, we used well-known redox active organometallic probes, whose iron-carbon, iron-nitrogen, and iron-sulfur bonds vibrational modes are active in the FIR region. Thus, we observe an enhancement of the signal from these vibrational modes in the FIR spectrum when these gold nanostructures are in close interaction with these probes. Also, this absorption enhancement benefits the use of this approach in aqueous medium electrochemistry, probing more clearly the role of the metallic atom redox state on the whole organometallic structure. Based on these observations of such control of the vibrational modes in the FIR spectroscopy by electrochemistry, this approach might also be helpful to further investigate organometallic interaction within biological relevant molecules such as metalloproteins.

CM03.15.06

***In Situ* Study of the Reaction Processes and Mechanisms of Nanocatalysis by Enhanced Raman Spectroscopy** Chen Wang; Xiamen University, Xiamen, China.

In-situ dynamic monitoring of nanocatalytic processes is of significant importance for the insightful understanding of reaction mechanisms and structure-activity relationships. Raman spectroscopy can provide fingerprint structural information. However, its sensitivity is too low to achieve the *in-situ* detection of trace amount of surface species on catalysts. To solve this long-standing problem, we develop a SHINERS-satellites strategy which can be used to *in-situ* track the nanocatalytic processes based on shell-isolated nanoparticle-enhanced Raman spectroscopy (SHINERS). In the SHINERS-satellites strategy, nanocatalysts are assembled on shell-isolated nanoparticles (SHINs), leading to the formation of SHINERS-satellites nanocomposites (Au core-silica shell-catalyst satellites). The Au cores can generate strong electromagnetic field to enhance the Raman signals of the species adsorbed on the catalysts, while the silica shells can isolate the influence of the Au cores on the catalysts and reactions. Therefore, SHINERS-satellites strategy can be used to *in-situ* detect the trace amount of active species and intermediates during nanocatalytic reactions. It is a general strategy and can be used for different kinds of nanocatalysts including monometal, bimetal, trimetal, oxide, etc. With SHINERS-satellites strategy, the reaction processes of CO oxidation on Pt- and Pd-based nanocatalysts are *in-situ* monitored. The intermediates including active oxygen species, Pt-C, Pd-C, etc. are *in-situ* detected, and the reaction mechanisms as well as structure-activity relationships are revealed at a molecular level. Furthermore, SHINERS-satellites strategy has also been used in the *in-situ* study of catalytic hydrogenation using the conversion of pNTP to pATP as a probe reaction. Direct spectroscopic evidences for the hydrogen spillover at interfaces are obtained, and the influence of the interfacial structures on the hydrogen spillover and reaction pathways has been revealed. At the same time, the transportation of hot electrons generated on plasmonic nanomaterials in different materials has been studied using SHINERS. It is found that hot electrons can only be transferred via semiconductors and then trigger photocatalytic reactions. This study provides not only a new strategy for the *in-situ* study of nanocatalysis but also molecular information of the reaction mechanisms and structure-activity relationships, thus greatly helps the rational design and development of highly efficient nanocatalysts.

CM03.15.07

Characterizing the Mechanical Failure of Solid Electrolytes Through *Operando* X-Ray Tomography Jared Tippens², Matthew McDowell^{1,2}, Francisco Javier Quintero Cortes¹, John Lewis¹, Christopher Saldana², John Miers² and Haipeng Qiao²; ¹School of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, Georgia, United States; ²George W. Woodruff School of Mechanical Engineering, Georgia Institute of Technology, Atlanta, Georgia, United States.

Solid state batteries have attracted growing interest due to their increased safety and potentially high energy density when compared with traditional lithium-ion batteries with liquid electrolytes. Solid electrolytes have been shown to offer a greater resistance to lithium dendrite growth when using a lithium metal anode, but recent studies demonstrate that metal growth and mechanical degradation can still occur when using a ceramic ion-conducting membrane. The low fracture toughness of ceramic solid electrolytes suggests that they are susceptible to mechanical failure, particularly after cracks are initiated in the material. While several studies have been conducted to characterize the mechanical properties of solid electrolytes, little work has been done to characterize and understand the fracture process during electrochemical cycling. In this work, we use *operando* x-ray tomography with a lab-scale computed tomography (CT) instrument to investigate the mechanical degradation process in $\text{Li}_{1.5}\text{Al}_{0.5}\text{Ge}_{1.5}(\text{PO}_4)_3$ (LAGP), a NASICON-type solid electrolyte during cycling. NASICON electrolytes have garnered interest due to its high ionic conductivity. A symmetric cell with lithium metal electrodes was cycled galvanostatically, and 3D images were collected showing the morphology of the solid electrolyte at different stages of electrochemical cycling. A voxel resolution of 18 μm was obtained, allowing for thorough characterization of the microstructural evolution during the experiment. Through this methodology, the locations of crack initiation and the process of crack growth can be tracked voxel by voxel as a function of the number of galvanostatic cycles. The results show the potential for using this non-invasive method to investigate the mechanical degradation behavior of various solid electrolytes. This information paves the way to future studies in which protection layers between the electrolyte and electrodes could be applied to prevent or retard mechanical failure in solid electrolytes to prolong battery life.

CM03.15.08

XPS on Li Battery Related Compounds—Analysis of Inorganic SEI Phases and a Methodology for Charge Correction Kevin N. Wood^{1,3}, Sang-Don Han¹, Andrew L. Davis², Yun Xu¹, Andriy Zakutayev¹, Neil P. Dasgupta² and Glenn Teeter¹; ¹National Renewable Energy Laboratory, Lakewood,

Colorado, United States; ²University of Michigan, Ann Arbor, Michigan, United States; ³San Diego State University, San Diego, California, United States.

Accurate identification of chemical phases associated with the electrode and solid-electrolyte interphase (SEI) is critical for understanding and controlling interfacial degradation mechanisms in lithium-containing battery systems. To study these critical battery materials and interfaces, X-ray photoelectron spectroscopy (XPS) is a widely used technique that provides quantitative chemical insights. However, due to the fact that a majority of chemical phases relevant to battery interfaces are poor electronic conductors, phase identification that relies primarily on absolute XPS core level binding-energies (BEs) can be problematic. Charging during XPS measurements leads to BE shifts that can be difficult to correct. These difficulties are often exacerbated by the coexistence of multiple Li-containing phases in the SEI with overlapping XPS core levels. To facilitate accurate phase identification of battery-relevant phases (and electronically insulating phases in general), we propose that BE separations between core levels present in a particular phase (e.g. BE separation between the O 1s and Li 1s core levels in Li₂O) should be used as an additional constraint in order to significantly improve reliability of phase identification. This approach is applied to XPS data acquired from six battery-relevant inorganic phases including lithium metal (Li⁰), lithium oxide (Li₂O), lithium peroxide (Li₂O₂), lithium hydroxide (LiOH), lithium carbonate (Li₂CO₃) and lithium nitride (Li₃N). To demonstrate the practicality of this approach, we apply the charge-correction methodology to *ex-situ* and *operando* XPS data acquired on solid electrolytes and Si anodes materials.

CM03.15.09

Origin of Contraction Force in Artificial Muscle Based on Conducting Polymers Keiichi Kaneto, Fumito Hata and Sadahito Uto; Osaka Institute of Technology, Osaka, Japan.

Artificial muscles are interested in the application to human friendly robots, because of the noiseless and simple structure for complicated motions. Among various materials, conducting polymers are superior in operation voltage, magnitude of deformation and contraction force. These features originate from the mechanism of deformation, as well as the high electrical conductivity, flexibility and toughness of conducting polymers. Electrochemical oxidation and reduction of conducting polymers induces the electrochemomechanical deformation (ECMD) by insertion and exclusion of ions. It has been shown that the magnitude of deformation is determined by the total volume of inserted bulky ions, being up to 40% and larger than skeletal muscle of 25%. The contraction force is several tens MPa, being larger than that of skeletal muscle of 0.4 MPa. However, little is known about the origin of contraction force. The strain of ECMD in the polymer films was measured in-situ as the function of tensile stress using a laser displacement meter. The strain decreased with increasing the tensile stress, which gave the EC stress-strain curve. In this talk, the origin of EC contraction force is discussed based on EC stress-strain curves, taking the Young's moduli into account in polypyrrole and polyaniline films.

CM03.15.10

CO₂ Bubble Engineering During Electrochemical Reduction of CO₂ Sami Khan, Jonathan Hwang, Yang Shao-Horn and Kripa K. Varanasi; Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

Electrochemical reduction of CO₂ is a promising approach towards reducing the atmospheric CO₂ levels and converting CO₂ to usable fuels. While a variety of electrocatalysts have been developed for CO₂ reduction, a major challenge remains in minimizing co-evolution of hydrogen as well as maintaining a sufficiently high CO₂ concentration in the electrolyte. Herein we report the effect of CO₂ bubbles on the current density and product distribution mix during CO₂ reduction. We compare and contrast against standard approaches using CO₂ atmospheres and demonstrate high faradaic efficiency towards carbonaceous products using copper catalyst, as well as a sustained higher current density and propose broader implications towards scaling up.

CM03.15.11

Rechargeable Li-Ion Cell State of Charge and Health by *In Operando* Inside-Out Magnetic Resonance Imaging Mohaddese Mohammadi, Alexej Jerschow and Emilia Silleto; New York University, New York, New York, United States.

One of the biggest obstacles in the way of battery technology development is the limited amount of information that one can obtain from the battery mechanism without taking it apart. Here we are presenting a novel nondestructive battery assessment technology that is capable of obtaining crucial information from batteries even when the cells are encased in conductive material. One important application is commercial-type cell-phone batteries, which can be analyzed with this method. The technique is based on measuring the magnetic susceptibility of active ingredients inside an electrochemical cell that is affected by the oxidation state of the materials to give insights into the state of charge (SOC) of the battery, its failure mechanisms and the current distributions. The technique has been demonstrated on various cell types, defects, chemistries, and current level. The measurement is fast (a couple of seconds), and could be adapted to a range of cell types. Overall, it is hoped that this new noninvasive methodology will provide much-needed tools for the development of new battery materials and cell designs that address current and future needs.

CM03.15.12

***In Situ* Identification of High-Efficient Phosphide-Based Catalysts for Bi-Functional Overall Water Electrolysis** Sung-fu Hung; Chemistry, National Taiwan University, Taipei, Taiwan.

Phosphide-based electrocatalysts exhibit high activities in alkaline solution toward bi-functional overall water electrolysis. However, the stable phase of non-oxides during the catalysis were merely directly identified, leading to the inappropriate development in material assignment and theoretical simulation. In this work, the synthesized iron-doped cobalt phosphides showed superb activity in hydrogen evolution reaction ($\Delta\eta = 114$ mV), oxygen evolution reaction ($\Delta\eta = 66$ mV), and bi-functional overall water electrolysis ($\Delta\eta = 199$ mV) in comparison to pristine cobalt phosphides. *In-situ* transmitted X-ray diffraction and X-ray absorption spectroscopy identified that iron dopants stabilized the phosphide phase, restraining the transformation into hydroxides that impedes the active substance in the case of pristine cobalt phosphide, and thus swiftly converted into active oxyhydroxide for OER as well as preserved the active phosphide phase for HER to achieve high bi-functional activity. These results would reveal the true materials during the catalysis when dealing with non-oxide materials and reflect the proper mechanism of catalysis to facilitate the electrocatalytic applications.

CM03.15.13

***In Situ* TEM Investigation of 3D Vertical RRAM Array** Min-Ci Wu, Tsung-Eong Hsieh and Wen-Wei Wu; Materials Science and Engineering, National Chiao Tung University, Hsinchu, Taiwan.

Resistive random access memory (RRAM) is considered as a promising candidate for the next-generation nonvolatile memories (NVM) due to its high storage density, reduced power consumption, and fast switching speed. Transition metal oxides are widely utilized to RRAM as insulator, which exhibit stable structure, high endurance and retention, and shrinking ability under several nanometers. In order to realize higher endurance and stability while reducing the size, knowing the mechanism of filaments formation and the interaction between adjacent nanodevices are essential. In this work, three-dimensional vertical RRAM (VRRAM) array architectures were built to access and organize data, which are expected to high density application potential. In our simple MIM structure, ZnO is the insulator, and Ag and Pt are served as active electrode and inert electrode, respectively. Each electrodes

intersection contains two types of RRAM devices (Ag/ZnO/Pt, Pt/ZnO/Pt). By utilizing in-situ transmission electron microscope (TEM), we could observe the dynamic switching behaviors of two neighboring devices and realize the interaction between them. While the devices sizes scale down to few nanometers scale, the evolution of different types of filaments provides important information to improve the stability and performance of the devices.

CM03.15.14

Mechanical Behavior of Silicon Dioxide (SiO₂) Thin-Film Coatings During Electrochemical Lithiation/Delithiation Cycling Subhajit Rakshit, Akshay Shailendra Pakhare and Siva P. Nadimpalli; Mechanical Engineering Department, New Jersey Institute of Technology, Newark, New Jersey, United States.

Oxide (SiO₂) coatings have been shown to improve the cyclic performance of high-energy density electrode materials such as Si. However, no study exists on the mechanical characterization of these oxide coatings. Here, thin film SiO₂ electrodes are cycled under galvanostatic conditions in a half-cell configuration with lithium metal foil as a counter/reference electrode, with 1 M LiPF₆ in ethylene carbonate, diethyl carbonate, dimethyl carbonate solution (1:1:1, wt%) as an electrolyte. Stress evolution in the oxide films during electrochemical lithiation/delithiation is measured in situ by monitoring the substrate curvature using a multi-beam optical sensing (MOS) method. Upon lithiation SiO₂ undergoes extensive inelastic deformation, with a peak compressive stress of 3.1 GPa, and upon delithiation, the stress became tensile with a peak stress of 0.7 GPa. A simple plane strain finite element model of Si nanotube coated with SiO₂ shell was developed to understand the mechanical response of the core-shell type microstructures under electrochemical cycling. The results reported here provide insights and quantitative understanding as to why the highly brittle SiO₂ coatings are able to sustain significant volume expansion (300%) of Si core without fracture and enhance the cyclic performance of Si reported in the literature. The basic mechanical properties presented here are necessary for future design and development of durable Si/SiO₂ core-shell structures or SiO₂-based electrodes.

CM03.15.15

In Situ Measurement of the Effect of Stress on Chemical Diffusion Coefficient of Large Volume Change Electrodes Siva P. Nadimpalli, Rajasekhar Tripurani and Subhajit Rakshit; New Jersey Inst of Technology, Newark, New Jersey, United States.

The effect of stresses on the measured chemical diffusion coefficient in battery electrodes has not been characterized previously. In this study, sputter deposited Ge films were subjected to potentiostatic intermittent titration technique (PITT) and galvanostatic intermittent technique (GITT) conditions while simultaneously measuring the stress evolution in the electrodes. It was observed that the diffusion coefficient value increased considerably with Li concentration; however, diffusion coefficient values obtained during delithiation are at least two times greater than those obtained during lithiation at any given Li concentration. This difference is attributed to the stress state, i.e., tensile stress during delithiation leads to higher D values compared to the compressive stresses during lithiation. The data and observations presented here will be helpful in developing and using electrochemomechanical models in producing optimized electrode structures.

CM03.15.16

Bismuth as Rechargeable Lithium-Ion Battery Anode—A Fundamental Study Using In Situ Synchrotron XRD and In Situ TEM Yifei Yuan¹, Wentao Yao¹, Vitaliy Yurkiv¹, Lu Ma², Tongchao Liu², Farzad Mashayek¹, Jun Lu², Khalil Amine² and Reza Shahbazian-Yassar¹; ¹University of Illinois at Chicago, Chicago, Illinois, United States; ²Argonne National Laboratory, Argonne, Illinois, United States.

Materials storing energy via alloying reaction are promising anode candidate in rechargeable lithium ion batteries due to their much higher energy density than current graphite anode. Among these materials, bismuth provides a high theoretical volumetric capacity of 3800mAh/cm³ when it alloys with Li⁺ to form Li₃Bi. Yet, its further development has been hindered by the unclear alloying mechanisms with Li⁺. In this work, we carry out real-time study of the (de)alloying kinetics of Bi nanomaterials working as a LIB anode combining both *in situ* synchrotron XRD and *in situ* TEM. *In situ* synchrotron XRD reflects the phase transition information of the ensemble of many Bi nanoparticles, while *in situ* TEM demonstrates the structural evolution of single Bi nanoparticle at both high spatial resolution and high temporal resolution. Both two methods reveal that the Li-Bi alloying is a two-step process featuring two two-phase reactions with formation of Li₃Bi as the intermediate phase. More importantly, our work reveals an energetically favorable lithiation pathway along Bi-(012) planes during the Bi-Li₃Bi phase transition process, which is further theoretically understood by DFT calculations. The fundamentals discovered in this work are expected to further guide the design of Bi-based electrode materials for battery performance enhancement in the future.

CM03.15.17

Carrier Transfer from N-Type GaN Photoanode to Island-Like NiO-Catalyst for Water Oxidation Evaluated by Photoluminescence Katsushi Fujii¹, Kayo Koike¹, Takenari Goto², Shinichiro Nakamura², Takayo Ogawa¹ and Satoshi Wada¹; ¹RIKEN, RAP, Wako, Japan; ²RIKEN, Baton Zone Program, Wako, Japan.

The island-like NiO catalyst loaded on n-type GaN single crystal photoanode works perfectly to prevent the anodic corrosion [1]. The mechanism of NiO catalyst is, however, not fully understanding. Carrier transfer from GaN photoanode to NiO catalyst is expected for the prevention. The carrier transfer direction between the GaN surface and NiO-islands was proposed from our experiments recently [2].

In this report, the in-situ and ex-situ photoluminescence (PL) was used for the evaluation of the carrier transportation. The samples were island-like NiO-loaded n-type GaN and bare n-type GaN. The 325.0 nm He-Cd laser was used as the excitation light. The light was used for both PL and photoelectrochemical water splitting for the in-situ measurements. The electrolyte was 1.0 mol/L NaOH aqueous solution.

The major PL peaks of n-type GaN at room temperature (RT) are near-band-edge luminescence (XL) and deep-yellow luminescence (YL). From the ex-situ PL results, the intensities of XL and YL were similar for both island-like NiO-loaded and bare n-type GaN when the excitation intensity was relatively high at about 1.0 W/cm². The XL intensity of island-like NiO-loaded GaN decreased more than that of the bare n-type GaN when the excitation intensity was changed to 0.9 mW/cm², whereas the YL intensities were similar for both samples. This 0.9 mW/cm² excitation intensity is close to our commonly used photoelectrochemical excitation of 100 mW/cm² Xe lamp.

During the photoelectrochemical reaction, the XL intensity of the bare n-type GaN decreased from the intensity without the reaction. The amount of XL intensity decreasing was much larger than that for YL. For the PL results of island-like NiO-loaded GaN, the XL intensity did not change and the YL intensity showed small decreasing with photoelectrochemical reaction from that without the reaction.

The in-situ intensity change from the ex-situ intensity shows that the holes of bare n-type GaN are mainly used for the XL at the process without the photoelectrochemical reaction. On the other hand, the holes in the GaN of the island-like NiO-loaded GaN moves to the island-like NiO and would be consumed at the NiO by thermal recombination even without the photoelectrochemical reaction. The holes at the NiO are probably used for the water oxidation before the thermal recombination at the photoelectrochemical reaction. This probably shows that the holes in NiO can move more smoothly from the electrode to the reactant in the electrolyte than that in the bare GaN.

[1] K. koike et al., J. Electrochem. Soc. 163 (2016) H1091.

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CM03.15.18

In Situ Optical Absorption Spectroscopy for Investigating Point Ionic Defects Concentration and Kinetics in Mixed-Ionic-Electronic-Conductor Thin Films Dmitri Kalayev¹, Clement Nicollet¹, George F. Harrington^{1,2} and Harry L. Tuller¹; ¹Massachusetts Institute of Technology, Cambridge, Massachusetts, United States; ²Kyushu University, Fukuoka, Japan.

Mixed ionic electronic conducting (MIEC) oxides are extensively used as electrodes in energy, electronics and catalysis applications. In particular, point ionic defects concentrations in MIECs bulk and surface and their kinetics properties are important parameters in the design of solid oxide fuel cell electrodes. Typically, the point ionic defects properties are measured electrically as function of oxygen partial pressure change to reveal the defect model. The electrical measurement can be disadvantageous, in some cases, if the contacts alter significantly the material properties or if the electrical conductivity dominates over the ionic one. Additionally, there is an increased interest in using MIEC thin films in electronics and catalysis applications that impose an additional challenge for characterizing them by the classical impedance spectroscopy and other electrical measurement techniques.

We demonstrate how the ions with optical absorption, occurring naturally or inserted on purpose in the MIECs, can be used for the characterization of the point ionic defects concentrations and kinetics in the oxides thin films. The examples will include praseodymium substituted ceria (PCO) and praseodymium oxide thin film. In these materials the praseodymium ions can have different valence states showing significant visible light absorption in one of the states. The praseodymium ions concentration and changes in their valence state can be measured, *in-situ*, at elevated temperatures and under a controlled oxygen partial pressure.

Applying the optical measurement technique allows, among other, to measure the oxygen vacancies ordering associated phase transition in praseodymium oxide thin film, measured previously by thermal gravimetric analysis. Finally, measuring the properties of the point ionic defects from optical absorption in heterostructures of an interchanging layers of epitaxial PCO and SrTiO₃ thin films enables to study the effect of the space charge regions widths on the ionic defects concentration and the effect of a strain, induced by a lattice mismatch between the materials, on the ionic defects kinetic properties.

SESSION CM03.16: Batteries IV

Session Chairs: Andrej Singer and Chongmin Wang

Thursday Morning, November 29, 2018

Hynes, Level 3, Room 300

8:00 AM *CM03.16.01

Electrochemical Energy Storage Beyond Lithium—Mechanisms Revealed by *In Operando* Synchrotron Studies Helmut Ehrenberg, Qiang Fu, Sonia Dsoke, Sylvio Indris, Raheleh Azmi, Michael Knapp and Vanessa Trouillet; Karlsruhe Institute of Technology, Karlsruhe, Germany.

Electrochemical energy storage beyond lithium is of high relevance for a sustainable energy technology. However, qualitatively new concepts are needed for suitable electrodes, especially in the case of the intercalation of larger monovalent ions like Na⁺ or K⁺ or multivalent ions like Mg²⁺, Ca²⁺ or Zn²⁺. One example for a promising Na-ion battery is presented based on symmetrical NASICON-structured Na₂VTi(PO₄)₃ electrodes [1]. The contribution of *in situ* synchrotron diffraction and X-ray absorption spectroscopy to unravel the underlying sodium storage mechanism and charge compensation behaviour is presented.

Model systems for multivalent-ion insertion can also include hybrid batteries with two mobile metal ions in the electrolyte, where a metal like Mg is plated at the negative electrode, while Li- or Na-ions are inserted at the positive electrode [2,3]. This presentation summarizes some recent results on the underlying working mechanisms in such hybrid batteries as revealed by *in operando* diffraction using synchrotron radiation in combination with X-ray photoelectron spectroscopy (XPS).

[1] D. Wang, et al., Nat. Commun. 8 (2017) 15888.

[2] X. Bian, et al., Mater. Chem. A, 2017, 5, 600.

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8:30 AM CM03.16.02

***In Situ* Focused Ion Beam-Scanning Electron Microscope Study of Microstructural Evolution of Single Tin Particle Anode for Li-Ion Batteries** Xinwei Zhou¹, Tianyi Li¹, Yi Cui¹, Yuzi Liu² and Likun Zhu¹; ¹Department of Mechanical and Energy Engineering, Indiana University-Purdue University Indianapolis, Indianapolis, Illinois, United States; ²Nanoscience and Technology Division, Argonne National Laboratory, Lemont, Illinois, United States.

Tin (Sn) has been considered a promising anode material for Li-ion batteries because it is non-toxic, abundant, and inexpensive and it has a theoretical specific capacity of 994 mAh/g. However, Sn electrode has large volume change during lithiation and delithiation, which causes fast capacity fading. In order to address this issue, it is necessary to understand the microstructure evolution and electrochemical performance of Sn electrode during cycling. In recent years, transmission X-ray microscopy has been used to investigate the microstructural evolution of Sn anode during cycling in *in-situ* cell setups.^[1] However, the Sn electrodes used in these *in-situ* studies were composed of Sn particles with different size and shapes. It is challenging to correlate the microstructural evolution of single Sn particle with the electrochemical performance of the whole cell. In recent years, *in situ* transmission electron microscopy (TEM) is also used to reveal the microstructural evolution and phase change of electrode materials.^[2] Although *in-situ* TEM allows real time microstructure investigation at atomic scale resolution, the *in-situ* cell rarely shows electrochemical performance of electrodes.

In this study, we developed an approach to build a single particle battery in the chamber of focused-ion beam-scanning electron microscope (FIB-SEM) to monitor the microstructural evolution of a single Sn micro-particle during cycling. The experiment was performed within a ZEISS Nvision FIB-SEM at the Center for Nanoscale Materials, Argonne National Laboratory. A tin particle was attached to the tungsten probe by carbon coating using FIB deposition as positive electrode. The lithium metal was placed on the top of SEM stage as negative electrode. One drop of ionic liquid electrolyte (ILE) was placed on the top of lithium metal. The ILE was made by dissolving the lithium salt, lithium bis (trifluoromethylsulfonyl) imide (LiTFSI), in a solvent of 1-butyl-1-methylpyrrolidinium bis (trifluoromethyl -sulfonyl) imide (P₁₄TFSI). The tungsten probe and the SEM stage were connected to a Keithley 6430 sub-femtoamp remote sourcemeter. Galvanostatic mode was used in all electrochemical cycling with a current of 300 pA. The particle was immersed in the ILE drop during cycling and lifted out for imaging at different states of charge. The particle was polished by FIB before imaging to remove ILE on the surface. Our results show the formation and evolution of cracks during lithiation, evolution of porous structure during delithiation and volume change during cycling. The electrochemical performance and the microstructural evolution of the Sn micro-particle during cycling are correlated.

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[2] Q. Li, P. Wang, Q. Feng, M. Mao, J. Liu, S. X. Mao, H. Wang, *Chemistry of Materials* **2014**, *26*, 4102-4108

8:45 AM CM03.16.03

Probing Electrochemical Phase Transformation Kinetics by *In Situ* TEM Kai He; Clemson University, Clemson, South Carolina, United States.

In situ transmission electron microscopy (TEM) as a fast-growing technique has attracted tremendous attention in diverse scientific research because it can acquire dynamic information and allow for mechanistic understanding of various physical and chemical processes and materials systems [1]. Specifically, the advancement of *in situ* TEM in chemically reactive environments has enabled the direct real-time observation of electrochemical reactions in electrode materials for lithium ion batteries [2]. Previous studies have found different types of electrochemical reactions with lithium via various mechanisms such as intercalation, alloying, and conversion, which confirmed the lithiation processes following the thermodynamic reaction pathways. In addition to that, we would like to utilize *in situ* TEM imaging and spectroscopy approaches to build direct correlations between microstructure and electrochemistry on atomic to nanoscale and reveal the kinetics of phase transformations during the electrochemical reactions.

We primarily focus on transmission metal oxides and sulfides with a large number of openings in their crystal framework, such as the spinel (Fe_3O_4) and 2D layered (CuS) structures [3, 4], to accommodate the uptake of guest Li ions. Although it is generally believed that these materials should follow the conversion reaction, we found the intermediate lithiated phases resulted from the intercalation reactions at the beginning; and more importantly, such phase transformations are sensitive to the reaction kinetics that are common in realistic battery coin cells. With further performance tests of coin-cells at various charging rates, we are able to explicitly establish the relationship that crosslinks the structure evolution, electrochemical properties, and the reaction pathways on the atomic level, and address the importance of the effects of kinetics and dimensionality on the phase transformation. Our findings provide insights into understanding phase transformation mechanisms in spinel and layered structures, and also show implications for improving performance in future design of battery electrodes.

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[3] K. He, *et al*, *Nature Commun.* **7**, 11441 (2016).
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9:00 AM CM03.16.04

Investigation of Dynamic Phase Transformation of Selenium-Doped Germanium Anode During (De)Lithiation Processes Using *In Operando* Synchrotron X-Ray Diffraction Tianyi Li^{2,1}, Yi Cui^{2,1}, Xinwei Zhou^{2,1}, Melissa Meyerson³, Alan Guo³, Charles Mullins³, Yang Ren⁴, Qi Liu⁴, Yongzhu Fu² and Likun Zhu²; ¹Department of Mechanical Engineering, Purdue University, West Lafayette, Indiana, United States; ²Department of Mechanical and Energy Engineering, Indiana University Purdue University Indianapolis, Indianapolis, Indiana, United States; ³Department of Chemical Engineering, The University of Texas at Austin, Austin, Texas, United States; ⁴Argonne National Laboratory, Argonne, Illinois, United States.

Germanium (Ge) is an attractive candidate for high-capacity Li-ion battery anode due to its high theoretical capacity of 1384 mAh/g (for the charged $\text{Li}_{15}\text{Ge}_4$ phase), low operation voltage, fast bulk Li diffusion, and high electrical conductivity. However, the major challenge in the development of Ge anode is the large volume change involved in the reaction scheme, which could result in particle fracture and electrode delamination from the current collector, thereby leading to rapid loss of specific capacity. Klavetter *et al.* recently reported that selenium (Se)-doped Ge (GeSe) forms an inactive phase that buffers the volumetric expansion of Ge which provides better cycling life and performance [1]. Therefore, it is essential to understand the mechanisms and dynamic phase transformation that occur during battery cycling processes.

The *in-operando* experiment conducted by Lim *et al.* has shown crystal $\text{Li}_{15}\text{Ge}_4$ as the final product of lithiation and amorphous Ge at the end of Delithiation [2]. However, the crystalline change of GeSe anode material is still unclear which needs further investigation. In this study, we examined and compared the dynamic phase evolution of Ge and GeSe electrodes made of micro-particles (~5 μm in diameter) via Synchrotron X-ray diffraction (XRD) at the beamline 11-ID-C of the Advanced Photon Source at the Argonne National Laboratory. To investigate the crystalline evolution of Ge and GeSe particles, a synchrotron X-ray diffraction with a wave length 0.1173 \AA was employed to obtain diffracted data of the electrodes during *in-operando* condition to monitor and quantify crystalline change of active materials. Similar to Lim's results, $\text{Li}_{15}\text{Ge}_4$ was observed as the single crystalline at the end of lithiation and no crystal Ge peak was found at the end of delithiation process for Ge. However, GeSe became amorphous at the end of the first lithiation and no crystal phase was observed thereafter. We believe that the different phase evolution is caused by the formation of a network of Li-ion superconducting and inactive Li-Ge-Se phase at the beginning of the lithiation process.

<!--[if supportFields]> ADDIN EN.REFLIST <![endif--> [1] K.C. Klavetter, J. Pedro de Souza, A. Heller, C.B. Mullins, High tap density microparticles of selenium-doped germanium as a high efficiency, stable cycling lithium-ion battery anode material, *Journal of Materials Chemistry A* **3**(11) (2015) 5829-5834.

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9:15 AM CM03.16.05

Deep Learning of Solid-State Reactions on Atomic Level Maxim Ziatdinov, Ondrej Dyck, Artem Maksov, Andrew Lupini, Stephen Jesse and Sergei V. Kalinin; Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States.

Solid-state reactions underpin virtually all aspects of materials synthesis, operation of batteries and fuel cells, as well as ionic information technology devices. However, despite extremely high significance, these processes were traditionally studied only on the macroscopic level or via scattering techniques, providing only average information. Recent advances in scanning transmission electron microscopy (STEM) allow the visualization of solid-state transformations in materials, including those induced by electron beam influence and temperature, in real time with atomic resolution. However, the existing analytical tools allow extracting only a very small (and insufficient) portion of relevant physical and chemical information from the experimental data. Here we demonstrate a deep learning framework for full data analysis of the atomic defect dynamics and evolution from dynamic STEM data and illustrate its application for STEM "movies" from graphene and WS_2 . The developed framework allows us to create a library of defects, map chemical transformation pathways at the atomic level, including detailed transition probabilities, and explore subtle distortions in local atomic environment around the defects of interest. In particular, we were able to extract parameters of diffusion for the sulfur vacancies and transition probabilities associated with switching between different configurations of defect complexes consisting of Mo dopant and sulfur vacancy in WS_2 (arXiv:1803.05381), as well as to analyze evolution of topological defects in graphene. Overall, our approach allows an unprecedented insight into the nature and mechanisms of solid-state

reactions and electron-beam-matter interactions on the atomic level.

9:30 AM BREAK

SESSION CM03.17: Battery Cathodes
Session Chairs: Andrej Singer and Chongmin Wang
Thursday Morning, November 29, 2018
Hynes, Level 3, Room 300

10:00 AM CM03.17.01

Structural Analysis of Layered Li_2RuO_3 via *Operando* X-Ray Absorption Spectroscopy and X-Ray Diffraction Kipil Lim^{1,2}, Jihyun Hong^{1,2}, William Gent¹, Peter Csernica¹, Iwnetim I. Abate^{1,2}, William Chueh¹ and Michael F. Toney²; ¹Stanford University, Stanford, California, United States; ²SLAC, Menlo Park, California, United States.

In the last decades, lithium-ion batteries (LIB) have significantly contributed to technological progress.[1] Recently, Li-excess layered materials are attracting interest since they exhibit high energy densities and capacities significantly higher than the commercially available layered NMC oxides.[2] Unlike conventional layered oxides where the only redox center is transition metal cations, an oxygen anion redox in the Li-excess layered material plays an important role to achieve high capacity.[3] Even though several research groups have suggested theories and tried to explain the mechanism of anion redox, the anion redox in the Li-excess layered material is still not fully understood.

Understanding the electronic structural evolution of the Li-excess layered oxide is the key to understand the mechanism of the anion redox. Recently, our group reported a strong coupling between the anion redox and the transition metal migration into the Li layer during cycling in the $\text{Li}_{1+x}[\text{Ni,Co,Mn}]_{1-x}\text{O}_2$ material.[4] Their simulation predicted a reshuffling of the electronic states by the migrated transition metal and the oxidized oxygen, and the hypothesis was proved by the resonant inelastic X-ray spectroscopy (RIXS) analysis which showed a distinctive feature at the oxygen K edge spectra. Therefore, understanding the precise crystal structure is important to explain RIXS feature and understand the nature of anion redox. To build upon this work, we have selected Li_2RuO_3 is a model system, due to its good electrochemistry properties and the presence of only a single transition metal. In this work, we present how different synthesis conditions dramatically impact the properties of Li_2RuO_3 . We present a combination of advanced techniques, including operando X-ray absorption spectroscopy (XAS), operando extended X-ray absorption fine structure (EXAFS), and high-resolution synchrotron X-ray diffraction to obtain a complete picture of the electronic and structural changes during cycling. This accurate structural information will be compared with the RIXS analysis to identify the mechanism of the anion redox in the Li_2RuO_3 material.

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10:15 AM CM03.17.02

Understanding Oxygen Redox Activity in Li-Rich Cathode Materials—Experimental and Theoretical Core-Level Spectroscopy Liang Li¹, Eungje Lee¹, Haifeng Li², Teak D. Boyko³, John w. Freeland¹, Tim Fister¹, Jordi Cabana², Michael M. Thackeray¹ and Maria K. Chan¹; ¹Argonne National Laboratory, Lemont, Illinois, United States; ²University of Illinois at Chicago, Chicago, Illinois, United States; ³Canadian Light Source, Saskatoon, Saskatchewan, Canada.

Using oxygen redox reactions to obtain higher capacity in Li-ion batteries (LIBs) is an intriguing route. Despite numerous experimental and theoretical attempts to unravel the electronic origin of oxygen redox behavior, whether the oxidation of oxygen occurs via the formation peroxy-like species or depletion of electrons from non-TM-bonding states is still, however, an open question. It is also unclear how the electron-depleted oxygen states manifest themselves in experimental observations. In this study, using Li-rich layered 4d/5d transition metal oxides and three dimensional cationic disordered cathodes as model systems, we performed density functional theory (DFT) and *ab-initio* molecular dynamics (AIMD) simulations to investigate the structural response of oxygen matrix to delithiation. The oxygen K-edge X-ray absorption near-edge spectra (XANES) were modeled using Bethe-Salpeter Equation (BSE) approach and compared with experiments, from which the oxygen redox mechanism is uncovered. This work demonstrates the effectiveness of combining experimental core-level spectroscopy with first-principles simulations to unambiguously identify the signature of oxygen reactivity, and has profound implications in understanding and exploiting the oxygen capacity in Li-rich LIB systems.

10:30 AM *CM03.17.03

Investigating the Nanoscale Heterogeneity of Solid Electrolyte Interphase on Amorphous Silicon from Tip Enhanced Raman Spectroscopy (TERS) Jagjit Nanda¹, Guang Yang¹, Dmitry Voylov³, Michael Naguib², Rose Ruther¹, Gabriel Veith¹ and Alexei Sokolov³; ¹Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States; ²Tulane University, New Orleans, Louisiana, United States; ³The University of Tennessee, Knoxville, Tennessee, United States.

A key challenge of using silicon as an anode in a Li-ion battery is the dynamic nature of the solid electrolyte interphase (SEI) layer that constantly breaks and reforms due to the enormous volume changes during electrochemical cycling resulting in the loss of lithium inventory. Recent literature studies report a highly heterogeneous and multiphase nature of SEI that evolves under continuous electrochemical cycling. In this work, we report Tip Enhanced Raman Spectroscopic (TERS) study of SEI on cycled amorphous silicon (a-Si) for the first time. Amorphous silicon anode (50 nm in thickness on copper current collector) was cycled in a commercial lithium-ion battery electrolyte (1M LiPF₆ in EC:DEC, 1:1 vol). TERS analysis on cycled amorphous silicon sample indicates that the nanometer scale SEI “islands” are unevenly distributed on the Si anode surface. Even for the same SEI “island”, the composition is different from point to point with inter-point distance smaller than 10 nm. In addition, the TERS spectra and mapping obtained from a-Si of differing cycle numbers suggests different SEI local compositions. The a-Si cycled for once (denoted as 1X a-Si) has rich local SEI species containing poly (ethylene oxide) (PEO) - like oligomer and lithium ethylene dicarbonate (LEDC, (CH₂OOCOLi)₂). In sharp contrast, the bulk chemical information of the SEI for 1X a-Si probed by FT-IR only indicates the existence of the Li₂CO₃. Moreover, different vibrational modes from the same species such as LEDC have differing TERS activity. This is due to different alignments of the enhanced near field vector versus the Raman scattering tensor of the given vibrational modes. The SEI on 5X a-Si is dominated by the LEDC species, although Raman bands assigned to PEO oligomer and carboxylate compounds also show up. For 20X a-Si, the dominant species in the SEI is carboxylate compounds. The bands between 1450 cm⁻¹ and 1650 cm⁻¹ which are related to the -COO stretching and C=O stretching modes were analyzed in details for the first time. Due to its excellent spectral resolution on this type of compound, as

compared to its IR counterparts, TERS is capable of probing the conformational change of the carboxylates upon their coordination to Li⁺ cations with nanoscale spatial resolution in sample plane.

Acknowledgement

This research was conducted at Oak Ridge National Laboratory, managed by UT Battelle, LLC, for the U.S. Department of Energy (DOE) under contract DE-AC05-00OR22725, is funded by Asst. Secretary Energy Efficiency and Renewable Energy (EERE) Vehicle Technologies Office (VTO).

11:00 AM *CM03.17.04

Multiscale Heterogeneity in Single Particles of Li-Ion Battery Cathodes Visualized with X-Ray Imaging Jordi Cabana; University of Illinois at Chicago, Chicago, Illinois, United States.

The existing performance limitations of Li-ion batteries can be tracked to slow transport and irreversibilities in the changes undergone by the electrode materials, often coupled with mechanical events. Tools that provide insight into the onset and propagation of these transitions are critical to identify the mechanisms of electrochemical function. This information must be generated at the level of single particles, where irreversibilities trigger degradation of the electrode architecture. Synchrotron-based X-ray microscopy currently combines high spatial resolution with a suite of possible mechanisms of chemical contrast, such as diffraction and spectroscopy. In this talk, we will discuss recent developments to image, using X-rays, electrochemical reactions in single particles of battery electrodes, with a focus on the prospects of capturing and assessing the relevance of time-resolved phenomena using *operando* measurements. These measurements avoid relaxation of components from the kinetically controlled functional state to one that is more stable under open circuit conditions. The talk will highlight the new fundamental insight generated by the tools, involving mechanisms of transformation and local dynamics of heterogeneity.

11:30 AM CM03.17.05

An *Operando* Study of Rechargeable MnO₂ Cathodes for Low Cost, High Energy Density Aqueous Batteries Joshua W. Gallaway¹, Gautam Yadav², Damon Turney² and Sanjoy Banerjee²; ¹Northeastern University, Boston, Massachusetts, United States; ²City College of New York, New York, New York, United States.

This talk will outline the complex cycling pathways of electrolytic manganese dioxide in alkaline electrolyte, as studied by *operando* characterization in "real world" electrodes of high areal capacity. The alkaline MnO₂ system is one of the safest and most inexpensive battery materials ever discovered, and is well known in primary batteries. Deeply cycling MnO₂ has the potential to provide battery storage of high safety, high energy density, low toxicity, and low cost, for applications such as intermittent renewable generation backup at the scale of the power grid. Deep cycling is defined as reduction through nearly all of the theoretical capacity from Mn^{IV} to Mn^{II}, or 617 mAh/g-MnO₂, while remaining reversible. Modification of MnO₂ by Bi is known to impart rechargeability, through a cycling pathway with the layered polymorph δ-MnO₂ as the end member.[1-3] The molecular mechanism of this effect has previously been unknown, and typically works well only in thin electrodes of low areal capacity, lessening the potential for use in applications. However, it has recently been reported that modification by both Bi and Cu imparts rechargeability even in thick electrodes, promising high impact if this chemistry is successfully developed into practical batteries.[4]

The MnO₂ proton insertion reaction involves both unit cell dilatation and multiple phase changes, which are often spatially inhomogeneous throughout the electrode.[5] We use the correlation of energy dispersive X-ray diffraction (EDXRD) to a multiscale electrochemical model to demonstrate that a phase change to MnOOH leads to spinel formation, but this reaction is suppressed with Bi. EDXRD using high energy white beam photons allows spatially-resolved diffraction to be collected in real time within batteries through the cell containment. We further demonstrate two distinct regimes of Mn(OH)₂ formation, with Bi causing a shift from amorphous to highly crystalline discharge product. These phenomena have not previously been observed through *ex situ* analysis. We further use a cell modified for X-ray transparency to follow the concentrations and redox states of Mn, Bi, and Cu spatially, in real time. This is done via *operando* X-ray fluorescence mapping (XRF) and micron-sized spot XANES (μ-XANES). All experiments were performed on electrodes with areal capacities of >20 mAh/cm². Modeling indicates that such cathodes have potential to result in high energy density aqueous, rechargeable batteries when paired with zinc anodes meeting the requirements for a collection of emerging applications, namely grid-scale electrical storage.[6]

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11:45 AM CM03.17.06

Cation Ordering and Oxygen Release in LiNi_{0.5-x}Mn_{1.5+x}O_{4-y} (LNMO)—*In Situ* Neutron Diffraction and Performance in Li-Ion Full Cells Burak Aktekin¹, William Brant¹, Mario Valvo¹, Fernando L. Marzano², Wolfgang Zipprich³, Daniel Brandell¹ and Kristina Edstrom¹; ¹Department of Chemistry – Ångström Laboratory, Uppsala University, Uppsala, Sweden; ²Scania CV AB, Södertälje, Sweden; ³Volkswagen AG, Wolfsburg, Germany.

LiNi_{0.5}Mn_{1.5}O₄ (LNMO) is a promising spinel-type positive electrode for lithium ion batteries as it operates at high voltage and possesses high power capability. However, rapid performance degradation in full cells, especially at elevated temperatures, is a problem. There has been a considerable interest in its crystal structure as this is known to affect its electrochemical performance. LNMO can adopt a *P4₃32* (cation ordered) or *Fd-3m* (cation disordered) arrangement depending on the synthesis conditions. Most of the studies in literature agree on better electrochemical performance for disordered LNMO [1], however, a clear understanding of the reason for this behaviour is still lacking. This partly arises from the fact that synthesis conditions leading to disordering also lead to oxygen deficiency, rock-salt impurities and therefore generate some Mn³⁺ [2]. Most commonly, X-ray diffraction is used to characterize these materials, however, accurate structural analysis is difficult due to the near identical scattering lengths of Mn and Ni. This is not the case for neutron diffraction. In this study, an *in-situ* neutron diffraction heating-cooling experiment was conducted on slightly Mn-rich LNMO under pure oxygen atmosphere in order to investigate relationship between disordering and oxygen deficiency. The study shows for the first time that there is no direct relationship between oxygen loss and cation disordering, as disordering starts prior to oxygen release. Our findings suggest that it is possible to obtain samples with varying degrees of ordering, yet with the same oxygen content and free from impurities. In the second part of the study, highly ordered, partially ordered and fully disordered samples have been tested in LNMO||LTO (Li₄Ti₅O₁₂) full cells at 55 °C. It is shown that differences in their performances arise only after repeated cycling, while all the samples behave similarly at the beginning of the test. The difference is believed to be related to instabilities of LNMO at higher voltages, that is, in its lower lithiation states.

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SESSION CM03.18: Batteries V
Session Chairs: Joshua Gallaway and Guang Yang
Thursday Afternoon, November 29, 2018
Hynes, Level 3, Room 300

1:30 PM *CM03.18.01

Nucleation of Dislocations and Their Dynamics in Layered Oxides Cathode Materials During Battery Charging Andrej Singer; Department of Materials Science and Engineering, Cornell University, Ithaca, New York, United States.

Lithium-rich layered oxides (LRLO) are among the leading candidates for the next generation cathode material for energy storage, delivering 50% excess capacity over commercially used compounds. Despite excellent prospects, voltage fade has prevented effective use of the excess capacity, and a major challenge has been the lack of understanding of the mechanisms underpinning the voltage fade. I will present our recent results, where using operando three-dimensional Bragg coherent diffractive imaging, we directly observe the nucleation of a mobile dislocation network in LRLO nanoparticles. The dislocations form more readily in LRLO as compared with a classical layered oxide, suggesting a link between the defects and voltage fade. We show microscopically how the formation of partial dislocations contributes to the voltage fade. The insights allow us to design and demonstrate an effective method to recover the original high voltage functionality. Our findings reveal that the voltage fade in LRLO is reversible and call for new paradigms for improved design of oxygen-redox active materials.

2:00 PM CM03.18.02

In Situ Synchrotron X-Ray Diffraction Studies on the P2- Manganese Based Sodium Layered Oxides—Structural Evolution During Cycling Elena Gonzalo¹, Wesley Dose², Neeraj Sharma⁴, Teofilo Rojo^{1,3} and Miguel Angel Muñoz-Marquez¹; ¹CIC Energigune, Miñano, Spain; ²Chemical Sciences and Engineering (CSE) Division, Argonne National Laboratory, Lemont, Illinois, United States; ³Departamento de Química Inorgánica, Universidad del País Vasco UPV/EHU, Bilbao, Spain; ⁴School of Chemistry, University of New South Wales, Sydney, New South Wales, Australia.

Na-ion battery research has been under focus lately due to its advantages in specific applications such as large scale power grid systems [1,2]. Among the candidates of cathode materials, layered oxides with the general formula: NaT_mO_2 ($T_m = \text{Cr, Mn, Fe, Co, Ni, etc.}$) exhibit one of the largest theoretical capacities along with simple crystal structures.[3,4]

Co- and Ni- free P2-manganese based systems possesses excellent cathode characteristics for Na-ion batteries due to combination of environmentally benign, economically favorable transition metals and high capacity, although some issues such as the Jahn-Teller distortion effect, ascribed to Mn^{3+} , has to be taken into account.[5] The importance of considering this issue has been widely studied by our group,[6,7] as well as mitigation strategies – such as doping with electrochemically active (Fe)[8] and inactive elements (Ti).[9]

Here we report the in situ synchrotron X-Ray diffraction study we have carried out to shed light on the relationship between electrochemical performance and structural evolution of different P2- $\text{Na}_{2/3}\text{Mn}_{1-x}\text{Fe}_x\text{O}_2$ phases ($0.1 \leq x \leq 0.67$) upon cycling. Lattice parameter evolution, phase fractions and sodium content in the crystal structure as a function of the charge/discharge process and at different current rates will be shown. The effect of dopants such as Ti and the mitigation of structural changes during cycling will be examined in detail.

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2:15 PM CM03.18.03

In Operando Tracking Ion Intercalation into 2D MXenes in Aqueous Electrolytes Qiang Gao¹, Xin Li¹, Weiwei Sun¹, Michael Naguib³, Stephen Jesse¹, Paul Kent^{1,2}, Arthur P. Baddorf¹ and Nina Balke¹; ¹Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States; ²Computer Science and Mathematics Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States; ³Department of Physics & Engineering Physics, Tulane University, New Orleans, Louisiana, United States.

Supercapacitors have drawn considerable attention for a variety of applications in portable electronics, grid and transportation systems due to their rapid power delivery and an almost unlimited cycle life. To enhance the energy stored, the intensive efforts have been devoted to exploring new electrode materials, new electrolytes, and novel cell configurations. In search for new electrode materials, two dimensional (2D) transition metal carbides-MXenes, are of particular interest owing to their excellent electrical conductivity and high volumetric capacitance^{[1][2]}. The mechanism for high capacitance was essentially described as intercalation pseudo-capacitance arising from redox reactions of the Ti atoms. Similar to graphite or other electrode materials, MXene electrodes also show a significant change in volume when ions are intercalated. This electro-chemo-mechanical coupling can be used to get unprecedented insight into ion intercalation pathways with lateral resolution of 10's of nm using Scanning Probe Microscopy (SPM) techniques. In this communication, we introduce contact resonance SPM which allows to extract mechanical properties and its changes under electrochemical control when ions are intercalated into MXene^{[3][4]}. Therefore, it is of great importance to explore the different intercalation contributions with varying aqueous cations to the mechanical properties variations of material itself, which is required to evaluate the electrochemical long-term stability of electrode materials. Of special interest to boost energy storage is the intercalation of multivalent ions which suffers from sluggish intercalation and transport kinetics due to its ion size. By combining electrochemical dilatometry and contact resonance atomic force microscopy, the synergetic effects of smaller ion size cation and larger

ion size cation are demonstrated to improve charge storage to maximize the utilization of electrode volume, as well as tune mechanical and actuation properties of Ti_3C_2 MXene^{[4][5]}. Our results have important implications for quantitatively understanding the charge storage processes in intercalation compounds and provide a new path for studying the mechanical evolution of a variety of electrochemical energy storage materials. The experiments and sample preparation in this work were supported as part of the Fluid Interface Reactions, Structures and Transport (FIRST) Center, an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences. The facilities to perform the experiments were provided by the Center for Nanophase Materials Sciences, which is a DOE Office of Science User Facility.

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2:30 PM *CM03.18.04

***In Situ* and *Ex Situ* Electron Microscopy and Spectroscopy Diagnosis Guided Designing of Electrode Materials for Better Battery** Chongmin N. Wang; Pacific Northwest National Laboratory, Richland, Washington, United States.

In-situ diagnosis appears to be one of the essential methods for gaining insights as how an electrode material failure, therefore feeding back for designing and creating new materials with enhanced performances. In this presentation, I will highlight recent progress on ex-situ, in-situ and operando S/TEM for probing into the structural and chemical evolution of energy storage materials. Both ex-situ and in-situ high resolution imaging enables direct observation of structural evolution, phase transformation and their correlation with mass and charge transport, providing insights as how active materials failure during the cyclic charge and discharge of a battery. In particular, I will broadly cover the frontier of the current understanding of the interfacial process in an electrochemical cell. In perspective, my presentation will target to stimulate this field of research to re-check what has been understood and what need to be done to tackle the technical challenges facing the application of the layer structured cathode and high capacity silicon based anode.

3:00 PM BREAK

SESSION CM03.19: Mechanics of Battery Materials
Session Chairs: Joshua Gallaway and Guang Yang
Thursday Afternoon, November 29, 2018
Hynes, Level 3, Room 300

3:30 PM CM03.19.01

***In Situ* Mechanical Characterization for Understanding the Coupled Electrochemical-Mechanical Behavior of Battery Electrode Materials** Yang-Tse Cheng; Chemical and Materials Engineering, University of Kentucky, Lexington, Kentucky, United States.

With an increasing demand for higher energy and power density of lithium ion batteries (LIBs), the coupled electrochemical-mechanical degradation of electrode materials becomes a more pressing problem. In particular, fracture and delamination of electrodes can occur during repeated charging and discharging of LIBs. An improved understanding of the mechanical behavior of electrode materials, which often evolves with the state-of-charge and cycle number, is therefore necessary for improving the performance and durability of the next generation LIBs. In this presentation, we will provide an overview of our recent work on using three complementary measurement techniques: (1) *in situ* electrochemical nanoindentation,¹ (2) peel adhesion and cohesion test,² and (3) electrode curvature measurement^{3,4} to help understand several coupled effects between mechanical and electrochemical behavior of materials on the performance and durability of high capacity electrodes. Examples include Si/polymer binder porous composite electrodes, lithium metal electrodes, and inorganic/polymer composite solid-electrolytes. The suite of complementary *in situ* mechanical characterization techniques can also be used to investigate mechanical behavior of a wide range of electrochemical energy storage materials under realistic working conditions.

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3:45 PM CM03.19.02

Real-Time Measurement of Phase Transformation in Electrode Materials by Integrating *In Situ* Picosecond Ultrasonics with Atomic Force Microscopy Shaghayegh Rezazadeh Kalehbasti, LiWei Liu, Humphrey Maris and Pradeep R. Guduru; Brown University, Providence, Rhode Island, United States.

Advances in mobile electronics, electric vehicles, and grid energy storage require the next generation of Lithium ion batteries (LIB) with higher energy capacity. Many of the LIB electrode materials go through phase transformation during lithiation/delithiation. Understanding the thermodynamics, mechanics, and kinetics of the phase transformation plays a critical role in modeling their performances. This study is focused on in situ measurement of the kinetics of phase transformation in silicon as an example of a high energy density electrode material. By integrating Picosecond Ultrasonics technique with an electrochemical setup, we have successfully monitored the position of the phase front at various stages of lithiation at a resolution of few nanometers and measured the velocity of the phase boundary propagation under well controlled electrochemical conditions while maintaining the simple geometry of a silicon wafer. Further examination of the volume expansion during lithiation of crystalline silicon and the growth rate of the lithiated layer is done by combining the experimental data with in situ AFM measurements. Our technique allows measurement of micron-scale thicknesses without sacrificing the resolution. A Deal-Grove type model is adopted to study the reaction rate at the interface. The extracted kinetic parameters are of significant importance in simulating the phase transformation behavior of more complicated structures such as silicon particles.

4:00 PM CM03.19.03

Probing Stress and Microstructural Evolutions of Silicon Nanowire Anodes for Next Generation Li-Ion Battery Using *In Situ* Synchrotron X-Ray Submicron Diffraction Arief S. Budiman¹ and Nobumichi Tamura²; ¹Singapore University of Technology & Design, Singapore, Singapore; ²Advanced Light Source (ALS), Berkeley Lab, Berkeley, California, United States.

Silicon is considered as a promising anode material for the next generation lithium-ion battery due to its high capacity at nanoscale. However, silicon expands up to 300% during lithiation, which induces high stresses and leads to fractures. To design silicon nanostructures that could minimize fracture, it is important to understand and characterize stress states in the silicon nanostructures during lithiation. Synchrotron X-ray microdiffraction has proven to be effective in revealing insights of mechanical stress and other mechanics considerations in small-scale crystalline structures used in many important technological applications, such as microelectronics, nanotechnology and energy systems. In the present study, an *in situ* synchrotron X-ray microdiffraction experiment was conducted to elucidate the mechanical stress states during the first electrochemical cycle of lithiation in single-crystalline silicon nanowires (SiNWs) in a lithium-ion battery test cell. Morphological changes in the SiNWs at different levels of lithiation were also studied using scanning electron microscope (SEM). It was found from SEM observation, that lithiation commenced predominantly at the top-surface of SiNWs followed by further progression towards the bottom of the SiNWs gradually. The hydrostatic stress of the crystalline core of the SiNWs at different levels of electrochemical lithiation was determined using the *in situ* synchrotron X-ray microdiffraction technique. We found that the crystalline core of the SiNWs became highly compressive (up to ~ -325.5 MPa) once lithiation started. This finding helps unravel insights about mechanical stress states in the SiNWs during the electrochemical lithiation, which could potentially pave the path towards the fracture-free design of silicon nanostructure anode materials in the next generation lithium-ion battery. The *in situ* synchrotron X-ray submicron diffraction methodology as a probe of stress and thus reliability of the novel silicon nanowire anode *in Li-ion* battery described is also novel and could lead to enable next generation, more robust Li-ion battery technology and thus enable next generation applied energy technologies for the world.

4:15 PM CM03.19.04

***In Situ* Measurement of Plane Strain Modulus of the Solid Electrolyte Interphase (SEI) on Lithium Metal Anodes in Ionic Liquid Electrolytes** Insun Yoon and Pradeep R. Guduru; Brown University, Providence, Rhode Island, United States.

Lithium metal anode can serve as a host-free electrode, and thus has the highest theoretical capacity compared to traditional graphite-based electrodes as well as advanced lithium-alloying anodes. The major challenge with the lithium anode is highly dendritic deposition, resulting in 'mossy' electrode and internal short-circuits. A part of underlying failure mechanisms is attributed to mechanical degradation of solid electrolyte interphase (SEI). Recent theoretical and experimental studies suggest that surface films with high elastic modulus and mechanical stability may mechanically suppress the dendrite formation. Stable lithium plating/stripping with ionic liquid (IL) electrolytes, which are known to form inorganic SEI supports the suggestion. This background motivates to develop an experimental platform to measure elastic moduli of SEI formed with various electrolytes. However, most previous experimental approaches are limited to the atomic force microscopy (AFM) indentation. The approach has several sources of uncertainties such as substrate influence and inaccurate contact area due to low thickness and roughness of SEI. As a result, reported elastic modulus of SEI has several orders of magnitude variation.

In this work, we use strain induced elastic buckling instability for mechanical measurement (SIEBIMM) approach to measure the plane strain elastic modulus of SEI formed with IL electrolytes. SEI layers (80 ~ 200nm) on polydimethylsiloxane (PDMS) substrates are prepared by letting thermally evaporated lithium thin films react with IL electrolytes. The formation of SEI result in large enough compressive residual stress induce elastic buckling. *In situ* AFM measures the thickness of SEI and the characteristic wavelength of the buckling topography to extract the plane strain modulus. The distinguishing feature of this approach is the formation of SEI on an extremely compliant substrate without any current collector or residual lithium which eliminates several sources of uncertainties associated with conventional approaches.

4:30 PM CM03.19.05

Controlled Investigations of Chemo-Mechanical Degradation of the Solid Electrolyte Interphase on Silicon Electrodes Wei Zhang, Ravi Kumar, Kai Guo, Huajian Gao and Brian W. Sheldon; School of Engineering, Brown University, Providence, Rhode Island, United States.

Silicon is a promising electrode material because its full storage capacity is an order of magnitude larger than the graphite materials that are used in most rechargeable lithium-ion batteries (LIBs). However, this high capacity is accompanied by an extremely large volume change (>300%) which leads to a number of problems. In particular, mechanical degradation of the solid electrolyte interphase (SEI) is widely recognized as a major cause of short cycle life in Si-containing LIBs. To directly investigate the relationship between capacity loss and the mechanical strain in the SEI, we developed a novel method based on patterned silicon thin films that consist of isolated small islands (10-40 μm in diameter). This configuration makes it possible to apply controlled in-plane strains to SEI films that form on top of the Si. Electrochemical data from patterned Si islands with different sizes were compared to continuous Si thin films. Based on detailed analyses of these results, the strain-induced SEI losses were determined as a function of the state of charge of the electrodes. This leads directly to maps of irreversible capacity evolution as a function of strain in the SEI. These results were further supported with *in situ* AFM and electron microscopy, and more detailed solid mechanics modeling. This approach was then employed to investigate the impact of FEC additions to the electrolyte, and surface films created with atomic layer deposition.

4:45 PM CM03.19.06

Stress Evolution in the Solid Electrolyte Interphase and Its Impact on the Performance of Lithium Metal Batteries Jung Hwi Cho¹, Xingcheng Xiao² and Brian W. Sheldon¹; ¹Brown University, Providence, Rhode Island, United States; ²Global R&D Center, General Motors, Warren, Michigan, United States.

The potential advantages of lithium (Li) metal anodes have been widely touted (lowest reduction potential, etc). However, the poor stability of Li metal / liquid electrolyte interfaces leads to chronic problems, such dendrite formation and capacity loss. The possible impact of mechanical effects on interface stability and dendrite formation are difficult to probe directly. In this study, stress evolution during lithium plating and stripping was monitored with precise *in-situ* measurements. The data obtained with different film thicknesses made it possible to separate the stresses associated with the lithium metal and the solid electrolyte interphase (SEI). Ex-situ morphological characterization also provided additional information. The results show that significant stresses are created in the SEI films. A basic model of the experiments provides further understanding of the stress contribution from the SEI. An analysis of the relationship between stress in the SEI and morphological stability is also presented.

8:00 AM CM03.20.01

Mechanistic Insights into the Promotional Effect of Ni Doping on Mo and W Carbide Systems @NPGC for Highly Enhanced Overall Water Splitting Soumyabrata Roy^{1,2}, Debabrata Bagchi^{1,2}, Saurav C. Sarma^{1,2} and Sebastian C. Peter^{1,2}; ¹New Chemistry Unit, Jawaharlal Nehru Centre For Advanced Scientific Research (JNCASR), Bangalore, India; ²School of Advanced Materials (SAMat), Jawaharlal Nehru Centre for Advanced Scientific Research, Bangalore, India.

Hydrogen is steadily emerging as the next generation fuel owing to its high gravimetric energy density (143 kJ kg⁻¹) and environmentally benign nature. The electrocatalytic process of H₂ generation involves various mechanistic steps at the catalyst surface (adsorption, desorption, spilling and electron transfer) which govern a catalyst's activity. Transition metal (Mo, W) carbide systems are well known for electrocatalytic hydrogen evolution reaction (HER) due to their optimum proton adsorption energy (del G_{Hads}) and good electrocatalytic stability. However, there is still huge scope for improving the activities of carbide systems in terms of electrical conductivity, current densities and onset potentials for HER. We have adopted a one-step in-situ synthetic method to form Ni-doped WC and MoC nano-systems dispersed on nitrogen and phosphorus doped graphitic carbon (NPGC). The catalysts, both Ni-doped WC and MoC, have shown multi-fold improvement in activity both in terms of current densities and onset values than the undoped ones. While the NPGC enhances the electrical conductivity of the catalyst, Ni, as evident from theoretical calculations, optimises the d-band centre and free energy for proton adsorption to yield high activities. Three different percentages of Ni (5:1, 5:2 and 5:3-W/Mo: Ni precursor ratio) were doped to study the promotional effect of Ni doping. Interestingly, the doping percentage and the primary carbide phase was modulated by the extent of milling of the precursors, owing to the differential Ni-diffusion into the carbide lattice. The best electrocatalytic HER activity was observed in the non-ball milled Ni-doped MoC sample (MoC-Ni(5:1)_NBM) with an onset overpotential of 120 mV and a current density of 130 mA/cm² at -370 mV (v RHE), stable up to 10000 cycles. However, the WC-Ni(5:1)_BM sample showed the best activity among WC samples with a similar onset but a lesser current density of 90 mA/cm². The electronic interactions of Ni with the metal carbide motifs and the nature of the graphitic carbon were studied through XAFS, XPS and Raman studies. Both samples showed enhanced OER activity in alkaline medium with good onset values of about 1.5 V (v RHE) and current densities as high as 150 mA/cm² at 1.86 V with good stability. Thus their activity as overall water splitting catalysts triggered us to fine tune the electrolytic pH for both HER and OER activities to construct a H₂O electrolyzer with a minimum E_{cell} using them as bifunctional catalysts. The activities of the best MoC and WC catalysts are comparable to commercial Pt/C for HER and better than IrO₂ in case of OER. The electronic and structural roles of Ni in enhancing the catalytic activity has been studied through DFT calculations, XPS and in-situ quick EXAFS studies. These studies elucidate, in real time picture, how the adsorption energies of intermediates and reaction kinetics are modulated at different catalytic sites with the promotional effect of Ni doping.

8:15 AM CM03.20.02

Spectroscopic Observation of an Electrochemically Inert CO Sub-Population on Cu Electrodes Under CO Reduction Conditions in Alkaline pH Charuni M. Gunathunge¹, Vincent Ovalle¹, Yawei Li², Michael Janik² and Matthias Waegele¹; ¹Chemistry, Boston College, Chestnut Hill, Massachusetts, United States; ²Chemical Engineering, The Pennsylvania State University, University Park, Pennsylvania, United States.

Copper is the only pure metal capable of reducing carbon dioxide to hydrocarbons at significant rates in an aqueous electrochemical environment. Therefore, it is a prototypical catalyst for the electroreduction of carbon dioxide to various economically valuable hydrocarbons, such as methane and ethylene. Surface-adsorbed CO has been identified as a common on-pathway intermediate to hydrocarbons and its reduction corresponds to the potential-determining step of the overall process. While CO can adsorb on different adsorption sites (e.g. top or bridge) on the Cu surface, in situ spectroscopy of the copper/electrolyte interface has mostly been focused on atop-bound CO. Herein, we employ a combination of interface-selective infrared (IR) and Raman spectroscopies and DFT calculations to study the reactivity and surface dynamics of atop- and bridge-bonded CO on Cu electrodes. We show for the first time that (1) a fraction of the atop-bound CO population shifts to bridge sites when the total surface coverage is lowered below the saturation coverage (2) in contrast to atop-bound CO, bridge-bonded CO is electrochemically stable against reduction at a potential of -1.75 V vs. SHE. Our DFT calculations further reveal an unfavorable effect of the interfacial electric field on the activation barrier for the reduction of bridge-bonded CO as the underlying mechanism of the observed reactivity. In systematic pH studies, we further identify a pH-induced reconstruction of the Cu surface under operating conditions as the likely origin of the conversion of CO from atop- to bridge-sites. We will further discuss the implications associated with the co-existence of the two distinct CO populations on the electroreduction of atop-bound CO.

8:30 AM *CM03.20.03

Operando XAFS Measurements of Water Splitting Photocatalysts Takashi Hisatomi² and Kazunari Domen^{1,2}; ¹University of Tokyo, Tokyo, Japan; ²Center for Energy & Environmental Science, Shinshu University, Nagano-shi, Japan.

Water splitting using semiconductor photocatalysts has attracted much attention as a means of renewable hydrogen production on a large scale [1]. When a particulate semiconductor photocatalyst absorbs a photon, an electron is excited from the valence band to the conduction band, and a positive hole is left in the valence band. These excited electrons and holes can drive reduction and oxidation reactions on each photocatalyst particle, respectively. To drive the water splitting reaction efficiently, it is necessary to load nanoparticulate metals and metal oxides, denoted as cocatalysts, on the photocatalyst as active sites for the hydrogen evolution reaction and the oxygen evolution reaction. Otherwise photoexcited electrons and holes just recombine without contributing to the reaction. It is also important to suppress backward reactions such as formation of water from product hydrogen and oxygen and the oxygen reduction reaction. The authors' group has developed rhodium chromium oxide (RhCrO_x) and core/shell structured Rh/Cr₂O₃ as cocatalyst effective for the overall water splitting reaction [2-5] and has revealed the structure and working mechanism.

Al-doped SrTiO₃ (SrTiO₃:Al) loaded with a rhodium chromium oxide (RhCrO_x) as a cocatalyst (RhCrO_x/SrTiO₃:Al) decomposes water into hydrogen and oxygen with an apparent quantum yield of 56% at 365 nm [6]. The activity of the photocatalyst starts to decrease in 10 h when the reaction is conducted at an atmospheric pressure; however, co-loading of cobalt oxide species (CoO_x) drastically improves the durability. It is suspected that CoO_x species serves as an oxygen evolution cocatalyst and extracts holes from the photocatalyst to prevent oxidative dissolution of the Cr component in the RhCrO_x cocatalyst. In order to discuss the function of the cocatalyst species, the X-ray absorption fine structure (XAFS) of RhCrO_x and CoO_x species loaded onto SrTiO₃:Al were investigated operando, i.e., in water under UV light irradiation.

In this talk, recent progress and understanding of the structures, chemical states, and functionality of the cocatalysts are to be discussed

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9:00 AM CM03.20.04

Visualizing Electrochemical Reactions at the Nanoscale by *In Situ* TEM Huolin L. Xin, M. Ge and Yong Chu; Brookhaven National Laboratory, Upton, New York, United States.

Over the past five years, we have witnessed a rapid growth in liquid and gas flow holders for TEM and X-ray microscopes. These holders have enabled direct imaging of material transformations in liquid and gaseous environments with submicron-scale to atomic-scale spatial resolution. In particular, research regarding electrode materials in lithium ion batteries and nanocatalysts in heterogeneous catalysis has greatly benefited from the emergence of these capabilities. Despite their initial success in in-situ battery studies, similar class of problems in electrocatalysis has been rarely addressed using existing liquid electrochemical holders. In this talk, I will showcase the capability of direct nanoscale visualization of electrochemical formation and degradation of electrocatalysts utilizing an operando TEM liquid holder and I will also discuss existing challenges that the in-situ EM field need to address.

The research used resources of the National Synchrotron Light Source II and the Center for Functional Nanomaterials, a U.S. Department of Energy (DOE) Office of Science User Facility operated for the DOE Office of Science by Brookhaven National Laboratory under Contract No. DE-SC0012704. The electron microscopy experiment was performed at the Center for Functional Nanomaterials. This research is also partially supported by Laboratory Directed Research and Development (LDRD15-037) program at the Brookhaven National Laboratory.

9:15 AM CM03.20.05

Uncovering Biaxial Strain Effect on Kinetics of Metal Nanoparticle Catalyst Exsolution on Thin-Film Perovskite Oxides Jiayue Wang¹, Alexander K. Opitz^{1,2}, Roland Bliem¹, Xiahui Yao¹, Guln Vardar¹, Dongha Kim¹, Iradwikanari Waluyo³, Adrian Hunt³, Ethan J. Crumlin⁴ and Bilge Yildiz¹; ¹Massachusetts Institute of Technology, Cambridge, Massachusetts, United States; ²Institute of Chemical Technologies and Analytics, Vienna, Austria; ³Brookhaven National Lab, Upton, New York, United States; ⁴Lawrence Berkeley National Laboratory, Berkeley, California, United States.

Environment-friendly approaches are being advanced to synthesize carbon-neutral fuels. Some of these technologies rely on catalytically highly active nanoparticles that are supported on oxides. These nanostructured catalysts exhibit enhanced activity towards desired reactions due to their high specific area, and thus, increase the efficiency of the respective system. A recent advance in such catalyst design is to exsolve catalytic metal nanoparticles at the surface of a supporting oxide. Unlike traditional deposition 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 deposited ones. In addition, the exsolved particles also open up the possibility of regeneration of catalysts.

While being an exciting and promising pathway for high-performance oxide-metal composite catalysts, the approach towards exsolution has thus far been an empirical one, without a clear understanding and control of the underlying mechanisms to optimize catalyst composition, size and dispersion. Studies in the literature indicate that the exsolution products depend on both the surface chemistry (i.e. stoichiometry and composition) and bulk chemistry (i.e. composition and extended defects) of the parent oxide. However, it remains unclear how these parameters affect the exsolution process.

In this work, we aim to uncover how biaxial strain affects the exsolution process. Our hypothesis is that elastic strain in thin films can alter the reducibility (oxygen stoichiometry) and surface composition, and thereby affect the metal exsolution process. We quantified the strain effect on the materials' reducibility and on surface cation composition. $\text{La}_{0.6}\text{Sr}_{0.4}\text{FeO}_{3.8}$ (LSF64) thin films are employed as model systems due to the well-studied defect chemistry of LSF64, and the possibility to exsolve metallic Fe on the surface without decomposing the perovskite lattice. Biaxial strain is introduced by growing LSF64 thin films epitaxially on substrates with different lattice constants. *In-situ* ambient pressure X-ray spectroscopy is employed to probe defect chemistry, surface composition, and exsolution rate on LSF64 thin-film samples at different temperatures. Coupling surface chemistry with morphological information from atomic force microscopy, we found that in-plane biaxial strain can be a powerful tool in optimizing both the onset temperature of exsolution as well as the particle dispersion of the exsolution products. The observed strain dependence of exsolution advances our abilities to control them and enhance the performance of catalysts for clean energy technologies.

9:30 AM BREAK

SESSION CM03.21: Fuel Cells and Oxides
Session Chairs: Matthew McDowell and Mehdi Mehdi
Friday Morning, November 30, 2018
Hynes, Level 3, Room 300

10:00 AM CM03.21.01

***In Situ* Evidence of a Segregation Driven Metal-Insulator Transition at the Surface of an Epitaxial Semiconducting Manganite Thin Film** Arthur P. Baddorf, Rama K. Vasudevan, Hemant Dixit, Alexander Tselev, Valentino Cooper, Panchapakesan Ganesh and Sergei V. Kalinin; Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States.

We have established the ability to alter the conductivity and magnetism of $\text{La}_{5/8}\text{Ca}_{3/8}\text{MnO}_3$ film surfaces by tuning the degree of Ca segregation and the termination, which determine the Jahn-Teller distortion. This is of interest since doped manganese oxides (manganites) exhibit a rich response to an electric field, mixing electron and ionic transport and resulting in structural or electronic phase transitions. Manganites are consequently intriguing components in electrocatalysts, memristors, sensors, and solid oxide fuel cells. Interfaces, which play a key role in applications, introduce strain, off-stoichiometry, surface cation segregation, changes to octahedral rotations and Jahn-Teller coupling which open opportunities to tailor properties.

We have grown $\text{La}_{5/8}\text{Ca}_{3/8}\text{MnO}_3$ films by pulsed laser deposition and examined the surface structure, composition, and metallicity with in-situ studies using scanning tunneling microscopy and spectroscopy (STM/S), x-ray photoelectron spectroscopy, and first principles computation. Background oxygen pressure during growth has a strong effect on surface structural and electronic features. Deposition at 20 mTorr O_2 leads to a predominantly B-site (MnO_2) terminated surface with less A-site (La,Ca)O termination. Increasing the O_2 pressure modestly to 50 mTorr produces mixed termination and atomically imperfect surfaces. Both growth modes result in excess Ca at the surface, with greater segregation at higher growth pressures.

STM images show that B-site surfaces have bulk surface structure, whereas A-site terminations are reconstructed. STS demonstrates that both surfaces are metallic (gapless) even though the film bulk remains semiconducting. Density functional theory (DFT) provides understanding of how two experimentally

observed structural conditions lead to metallicity. First, computation reveals that the bulk ferromagnetic (FM) ordering is replaced by antiferromagnetic (AFM) ordering with increasing Ca concentration in the top layer and is more stable for 50% Ca as observed in experiments due to segregation. Second, DFT finds that $(\sqrt{2}\times\sqrt{2})R45^\circ$ reconstructed surfaces, where half of apical oxygen are present, are insulating with a band gap of ~ 0.8 eV. This apical oxygen increases the electron-phonon coupling, specifically a Jahn-Teller distortion, leading to insulating behavior. This information can enable better control over of manganite interfaces in a number of applications.

Research was sponsored the US Department of Energy, Office of Science, Basic Energy Sciences, Materials Sciences and Engineering Division and the Office of Science Early Career Research Program. Research was conducted at the Center for Nanophase Materials Sciences, which is a DOE Office of Science User Facility.

10:15 AM CM03.21.02

***In Situ* Negative Cs HRTEM Imaging of Topotactic Phase Transformation from Perovskite SrFeO₃ to Brownmillerite SrFeO_{2.5}** Yaolong Xing¹, Kyeong Tae Kang², Zhen Wang¹, Bumsu Park¹, Jinsol Seo¹, Jong Chan Kim³, Hu Young Jeong³, Woo Seok Choi² and Sang Ho Oh¹; ¹Department of Energy Science, Sungkyunkwan University, Suwon, Korea (the Republic of); ²Department of Physics, Sungkyunkwan University, Suwon, Korea (the Republic of); ³School of Materials Science and Engineering, Ulsan National Institute of Science and Technology, Ulsan, Korea (the Republic of).

SrFeO₃, a candidate oxide electrode for solid oxide fuel cell, undergoes topotactic phase transition reversibly to SrFeO_{2.5} at relatively low temperatures compared to other known similar class of materials due to the small difference in Gibbs free energy between the two phases. The phase transition is referred to as topotactic as the cation sublattice remains almost unchanged while oxygen ions (or vacancies) diffuses through the lattice along the specific crystallographic channels to modify the local coordination and valence states of cations. Previously X-ray diffraction and sequential STEM HAADF imaging have been used to characterize the phase transition of this type of materials. However, neither of these methods can directly observe the channeling of oxygen vacancies, which is extremely difficult due to the low scattering power of oxygen atoms. Here, we report *in situ* high resolution transmission electron microscopy observation of the phase transition of a 30 nm-thick SrFeO₃ epitaxial thin film to SrFeO_{2.5} brownmillerite phase at elevated temperatures in a Cs-corrected TEM (Grand ARM300F) operated at 300 kV. The TEM lamellas were prepared by focused ion beam milling and attached on the Si MEMS chip for heating using a DENSolutions Wildfire TEM holder. By using negative spherical aberration imaging (NCSI) technique, we successfully imaged all types of atomic columns in SrFeO₃ over a quite large area, which makes it possible to observe the oxygen vacancy channeling and formation and growth of SrFeO_{2.5} brownmillerite phase during heating. Although real-time NCSI HRTEM movies clearly resolve the oxygen columns, it is still difficult to measure local concentration of oxygen vacancy and sublattice change by looking at dynamically varying oxygen intensity, because of the topotactic phase transformation. We have applied several analysis methods to quantitatively measure the intensity of oxygen columns and cation sublattice to visualize local dynamic motion of transition process. Besides, the inverse Fourier filtered image formed by selecting the reflections from brownmillerite phase visualizes the dynamic motion of phase distribution. It was observed that brownmillerite SrFeO_{2.5} phase forms and grows from many different locations simultaneously, resulting in the formation of anti-phase boundaries at junctions.

10:30 AM CM03.21.03

Dynamic Control and *In Situ* Measurements of Oxygen Nonstoichiometry and Phase of Layered Cuprate-Based Thin Films by Electrochemical Pumping Chang Sub Kim and Harry L. Tuller; Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

Three major criteria are essential for a good solid oxide fuel cell (SOFC) electrode: 1) mixed ionic and electronic conductivity, 2) electrocatalytic activity towards oxygen surface exchange reaction, and 3) chemical and chemo-mechanical stability. Conventional method of assessing these electro-chemo-mechanical properties requires doping different concentrations of aliovalent cations and/or controlling atmosphere. These, however, are constrained by solubility limits of dopants, the range of oxygen partial pressures readily experimentally achievable, and require knowledge of the applicable defect chemical model. In this study, we control and measure oxygen defect types, concentrations, and phases in promising rare earth cuprate (RE₂CuO₄; RE = rare earth) SOFC cathode materials by electrochemical pumping of oxygen through an yttria-stabilized zirconia supporting electrolyte. These layered perovskites can incorporate both oxygen interstitials and vacancies, as well as two different crystal structures – T and T' – depending on the Cu-O coordination, thereby broadening the range of investigations. Oxygen nonstoichiometry values and crystal structures are determined by *in-situ* measurement of chemical capacitance and x-ray diffraction, respectively, and are correlated with surface kinetics, in-plane conductivities, ionic diffusivities, and chemo-mechanical properties.

10:45 AM CM03.21.04

***In Situ* Probing Effects of Phase Transition and Lattice Ordering on Surface Exchange Properties** Yi-Lin Huang and Eric D. Wachsman; University of Maryland, College Park, Maryland, United States.

The performance and efficiency of high-temperature electrochemical conversion devices such as solid oxide fuel cells (SOFCs) and solid oxide electrolysis cells (SOECs) are strongly determined by the activity of electrocatalysts. However, due to the multiple reaction steps of the oxygen exchange process and the complex surface chemistry at high temperature, it is challenging to isolate the role of a single factor, such as ionic conductivity (σ_{ion}) and crystal structure, on the overall oxygen reduction reaction (ORR) and oxygen evolution reaction (OER). Here we utilized the polymorphic and anion ordering nature in bismuth oxide and doped bismuth oxide to correlate surface exchange properties with the structure as well as ionic conductivity using *in situ* gas phase isotopic oxygen exchange (GPIE) and electrochemical impedance spectroscopy (EIS). Bismuth oxide has multiple crystallographic polymorphs at different temperature regimes, affecting its ionic conductivity over orders of magnitude. The relationship between diffusion coefficient (D) and surface exchange coefficient (k) of different bismuth oxide phases is explored and possible rate-limiting steps are proposed. In addition, once anion ordering in doped bismuth oxides occurs, its ionic conductivity changes orders of magnitude without changing its crystal structure, chemical composition, and microstructure. This intrinsic change provides a unique opportunity to isolate the effect of σ_{ion} on the overall surface exchange properties. The role of the ionic conductivity conducting phase in the composite will also be discussed.

11:00 AM CM03.21.05

Optical Characterization of Chemical Expansion of PCO Thin Films for High-Temperature Applications Hendrik Wulfmeier¹, Silja Schmidtchen¹, Holger Fritze¹, Thomas Defferriere² and Harry L. Tuller²; ¹Institute of Energy Research and Physical Technologies, Clausthal University of Technology, Goslar, Germany; ²Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

High-temperature (HT) actuators for operating temperatures above 500 °C are needed to achieve process control in HT systems such as microreactors. A promising novel approach for achieving HT actuation is based on nonstoichiometric oxides that exhibit large values of chemical expansion resulting from exchange of oxygen between the material and its environment [1].

Praseodymium doped cerium dioxide Pr_xCe_{1-x}O_{2-δ} (PCO) shows the ability to reversibly release and take up substantial amounts of oxygen, even in the high oxygen partial pressure regime (ambient air down to about $p_{\text{O}_2} \approx 10^{-6}$ bar). While strain values of the order of 1 percent are achievable via chemical expansion and contraction, this results in dimensional changes of only on the order of 1-10 nm depending on the thickness of the PCO films. Such levels of chemical expansion are, however, sufficiently large to observe by optical means [2].

To achieve reasonable signal to noise ratios in measuring such small displacements, measurements benefit from periodic adjustment of the oxygen activity within the PCO films, achieved by electrochemical pumping of oxygen into and out of the film utilizing a Nernst cell of the form Pt/YSZ/PCO. Two cell geometries are examined, including (1) deposition of PCO films on yttrium stabilized zirconia (YSZ) single crystal substrates (300-500 microns thick) and (2) the deposition of PCO films on highly resistive substrates (e.g. Al₂O₃ or MgO) and subsequent coverage with a YSZ film to pump oxygen. In this work, the chemical expansion of Pr_{0.1}Ce_{0.9}O_{2-δ} films of up to about 2 microns thickness was investigated using Laser-Doppler Vibrometry (LDV). Here, round substrates were used as they facilitate the modeling of substrate deformation associated with the chemical expansion of the PCO thin films. In particular, the mechanical stresses in the PCO films were calculated using the Stoney equation as a function of film thickness and the deflection of the substrate/film sandwich. These results are compared with previous results using rectangular substrates and comparable PCO thin films. The application of geometry (1) with sinusoidal electrochemical pumping at 4 Hz in the voltage range between 0 and 0.5 V at 700 °C results in displacements of 1.5 to 4 nm for a 250 nm PCO film. The related kinetics of oxygen transport are known [3]. However, approach (2) requires further understanding of the oxygen transport in the YSZ films and at the interface YSZ/PCO. In a first step, the functionality of the YSZ film as oxygen sensor and pump was tested and showed nearly instantaneous response upon change in p_{O2}.

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11:15 AM CM03.21.06

The Influence of Alkaline-Earth Cation (Ca²⁺, Sr²⁺ and Ba²⁺) of Binary Phosphate Glasses on H⁺ Infiltration Rates Analyzed by *In Situ* FT-IR Spectroscopy Sumin Jeong, Yusuke Daiko, Sawao Honda and Yuji Iwamoto; Department of Life Science and Applied Chemistry, Nagoya Institute of Technology, Nagoya, Japan.

Proton conducting glasses have received interest for application in electrolytes of intermediate temperature fuel cells. In our previous study, we successfully fabricated a fast proton conducting glass with proton transport number $t_H = 1$ and fuel cell performance of ~5.0 mW/cm² at 500 °C [1]. Interestingly, this proton conducting glass had few protons just after the deposition of glass-melts, and the proton concentration of the glass increased markedly during a fuel cell operation. Then, we provided the first experimental evidence of the proton implantation by evaluation of the implantation quantities using originally developed *in-situ* FT-IR analysis [2]. The factors for fast proton implantation rates is very important with respect to enhance of fuel cell performance, because output current is a function of the electrode reaction rate. However, influence of glass modifier cations on proton implantation rates has not been evaluated yet. Here, we show how proton implantation rate changes by varying alkaline-earth species based on results about local structures around these cations (M²⁺). The changes in concentration of proton (as OH groups) were measured by the *in-situ* FTIR spectroscopy, and the local structures around M²⁺ was investigated via a combination of high energy x-ray diffraction data and Reverse Monte Carlo (RMC) modelling. 50 MO-50 P₂O₅ glass (50M, M = Ca, Sr and Ba) were prepared by a conventional melt-quench method and cut into a plate shape and polished. Then, platinum electrodes were sputtered on both sides of the glass plates. Changes in OH concentration were measured under hydrogen atmosphere (4%) and voltage application of 3 V at the temperature around 350 °C.

Computational: The RMC ++ code [3] has been used to model the atomic structure that agree with x-ray diffraction data. A model is defined as a set of 4000 virtual atoms in a box at the number density corresponding to that of the real material. The distance and the coordination for neighboring atoms used in the construction of the model were obtained from existing knowledge of metaphosphate glasses and X-ray diffraction data.

The absorbance of OH groups around 3000 cm⁻¹ increased only in humidified (~0.04 % of relative humidity) hydrogen atmosphere under applying the voltage. This suggests that protons are implanted only under fuel cell operating condition with humidity. The proton implantation rate of 50Sr glass was two times larger than that of 50Ca glass at 350 °C. The relationship between alkaline-earth cation species and proton implantation rates will be discussed from the viewpoint of the local structure around the metal cations.

References: [1] Y. Daiko et al., *Electrochemistry*, **82**, 901-905 (2014) [2] S. Jeong et al., Symposium conducted at Ceramic Society of Japan Annual Meeting 2017, 2C04 (2017) [3] O. Gereben et al., *J. Optoelectron. Adv. Mater.*, **9**, 3021-3027 (2007)

11:30 AM CM03.21.07

Sub-Micron Resolution X-Ray Spectroscopy and X-Ray Fluorescence Imaging at the NSLS-II SRX Beamline Andrew Kiss, Juergen Thieme and Yong Chu; National Synchrotron Light Source II, Brookhaven National Laboratory, Upton, New York, United States.

The NSLS-II is a recently built and commissioned synchrotron designed to accommodate experiments that require highly coherent and high brilliance X-rays. The generated X-ray light has a very low emittance of 0.6 nm-rad and 8 pm-rad in the horizontal and vertical directions, respectively, as well as a position stability of less than 10% of the source size in the horizontal and vertical. The ring current has been steadily increasing to provide more X-ray flux, with a current value of 375 mA and a design goal of 500 mA. Based on these storage ring parameters, NSLS-II is an ideal synchrotron for X-ray microprobe experiments. The Sub-micron Resolution X-ray Spectroscopy (SRX) beamline at NSLS-II 5-ID has been specifically designed to utilize the strengths of NSLS-II for sub-micron X-ray spectroscopy and X-ray fluorescence (XRF) imaging. Kirkpatrick-Baez (KB) mirrors focus the X-ray beam down to a sub-micron spot for high spatial resolution X-ray absorption near-edge structure (XANES) spectroscopy and XRF imaging experiments. Monochromatic X-rays ranging from roughly 4.5 to 25 keV illuminate the sample and enable XANES across a wide range of elements from titanium up to plutonium. The undulator source produces enough brilliance for roughly 10¹³ ph/s at the sample, data collection time is minimized. The high X-ray flux combined with fly-scan sample motion, allow XRF imaging to be rapidly collected. This is necessary for and enables *in situ* experiments which can provide researchers more realistic conditions for their samples. Combining spectroscopy and imaging techniques allow scientists to nondestructively investigate the elemental and chemical state of their samples. This presentation will introduce current applications of research performed at the SRX beamline, focusing on material science and energy materials, such as Li-ion batteries.

SESSION CM03.22: Electrodeposition and Corrosion

Session Chairs: Neil Dasgupta and Matthew McDowell

Friday Afternoon, November 30, 2018

Hynes, Level 3, Room 300

1:30 PM *CM03.22.01

Detailed Investigation of the Interfacial Electrolyte/Electrode Reactions and the Effect of Additives in Li-Ion, Li-Sulfur and Li-Air Batteries by *Operando ec*-(S)TEM B. Layla Mehdi^{1,2}; ¹University of Liverpool, Liverpool, United Kingdom; ²Pacific Northwest National Laboratory, Richland, Washington, United States.

The high demand for new energy storage nanomaterials has created the need for novel experimental techniques that can provide *real-time* information on the dynamic structural changes and reactions that occur locally at the electrode/electrolyte interface inside the battery. The development of *in-situ* liquid electrochemical stages for (scanning) transmission electron microscopes (*ec*-(S)TEM) enables fabrication of a “*nano-battery*” to study the details of electrochemical processes under *operando* conditions. However, the high complexity of electrochemical processes during battery cycling requires careful calibration of the system to circumvent *e*-beam damage and to control the side electrochemical reactions [1]. Here we demonstrate the application of this “*nano-battery*” approach to rechargeable Li-ion, Li-sulfur and Li-O₂ batteries. The full operation of these complex systems is yet not fully understood and typically involves multi-step electrochemical reduction/oxidation reactions, which often lead to lithium dendrite formation. There are many strategies to improve the interfacial stability of the Li anode and control/suppress Li dendrite growth, which is highly dependent on nature of electrolyte itself, such as mixture of different electrolyte solvents, salts and additives (e.g. HF, LiNO₃ etc). In one example, we investigate the role of electrolyte additives on the initial stages of Li deposition/stripping and the SEI layer formation. Under *operando ec*-(S)TEM conditions we can explore the role of the moisture that typically causes fast degradation of the electrolyte but here is used as a “catalyst” that controls the interfacial electrode/electrolyte reactions. With careful calibration of the water content, we obtain precise control of the interfacial reaction mechanism, which leads to suppression of the Li dendrite, increases Coulombic efficiency and to uniform Li grain growth [2]. Similar mechanisms have been observed with LiNO₃ as an additive to control the mechanism of nucleation, growth and suppression of Li metal dendrites in Li-S batteries.

References:

[1] B. L. Mehdi, J. Qian, E. Nasybulin, C. Park, D. A. Welch, R. Faller, H. Mehta, W. A. Henderson, W. Xu, C. M. Wang, J. E. Evans, J. -G. Zhang, K. T. Mueller, N. D. Browning, *Nano Letters*, 15, (2015), 2168

[2] B. L. Mehdi, Andrew Stevens, Jiangfeng Qian, Chiwoo Park, Wu Xu, Wesley A Henderson, Ji-Guang Zhang, Karl T Mueller, Nigel D Browning, *Scientific Reports*, 6, (2016), 34267

[3] *This work was primarily supported by JCESR, an Energy Innovation Hub funded by DOE-BES. The development of the operando stage was supported by the Chemical Imaging LDRD Initiative at PNNL. PNNL is a multi-program national laboratory operated by Battelle for the U.S. DOE under Contract DE-AC05-76RL01830. A portion of the research was performed at the EMSL user facility sponsored by DOE-BER and located at PNNL. The multi-target tracking algorithm is supported by NSF-1334012.*

2:00 PM CM03.22.02

In Operando Investigations of the Surface Behavior of Cu Electrodeposition Suppressor Additives PEG and PPG Ryan Rooney¹, Kevin Schmitt¹, Frank von Horsten², Ralf Schmidt² and Andrew Gewirth¹; ¹University of Illinois at Urbana-Champaign, Urbana, Illinois, United States; ²Atotech Deutschland GmbH, Berlin, Germany.

Fabrication of microelectronics relies on the dual-Damascene process in order to create metal interconnects within dielectric materials. These interconnects allow for electrical connection between nanometer sized transistors and global-scale electrical contacts. The process allows for precise trench and via formation by lithographic techniques and superconformal filling by copper (Cu) electrodeposition. Superconformal filling is accomplished by tailored electrolytes including sulfuric acid, Cu salt, and different types of organic additives.

Suppressors are an important type of additive which prevent over-deposition on substrate surfaces, promoting growth within a trench/via. PEG and PPG are commonly used suppressor additives. In this talk we report on the surface behavior of PEG and PPG using Raman, *in-situ* surface enhanced Raman spectroscopy (SERS), and *in-situ* electrochemical quartz crystal microbalance (EQCM) measurements. Raman and SERS are used to determine the conformational behavior of PEG and PPG as pure materials, in solution/suspension, and at a roughened Cu surface *in-situ* during Cu electrodeposition. For both PEG and PPG, a clear spectroscopic trend emerges of increased intensity in higher wavenumber modes in the CH stretching region as the environment is changed from pure material to solution to surface. The spectral changes associated with PEG are larger than those associated with PPG, suggesting that the relatively more hydrophilic PEG undergoes more conformational changes with surface association relative to the more hydrophobic PPG. Calculations show that the observed spectroscopic trend is associated with increased gauche character in the polymer backbone. *In-situ* EQCM measurements show PEG only adsorbs to the surface in the presence of Cl⁻, consistent with previous studies of PEG. Alternatively, PPG adsorbed to the surface with and without Cl⁻, likely again because of the increased hydrophobic character associated with the molecule.

2:15 PM CM03.22.03

Revealing the Initial Stages of Metal Electrodeposition, Atom by Atom Richard Beanland¹, Haytham Hussein¹, Houari Amari^{2,1}, Reinhard Maurer¹, Jon J. Peters¹, Mark Newton¹ and Julie MacPherson¹; ¹University of Warwick, Coventry, United Kingdom; ²Engineering, University of Liverpool, Liverpool, United Kingdom.

Electrochemical deposition has yet to realize its full technological potential, despite its widespread use in many areas. Since it takes place in a liquid electrolyte very little is known about its initial stages, which occur at the atomic level. Many potential applications require precise control at this scale, such as energy storage and conversion electrodes for water splitting, fuel cells and electrochemical reduction of carbon dioxide. Here, we use scanning transmission electron microscopy to obtain snapshots of gold electrodeposition with a time resolution of tens of milliseconds, returning to examine the same areas time and again after each new electrodeposition. Being careful to quantify and account for electron-beam induced effects, we track the movement and behaviour of individual nanoparticles and indeed individual atoms. We show the importance of electrochemically driven atom transport, atom cluster formation, reassembly and growth into nanoparticles as well as deconstruction and atomic fluxes across the electrode surface via atom bridges. These show the limitations of existing models of growth, which typically assume the need for a critical particle size above which subsequent growth occurs irreversibly with direct atom addition.

2:30 PM CM03.22.04

Defect Formation, Coarsening and Morphological Instability of Passivating Oxide Film by Environmental Transmission Electron Microscopy Xiaoxiang Yu¹, Ahmet Gulec¹, Christopher Andolina³, Judith C. Yang³, John H. Perepezko², Peter W. Voorhees¹ and Laurence D. Marks¹; ¹Department of Materials Science and Engineering, Northwestern University, Evanston, Illinois, United States; ²Department of Materials Science and Engineering, University of Wisconsin-Madison, Madison, Wisconsin, United States; ³Department of Chemical and Petroleum Engineering, University of Pittsburgh, Pittsburgh, Pennsylvania, United States.

We report the results of *in-situ* and *ex-situ* transmission electron microscopy observations on the early stage oxidation of Ni-based alloys. At moderate temperature (~700 °C), an epitaxial rock-salt oxide Ni_{1-x}Cr_xO initiated at the surface of Ni-Cr and Ni-Cr-Mo alloys progressing by a layer-by-layer mode. Fast surface diffusion and slow bulk transportation of cations created vacancies firstly in the oxide film of Ni-Cr, coarsened into Kirkendall voids and then diffused to the metal-oxide interface, driven by the metal/oxide misfit stresses. The voids eventually formed cavities along the metal-oxide interface. For

Ni-Cr-Mo alloys, Kirkendall voids were inhibited by the fast formation of metastable $\text{Ni}_{2-x}\text{Cr}_x\text{O}_3$ (corundum structure) phase after the growth of rock-salt oxide. The results indicate that Mo doping may stabilize the cation vacancies and inhibit the Kirkendall voids formation by promoting the nucleation of corundum structure. Density functional theory calculations confirm that the thermodynamic driving force of phase transformation from rock-salt to corundum structure is increased by 0.6 eV per Mo atom.

At higher temperature (above 800 °C), however, the intrinsic morphological instability of rock-salt oxide thin film manifested due to surface stress. The nonlinear instability began at step edges by forming thicker regions and then retracted toward the thicker portion of the film, in effect “eating” a layer out of the thin film. Density functional theory calculations and continuum modeling of the elastic instability support the model for the process.

Collectively, our results provide new and deeper insights into defect formation, coarsening and morphological instability of protective oxide thin film during early stage oxidation, which is critical for better understanding and designing corrosion resistant alloys.

2:45 PM CM03.22.05

First Principles Approach to Model Electrochemical Reactions—Understanding the Fundamental Mechanisms Behind Mg Corrosion Mira Todorova, Sudarsan Surendralal and Jorg U. Neugebauer; Max-Planck-Institut fuer Eisenforschung, Duesseldorf, Germany.

Ab-initio modelling using density functional theory (DFT) provides important insights into reactions at electrochemical interfaces. Observation of reactions under conditions of applied potential presents, however, a major challenge. The reason is the lack of an easily available method within commonly used DFT codes with periodic boundary conditions, which allows tuning the electrode potential.

Utilising concepts from semiconductor physics we developed a novel potentiostat design. The new approach can be easily implemented in all existing periodic DFT codes. The potentiostat controls the electrode potential of the system by tuning the excess charge of the working electrode. Employing this method, we study the $\text{Mg}(0001)/\text{H}_2\text{O}$ interface under anodic polarisation conditions. The high corrosion rate under these conditions is a key obstacle to the technological application of Mg and its alloys. However, despite decade long numerous experimental and theoretical studies the mechanism behind the infamously fast corrosion rate could not be resolved. Our new approach allows to observe “in situ” the corrosion reactions at the Mg surface, such as dissociation events, proton transfer and H_2 evolution. Based on these insights we identify a novel and hitherto not considered reaction mechanism and explain the origins of the anomalous hydrogen evolution.

[1] S. Surendralal, M. Todorova, M.W. Finnis and J. Neugebauer, *Phys. Rev. Lett.* 120, 246801 (2018).

3:00 PM BREAK

SESSION CM03.23: Interfaces
Session Chairs: Neil Dasgupta and Matthew McDowell
Friday Afternoon, November 30, 2018
Hynes, Level 3, Room 300

3:30 PM CM03.23.01

Advances and Limitations of Composition Analysis by EDS for In Situ/Operando TEM Meiken Falke and Igor Nemeth; Bruker, Berlin, Germany.

Spectroscopy and element mapping capabilities using energy dispersive X-ray spectrometry (EDS) with silicon drift detectors (SDDs) in TEM/STEM and SEM are explored with a view on in situ analysis. Available instrumentation and its parameters important for in situ analysis as well as first application results will be discussed.

One certain request is speed, another the performance at elevated temperatures. Optimum photon detection geometry is crucial for efficient EDS in the electron microscope and includes a large solid and high take-off angle for photon collection, good collimation and suitable sample holders. The holders should not shadow the detector(s), holder materials and window materials need to be well known to ensure correct quantitative analysis. Multi-detector arrangements enable large solid angles at high take-off angle particularly well. Geometric optimization in combination with high brightness electron sources and aberration correction allows even the identification and tracking of single atoms at low accelerating voltages in STEM [1]. These prerequisites make in situ and certain in operando experiments possible or thinkable.

First EDS experiments at various temperatures, in liquid and with the electron beam as trigger of changes in the sample will be used to shed light on challenges of in situ spectroscopy and element mapping and possible solutions. E.g., heat radiation at elevated temperatures changes the low energy part of EDS spectra. Still, low energy element ID and phase analysis are available [2]. Liquid cells use windows and species investigated may also agglomerate at those windows, influencing quantitative analysis. Since EDS takes detector window materials into account anyway, liquid cell windows should be less of a challenge. Furthermore, dealing with constantly changing data streams demands new ways of data acquisition and processing.

[1] R. M. Stroud et al. *Appl. Phys. Lett.* **108** (2016) 163101

[2] T. T. van Omme et al., *Ultramicroscopy* **129** (2018) 14

3:45 PM CM03.23.02

In Situ Soft X-Ray Absorption Spectroscopy Characterization of Titanium Oxidation State in Ti_3C_2 MXene Ameer Al-Temimy^{1,2}, Babak Anasori³, Katherine A. Mazzio¹, Mohamad-Assaad Mawass¹, Florian Kronast¹, Sneha Choudhury¹, Simone Raoux^{1,4}, Mykola Seredych³, Yury Gogotsi³ and Tristan Petit¹; ¹Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, Berlin, Germany; ²Department of Physics, Freie Universität Berlin, Berlin, Germany; ³Department of Materials Science and Engineering, and A. J. Drexel Nanomaterials Institute, Drexel University, Philadelphia, Pennsylvania, United States; ⁴Institut für Physik, Humboldt Universität zu Berlin, Berlin, Germany.

MXenes are a new class of 2D materials consisting of transition metals carbides and nitrides that demonstrate extraordinary properties for electrochemical energy storage. In particular, Ti_3C_2 MXenes have shown very large capacitance in sulfuric acid due to a pseudocapacitive charging mechanism [1]. Monitoring the electronic structure of Ti_3C_2 MXenes *in situ/operando*, especially the oxidation state of the Ti atoms, could provide more insights into their energy storage mechanism. Furthermore, several reports have shown that MXenes can be oxidized naturally in various environments [2], therefore direct characterization in relevant media is necessary.

In this work, soft X-ray absorption spectroscopy (XAS) at the O K-edge and Ti L-edge has been applied to $\text{Ti}_3\text{C}_2\text{T}_x$ MXenes to study the oxidation state of Ti in various environments. The dried pristine $\text{Ti}_3\text{C}_2\text{T}_x$ MXenes have been characterized in vacuum by XAS in total electron yield mode (TEY) and X-ray

photoemission electron microscopy (X-PEEM). The X-PEEM is a powerful technique to record spatially resolved XA spectra at the Ti L-edge and O K-edge on individual MXene flakes. To evaluate the effect of solvation on the MXene oxidation state, $Ti_3C_2T_x$ MXenes dispersed in water have also been studied *in-situ* using silicon nitride membrane-based flow cell to enable good soft X-ray transmission. For dispersed samples, XA spectra at the Ti L-edge and O K-edge were recorded in total fluorescence yield (TFY) mode.

Finally, XAS characterization of $Ti_3C_2T_x$ MXenes deposited on gold-coated silicon nitride membrane enabled measurement under applied potential. *In-situ* characterization of $Ti_3C_2T_x$ MXenes under different bias voltages in 1M sulfuric acid at the Ti L-edge were performed. Partial fluorescence yield (PFY) measurements have been performed for these *in-situ* measurements.

The present work demonstrates that soft XAS can be applied to characterize MXenes in various conditions, which may provide new insights towards the understanding of their electrochemical charging mechanism. Advantages and limitations of the various XAS detection modes will also be discussed.

References:

- [1] M. R. Lukatskaya et al., *Adv. Energy Mater.*, 5, (2015) 1500589
- [2] C. J. Zhang et al., *Chem. Mater.*, 29 (11), (2017) 4848-4856

4:00 PM CM03.23.03

Direct *In Situ* Mechanism Study of Hierarchical ZnO Nanostructures Engineered by Facile Soft Solution Route Lili Liu, Xin Zhang, Elias Nakouzi, Zhizhang Shen, Maria Sushko, Jun Liu and James J. De Yoreo; Pacific Northwest National Laboratory, Richland, Washington, United States.

Hierarchical semiconductor nanostructures have been widely investigated as solutions to energy and environmental problems due to their excellent photocatalytic properties. For example, ZnO hierarchical structures with a range of morphologies have been adapted for photocatalytic applications, because of their low cost, non-toxicity and high quantum yields. However, little is known about the growth mechanisms and dynamics of these structures. Consequently, exploring these phenomena may provide new generalizable principles for hierarchical growth and aid in the development of new complex nanostructures as functional materials for applications in nanoscale devices. Here we report the results of *in situ* and *ex situ* electron microscopy investigations of the chemical and physical controls on growth of ZnO nanostructures. To decipher the growth mechanisms and quantify the kinetic parameters controlling growth rates, seed-free and seeded systems were examined in aqueous solutions at room temperature (RT) for a range of precursor concentrations. We employed $Zn(NO_3)_2$ and NaOH as sources of Zn^{2+} and OH^- , respectively, and varied their concentrations while keeping their ratios constant. We first characterized the resulting structures using *ex situ* SEM and high-resolution TEM (HRTEM). We found that a range of hierarchical wurtzite structures formed with morphologies that varied greatly with precursor concentration, ranging from flower-like structures to branched rods to inter-grown plates to hedgehog-like structures with increasing precursor concentration. The petals of the flower-like structures were elongated along the [001] direction, radiating from a central point in the unseeded system and appearing as branches in the seeded system. The branched structures that formed at low concentration exhibited a unique structural relationship between stem and branch, with the boundary defined by the (101) and (001) lattice planes. At the higher concentrations, faster growth along the [-1-1 0] than the [001] produced the complex structures of inter-grown plates, which have not been previously reported for growth in the aqueous solution at RT. At still higher concentration, the individual crystals within the hedgehog structures consisted of hexagonal nanorods that formed through fast growth along the [001] direction. *In-situ* liquid phase TEM at a range of electron dose rates was used to directly observe growth of the flower-like structures. We found that growth occurred in a diffusion limited regime at low dose rate and tended to switch to a mixed diffusion-reaction regime at high dose rate, with the flower like structure resulting from unstable growth at the corners of the initial hexagonal plates. Finally, results from liquid phase SEM experiments suggest that the inter-grown plates form mainly by means of monomer addition. These findings provide a systematic and comprehensive view of hierarchical ZnO growth.

4:15 PM CM03.23.04

Real-Time USAXS and WAXS Studies of Morphology Evolution in 3D Nanoporous Gold During Electrochemical Dealloying Samuel S. Welborn, John S. Corsi, Alexander Proschel and Eric Detsi; University of Pennsylvania, Philadelphia, Pennsylvania, United States.

Nanoporous (NP) metals with bicontinuous ligament/pore morphology are attractive for various applications including (electro)catalysis, actuation, sensing, plasmonics and electrochemical energy storage. Those NP metals are commonly produced by (*electro*)chemical dealloying, during which the less noble component of a parent alloy is selectively etched away and a 3D framework is left behind. In this talk, I will present a fundamental study on microstructural and crystallographic evolutions during electrochemical dealloying in combination with *in situ* and *operando* Ultra Small Angle X-Ray Scattering (USAXS) and Wide Angle X-Ray Scattering (WAXS) experiments that we have developed to measure structural change on several length scales in real-time. The experiment was realized with the simultaneous WAXS/SAXS capability of the University of Pennsylvania's multi-detector Dual Source and Environmental X-Ray Scattering (DEXS) facility. By controlling the voltage and measuring charge transferred, the length scale evolution of the system can be matched with the extent of dealloying. In addition, Weissmüller et al. have investigated the morphological similarities of nanoporous metal electron density and a Cahn's spinodal decomposition model based on a Gaussian Random Field.^{1,2} Using this model, we can map an autocorrelation function derived numerically to the USAXS data and glean important system parameters such as specific surface area and pore to void ratio. This information can also be used to visually reconstruct the nanoporous framework as it evolves through the dealloying process.

1. Cahn, J. W. Phase Separation by Spinodal Decomposition in Isotropic Systems. *J. Chem. Phys.* **42**, 93–99 (1965).

2. Soyarslan, C., Bargmann, S., Pradas, M. & Weissmüller, J. 3D stochastic bicontinuous microstructures: Generation, topology and elasticity. *Acta Mater.* **149**, 326–340 (2018).