

SYMPOSIUM ET03

Application of Nanoscale Phenomena and Materials to Practical Electrochemical Energy Storage and Conversion
November 26 - November 30, 2018

Symposium Organizers

Weiyang Li, Dartmouth College
Nian Liu, Georgia Institute of Technology
Bin Liu, Nanyang Technological University
Karthish Manthiram, Massachusetts Institute of Technology

* Invited Paper

SESSION ET03.01: Electrocatalysis Perspectives, Fundamentals and Case Study of Water Splitting
Session Chairs: Bin Liu and Karthish Manthiram
Monday Morning, November 26, 2018
Hynes, Level 3, Room 302

8:00 AM ET03.01.01

Enhanced Stability and Oxygen Evolution Electrocatalysis Activity of Heterostructured Anodes with Nanoscopically Thin Degenerately Doped Stannate and Titanate Epitaxial Layers John D. Baniecki¹, Catalin Harnagea², Dan Ricinchi³, Takashi Yamazaki⁵, Yoshihiko Imanaka⁴ and Hiroyuki Aso¹; ¹Next Generation Materials Project, Fujitsu Laboratories, Atsugi shi, Japan; ²INRS - Énergie Matériaux et Télécommunications, Varennes, Quebec, Canada; ³Innovator and Inventor Development Platform, Tokyo Institute of Technology, Yokohama, Japan; ⁴Digital Annealing Project, Fujitsu Laboratories Ltd., Atsugi shi, Japan; ⁵Fujitsu Laboratories Ltd., Atsugi shi, Japan.

Fuel produced from the electrochemical splitting of water can be used to power a wide variety of technologies including information communication technologies infrastructure. The slow kinetics of the oxygen evolution reaction (OER) is one of the performance-limiting factors for hydrogen production through electrolysis. OER catalysts are often unstable in alkaline environments exhibiting deactivation and structural transformation causing a significant challenge for use in photoelectrochemical cells and water electrolyzers. Moreover, in nanoscopically thin catalyst layers, OER activity also decreases due to inefficient charge transfer to the electrolyte-catalyst interface. Epitaxial heterostructures are promising to solve these issues, though recent attempts yielded improved stability only at the expense of greatly reduced OER activity. In this presentation, we elucidate the competing factors for deactivation of $\text{La}_x\text{Sr}_{1-x}\text{CoO}_3$ (LSCO) in nanoscopically thin layers supported on conducting perovskite substrates, and demonstrate heterostructured anodes with simultaneously high activity and stability during electrochemical water splitting in alkaline environments (pH = 13).

Epitaxial thin films of $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$, $\text{Ba}_{1-x}\text{La}_x\text{SnO}_3$, and $\text{Sr}_{1-x}\text{La}_x\text{TiO}_3$ were grown by pulsed laser epitaxy. Interface energetics were characterized using *in situ* X-ray and ultraviolet photoelectron spectroscopies. Scanning transmission electron microscopy and electron energy loss spectroscopy were used to resolve the atomic structures, and scanning nonlinear dielectric microscopy used to probe the nature of the charge carrier character on the heterostructured catalyst surface. Density functional theory calculations were used to assess the impact of the electronic structure of the heterostructured catalyst layers on the overpotential and OER catalytic activity.

While the LSCO undergoes dramatic structural and electronic changes during electrolysis, including leaching of La and Sr from the film to yield a layer of cobalt oxyhydroxide, the thickness dependence of the OER activity will be revealed to be due to inefficiency of charge carrier transport to active sites. We demonstrate engineering of depletion layers widths and chemical stability using heterostructures comprised of nanoscopically thin epitaxial layers of degenerately doped stannate and titanate perovskite structure oxides to yield low overpotentials ~ 300 mV at current densities (~10 mA/cm²) relevant for hydrogen production in electrolyzers and photo-electrochemical cells, at hundreds of hours operations in nanoscopically thin active layers. Implications of the results for applications of nanoscopically thin oxide heterostructures for designs of high activity and stable anodes for carbon neutral energy production via the electrochemical splitting of water will be discussed.

Acknowledgement

C.H. would like to thank the Japan Trust program of the National Institute of Information and Communication Technologies (NICT) for funding.

8:15 AM ET03.01.02

OER Catalyst Stability Investigation Using RDE Technique—A Stability Measure or an Artifact? Hany El-Sayed, Alexandra Weiß, Lorenz Olbrich, Garin Pratomo and Hubert A. Gasteiger; Chair of Technical Electrochemistry, Technical University of Munich, Garching, Germany.

The development of OER catalysts for PEM water electrolysis requires both activity and stability testing methods. The OER catalyst activity can be estimated by using rotating disk electrode (RDE), flow-channel methods, or in an electrolyzer. The evaluation of catalyst stability is realized using accelerated tests as testing over the whole lifetime (5-10 years) under realistic conditions is not practical.^{1,2} A protocol for the OER catalyst stability using RDE was proposed by the JCAP group and is now used by other researchers. In this protocol, a constant current is applied in a half-cell configuration and the change in potential is monitored until a sudden increase in potential indicates complete catalyst degradation.³ It was shown recently that the measured catalyst life-time depends on the nature of the electrode substrate onto which the catalyst powder is being supported. Based on this, it was recommended that Au and boron-doped diamond be used as they show better stability of the catalyst under investigation, while glassy carbon and fluorine doped tin oxide electrodes were deemed unsuitable in such stability test (St. T.).²

Here we present a careful examination of the use of RDE for investigating OER catalyst stability. Although the increase in potential in an RDE St. T. is thought to be due to catalyst degradation (dissolution), our findings provide a clear evidence that the change in potential is rather due to an experimental artifact. The source of this artifact are nano- and micro-bubbles formed within the pores of the catalyst layer during the OER that cannot be removed by electrode rotation. These bubbles accumulate and block the OER active sites, resulting in a potential increase, which is mistakenly interpreted as catalyst

degradation. Our findings indicate that almost no catalyst degradation takes place at the first phase of the St. T., which can last for several hours. In this phase, the bubbles accumulate and block the active sites, resulting in an artificial increase in the potential. The second phase of the St. T. starts once a threshold potential is realized, where a rapid potential increase is observed, due to catalyst dissolution at high potentials. Gas bubbles accumulation is responsible for the increase in potential, and ultimately resulting in the full degradation of the catalyst layer. A proper St. T. using RDE technique should avoid the accumulation of oxygen bubbles, which is currently under investigation and preliminary results will be also presented.

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8:30 AM *ET03.01.03

Nature Catalysis' Views on the Electrochemical Conversion and Storage of Energy [Marcal Capdevila-Cortada](#); Nature Catalysis, Berlin, Germany.

Modern societies face the challenge of supplying a continuously increasing energy demand. Intensive research is being conducted all around the globe to ensure that these needs can be satisfied while minimizing carbon emissions and other environmental threats. Electrochemistry holds promise to satisfy this requirement, either by using renewable energy to obtain fuels or store electricity or by converting fuels into electricity. Here catalysis research is pivotal, providing key advances in electrolyzers, fuel cells, and metal-air batteries.

Nature Catalysis, a new journal from the Nature Research group launched in January 2018, provides coverage of top research from the area of electrocatalysis, as well as all other areas of catalysis. Our broad scope, drawing from the work of scientists, engineers and researchers in industry and academia, ensures that published work reaches the widest possible audience. Nature Catalysis brings together researchers from across all chemistry and related fields, publishing work on homogeneous, heterogeneous, and biocatalysis, incorporating both fundamental and applied studies that advance our knowledge and inform the development of sustainable industries and processes.

9:00 AM *ET03.01.04

Catalyst and Electrode Development for Proton and Anion Exchange Membrane-Based Electrolyze Katherine Ayers, Chris Capuano, Luke T. Dalton and [Prasanna Mani](#); Proton OnSite, Wallingford, Connecticut, United States.

The need for a sustainable source of hydrogen has been widely recognized, not just as a potential transportation fueling vehicles, but to limit CO₂ production and fossil fuel consumption from existing industrial processes such as ammonia generation. Currently over 95% of hydrogen is made from fossil fuels through natural gas reforming or coal gasification. However, significant growth has occurred in recent years in water electrolysis research, especially in catalyst research for the hydrogen (HER) and oxygen (OER) evolution reactions. Proton exchange membrane (PEM)-based systems are relatively mature in that the technology has been commercialized, but further research and development can achieve significant impact; for example, order of magnitude reductions in catalyst loading. Anion exchange membranes based systems are still under development, with membrane and ionomer stability in the operating environment being a critical issue. In both the AEM and PEM case, there are complex interactions at the electrode level which need to be considered in catalyst and membrane development. First, the liquid electrolyte environment used for catalyst activity screening, where all of the catalyst surface is accessible to the reactant is often not comparable to a complex, 3-dimensional, ionomer-based electrode. Also, similar to automotive fuel cells, the operating environment is highly important and should be considered when claiming improvements over state of the art. For example, catalyst performance at very low current densities may indicate inherent activity but may not represent capability at typical device operating currents. Similarly, a membrane which cannot operate at differential pressure may be highly limited in utility even if more efficient than current commercial solutions. This talk will describe some of the complex interactions that need to be considered, typical operating requirements, and stages of development where relevant conditions should be introduced.

9:30 AM ET03.01.05

Highly Enhanced Electrochemical Water Oxidation Reaction Over Hyperfine β -FeOOH(Cl):Ni Nanorod Electrode by Modification with Amorphous Ni(OH)₂ [Tomiko M. Suzuki](#), Takamasa Nonaka, Kosuke Kitazumi, Naoko Takahashi, Satoru Kosaka, Yoriko Matsuoka, Keita Sekizawa, Akihiko Suda and Takeshi Morikawa; Toyota Central R&D Labs Inc, Nagakute, Japan.

The catalytic oxygen evolution reaction (OER) to extract electrons from water molecules is important for the artificial photosynthesis to generate useful chemicals such as hydrogen and organic compounds [1, 2]. In terms of elements strategy, utilization of abundant element for OER catalysts is remarkably advantageous for future low-costly artificial photosynthetic system. Fe-based OER catalysts, based on the fourth most earth-abundant element, are attractive, but are known to suffer from low OER activity due to limited electrical conductivity and non-ideal electronic structures near the surfaces of these catalysts.

Here, we report a highly crystalline, 10 nm-sized red rust OER catalyst composed of pure β -phase FeOOH(Cl) nanorods (ca. 3×13 nm) doped with Ni ions (β -FeOOH(Cl):Ni) [3] and surface-modified with amorphous Ni(OH)₂ (a-Ni(OH)₂, at a Ni to Fe ratio of 22 at.%), which shows the highest level of performance among Fe-rich oxides and oxyhydroxides. This catalyst can be synthesized by a facile one-pot process at room temperature, and colloidal aqueous solutions of the β -FeOOH(Cl)Ni/a-Ni(OH)₂ nanorods are very stable, with no apparent precipitation over a time span of at least one month. Electrochemical measurements for β -FeOOH:Ni/a-Ni(OH)₂ stacked nanorod anodes deposited on carbon paper (CP) were performed in a 3-electrode configuration using a Ag/AgCl reference electrode and a Pt wire counter electrode. The overpotential during the electrochemical OER over the anodes was 170 mV, and an OER current of 10 mA/cm² was obtained at an overpotential of 430 mV(+1.66 V vs. RHE) in 0.1 M KOH (without subtracting the iR drop). It is suggested that the surface modification with the a-Ni(OH)₂ lowered the OER overpotential of β -FeOOH(Cl):Ni, resulting in the very high current density at low potential compared with Fe-rich oxide and oxyhydroxide electrodes reported previously. Mössbauer spectroscopy also suggested electronic interaction between Fe and Ni species, which may be crucial evidence for the enhanced activity in the Fe-rich OER system [4]. The present cost-effective Fe-based OER catalysts can be widely applied to construct artificial photosynthetic systems for solar fuel generation by combination with CO₂ reduction catalysts.

References

- [1] T. R. Cook, et al., *Chem. Rev.*, 110 (2010) 6474. [2] C. C. L. McCrory, et al., *J. Am. Chem. Soc.*, 136 (2013) 16977. [3] T. M. Suzuki, T. Morikawa, et al., *Sustainable Energy Fuels*, 1 (2017) 636. [4] T. M. Suzuki, T. Morikawa, et al., *Bull. Chem. Soc. Jpn.*, 91 (2018) 778.

9:45 AM ET03.01.06

Unprecedented Impact of Charge on Electrochemical Reactions of Two-Dimensional Materials [Yuan Yue Liu](#), Donghoon Kim and Jianjian Shi; The University of Texas at Austin, Austin, Texas, United States.

Two-dimensional (2D) materials have attracted great interest in catalyzing electrochemical reactions such as water splitting, oxygen reduction, and carbon dioxide reduction. Quantum mechanical simulations have been extensively employed to study the catalytic mechanisms. However, these calculations typically assume that the catalyst has a zero/constant charge for computational simplicity, while in reality, the catalyst usually has a varying charge as the reaction proceeds due to the match between its Fermi level and the applied electrode potential. These contradictions urge an evaluation of the charge effects.

Here using grand canonical density functional theory calculations, we show that the charge on 2D materials can have a much stronger impact on the electrochemical reaction than the charge on 3D metals, which arises from the unique electronic properties of 2D materials. Our work calls for reconsideration of some of the previously suggested electrocatalytic mechanisms of 2D materials by incorporating the charge effects. [1]

[1] Donghoon Kim, Jianjian Shi, Yuanyue Liu, submitted

10:00 AM BREAK

10:30 AM *ET03.01.07

Hydroxide Exchange Membrane Electrolyzers (HEMELs) for Hydrogen Production Yushan Yan; University of Delaware, Newark, Delaware, United States.

One of the grand challenges facing humanity today is the development of an alternative energy system that is safe, clean, and sustainable and where combustion of fossil fuels no longer dominates. A distributed renewable electrochemical energy and mobility system (DREEMS) based on cheap renewable electricity could meet this challenge. At the foundation of this new energy system, we have chosen to study a number of electrochemical devices including fuel cells, electrolyzers, and flow batteries. We have been working on the development of hydroxide exchange membrane fuel cells (HEMFCs) and electrolyzers (HEMELs) which can work with nonprecious metal catalysts and inexpensive hydrocarbon polymer membranes. We have developed roadmaps for HEMFCs and HEMELs, the most chemically stable membranes, and the most active nonprecious metal catalysts. We have also studied why hydrogen oxidation and evolution reactions (HOR/HER) are slower in base than in acid for precious metal catalysts. For flow batteries we have developed novel designs, chemistries and cost models e.g., double-membrane aqueous flow batteries with high voltages (i.e., 3 V), single-element-mimic redox pairs, and user friendly physics-based analytical cost models. In this presentation, I will focus on our HEMEL work highlighting a new class of membranes, nonprecious metal catalysts and base/salt-free HEMEL cells for hydrogen production.

11:00 AM *ET03.01.08

Water Oxidation Mechanism of Assembled MnO Nanoparticles Ki Tae Nam; Department of Materials Science and Engineering, Seoul National University, Seoul, Korea (the Republic of).

Water splitting is regarded as a promising step towards environmentally sustainable energy schemes. The oxygen evolution reaction (OER) requires extremely high overpotential due to its slow reaction kinetics. The water oxidizing cluster in photosystem II, in the form of cubical Mn_4CaO_5 cluster, efficiently catalyzes water oxidation. Inspired by Mn_4CaO_5 cluster, we previously identified a new crystal structure, $Mn_3(PO_4)_2 \cdot 3H_2O$, and demonstrated its superior catalytic performance at neutral pH. We revealed that structural flexibility can stabilize Jahn-Teller distorted Mn(III), and thus facilitate Mn redox during catalysis. Additionally, we verified influence of Mn valency and asymmetric geometry on water oxidation catalysis using $Li_2MnP_2O_7$ and its derivatives.

Specific questions that we intensively focus for further applications include how to translate the underlying principles in Mn_4CaO_5 cluster into synthetic heterogeneous catalysts. Toward this vision, we have been developing a new catalytic platform based on sub-10 nm-sized MnO nanoparticles (MnO NPs) to bridge the gap between atomically defined biological catalysts, their metalloenzyme counterparts and the heterogeneous materials. In this approach, the local atomic geometry is controlled by the nitrogen surface modification by the specific ligand and the heterogeneous atom doping, that enhance the catalytic activity and selectivity. Furthermore, we detected key intermediate species, $Mn(IV)=O$, based on comprehensive electrokinetic and *in-situ* spectroscopic analysis. We revealed unique water oxidizing mechanism mediated by MnO different from bulk counterparts.

Here, we further conducted electrochemical impedance spectroscopy (EIS) analysis to decouple and investigate various rate-controlling factors in the MnO NPs film during OER. We proposed the transmission line model with Havriliak-Negami function to obtain physical parameters indicated complex electrochemical process such as surface catalysis and electron transport. Based on fitting analysis using our proposed model, we revealed that the surface catalysis was rate-limiting process for overall performance and electrons were transported with coupled manner of protons. Furthermore, our proposed circuit model could be applicable and generalized for not only MnO NPs but also various film-type electrocatalysts.

11:30 AM ET03.01.09

Ultrathin Pinhole-Free Molecular Wires-Embedded SiO₂ Membrane Connecting Incompatible Redox Reactions for Scalable Artificial Photosynthesis Won Jun Jo, Georgios Katsoukis and Heinz Frei; Lawrence Berkeley National Laboratory, Berkeley, California, United States.

Replacing fossil fuels with renewable resources to meet the global need requires a technology that is scalable to the unprecedented level of several terawatts. Natural photosynthesis is the sole existing technology that produces energy dense chemicals on the terawatt scale (> 100 TW). Its key design feature is the closed cycle of H₂O oxidation and formation of the primary reduction products on the shortest possible length scale, the nanometer scale, while separating the incompatible redox environments by an ultrathin membrane. This offers the advantage of minimizing efficiency-degrading mass transport processes and unwanted side reactions.

To incorporate the key feature into artificial photosystems, we assembled ultrathin (2 nm), pinhole-free, molecular wires-embedded SiO₂ membrane on planar and nanotube constructs. This membrane system spatially separates the H₂O oxidation CO₂ reduction, but enables (photo-)electrochemical communication between the incompatible redox reactions by transmitting protons and electrons in a precisely controlled manner, while preventing O₂ transport causing unwanted reverse reactions. This unique mass-transport behavior on planar and nanotube configurations was systematically studied via cyclic voltammetry, electrochemical impedance spectroscopy, and visible light-sensitized short circuit current experiments. The embedded molecular wires' integrity before and after the mass-transport process was confirmed by time-resolved optical spectroscopy and grazing angle ATR-FT-IR or IRRAS characterization.

11:45 AM ET03.01.10

Interesting Proton Conduction Environment within Thin Films of Fluorocarbon based Ionomers with Single or Multi-Acid Side Chains Shudipto K. Dishari; University of Nebraska--Lincoln, Lincoln, Nebraska, United States.

Polymer-catalyst interfaces control the energy efficiency of many energy conversion and storage device. The interfacial polymer layers are very thin (typically less than one micron thick). Many interesting structural, mechanical and transport properties in such thin ion containing polymer (ionomer)

layers evolve as a result of complex multimodal interfacial interactions, unusual hydration behavior and confinement. Especially ion conductivity at the interface can be drastically different from that in the bulk membranes and the route to this poor ion conduction behavior is not well-understood. It is thus highly needed to systematically study how the ion conduction environment and water uptake change with the change in ionomer structure and film thickness. In this work, three potential fluorocarbon based hydrogen fuel cell ionomers (Nafion, 3M PFIA, 3M PFSA) having single/multiple acids at side chain were studied in sub-micron thick films. All three ionomers have fluorocarbon (PTFE) backbones. The difference between Nafion and 3M PFSA is in the side chain structure, but both has single acid group at the side chains. On the other hand, 3M PFIA has bis(sulfonyl)imide group in addition to perfluorosulfonic acid which makes the polymer more acidic. By tracking the fluorescence response of photoacid dye HPTS incorporated within hydrated ionomer thin films, very interesting trends were obtained regarding the extent of proton transfer. The results, when combined with the information on nanoscale structure and water sorption, clearly indicated that there are many factors controlling the proton conduction behavior in thin ionomer films, in addition to water uptake.

SESSION ET03.02: Battery Fundamentals, Characterization and Modeling
Session Chairs: Weiyang Li and Nian Liu
Monday Afternoon, November 26, 2018
Hynes, Level 3, Room 302

2:00 PM *ET03.02.02

Nanoscale Characterizations and Material Designs for Rechargeable Lithium Batteries Yuan Yang; Columbia University, New York, New York, United States.

Nanoscale transport and materials are critical to electrochemical energy storage, such as power density, cycling life and safety. In this talk, I will present two examples on advanced tools and fabrication to understand nanoscale transport phenomena and designing of nanoscale materials. The first one is based on an emerging Stimulated Raman Scattering Microscopy, which is three orders of magnitude faster than traditional Raman microscopy. Therefore it can clearly track ion transport in electrolyte together with lithium dendrite, to illustrate their correlations. A positive feedback mechanism has been visualized, which guide methods to suppress lithium dendrite. The second example is through designing nanoscale modification of interfaces between battery electrodes and solid electrolyte. Therefore, the stability between electrodes and electrolyte and the cycling life of corresponding full cells are significantly improved.

2:30 PM ET03.02.03

Mechanistic Understanding of Phase Transformation Behavior during Lithiation of MoS₂ using Density Functional Theory Calculations Avinash M. Dongare¹, Jin Wang², Arthur Doble³ and C B. Carter^{1,4}; ¹University of Connecticut, Storrs, Connecticut, United States; ²University of Pennsylvania, Philadelphia, Pennsylvania, United States; ³EaglePicher Technologies, East Greenwich, Rhode Island, United States; ⁴Sandia National Laboratories, Albuquerque, New Mexico, United States.

The design/discovery of layered materials for applicability in next-generation battery technologies requires a fundamental understanding of the links between the atomic-scale structure, chemistry and the mechanisms and energetics of intercalation and de-intercalation reactions, and a consideration of other solid-state reactions that might compete. The goal of our research is to design/discover layered material microstructures as alternatives to graphite using an innovative combination of atomic-scale modeling, experimental in-situ characterization of the microstructural evolution during (de)intercalation reactions. Density functional theory (DFT) simulations are carried out to investigate the structural accommodation of the layered material during insertion and exertion of the intercalating species (energy barriers, volumetric expansion, and phase transformations). The structural stability of the 2H and 1T phases of MoS₂ during lithiation suggests that a phase transformation of the 2H phase of MoS₂ to the 1T phase may occur when MoS₂ is reacted with Li; the computational study allows different dosages of Lithium ion to be assessed with the aim of testing these the validity of these models using in-situ characterization of the solid-state reactions between Li and MoS₂ in the transmission electron microscope (TEM). The mechanisms of strain relaxation and the energetics of Li intercalation-induced phase transformations in MoS₂ at the atomic scales will be presented. This work is supported by NSF grant No. 1820565.

2:45 PM ET03.02.04

Mechanistic Understanding of Lithiation in MoS₂ by Atomic Scale Characterization Shalini Tripathi², Matthew T. Janish², William Moyer Mook¹, Katherine L. Jungjohann¹, Avinash M. Dongare², Arthur Doble³ and C B. Carter^{2,1,4}; ¹Center for Integrated Nanotechnologies (CINT), Sandia National Laboratories, Storrs, Connecticut, United States; ²Materials Science & Engineering Center, University of Connecticut, Storrs, Connecticut, United States; ³Yardney Division, EaglePicher Technologies LLC, East Greenwich, Rhode Island, United States; ⁴Chemical & Biomolecular Engineering, University of Connecticut, Storrs, Connecticut, United States.

Understanding the structure and phase changes associated with two-dimensional (2D) layered transition metal dichalcogenides (TMDs) is critical in optimizing performance in lithium-ion batteries. The large interlayer spacing in MoS₂ (~0.65nm) accommodates species such as alkali metal ions (Li⁺/Na⁺/K⁺) during intercalation. Intercalation is reported to change the electronic structure of the host molecule, resulting in variations in their electrical and optical properties. In this work, we examine the solid-state reactions between Li and MoS₂. Li⁺ ions can be inserted into vdW gap; the reaction is still unclear. Plan-view imaging has been extensively used, however, it is essential to visualize the process with the electron beam being parallel to the basal planes of the layer material to understand the reaction process. Lattice-fringe images have been discussed for several systems but relying on microtoming or simply using curved thin layers, the orientation of the specimen was less than ideally uncontrolled. Here, TEM specimens are made using FIB, and oriented for detailed study of the intercalation process. This study of TMDs uses a Tecnai F30 and a Cs/image-corrected Titan equipped with a direct electron detector camera, K2. This camera has two major advantages: the electron dose can be minimized and quick changes during reactions are recorded; both instruments have EELS and XEDS capabilities. DFT calculations are used to probe the structure and bonding changes during these reactions. Volumetric expansion, energy barriers, phase transformations and the role of doping, defects and interfaces can be modeled. The dynamics of the structural response are modeled using *ab initio* MD simulations. Electrochemical aspects can be monitored *in situ* in real-time and at atomic scale to provide understanding of lithium-ion storage mechanisms in these solid-state reactions and thus to test the modeling-based results.

In plan-view specimen, variations normal to the basal plane are not seen. Defects associated with the reactions were monitored real-time. As the reaction between MoS₂ and Li proceeds, white-line defects were observed under high-resolution imaging by TEM. Lower-magnification images show that the defects are not equally spaced and do not correspond to 'stage' development. These defects can cross several basal planes in the MoS₂ (either forwards or

backwards) but maintain essentially the same width after the step; they are not completely constrained to the vdW gap. This work is funded by NSF grant No. 1820565. MTJ is at LANL. TEM is at CINT, an Office of Science User Facility operated for the U.S. DOE. Sandia NL 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 NNSA under contract DE-NA-0003525. The views expressed in the abstract do not necessarily represent the views of the U.S. DOE or the U.S. Government.

3:00 PM BREAK

3:30 PM ET03.02.05

Gate-Tunable Electrochemical Kinetics on Back-Gated 2D Materials Yan Wang^{1,2} and Daniel Frisbie²; ¹Chemistry, University of Minnesota, Minneapolis, Minnesota, United States; ²Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, Minnesota, United States.

Electrochemical processes at electrode/electrolyte interfaces (e.g. electric double layer charging, heterogeneous charge transfer and surface binding of reaction species on the electrode) are of vital importance to energy conversion and storage systems including batteries, supercapacitors and electrocatalytic production of fuels. It has been widely acknowledged that the kinetics of the interfacial electrochemical processes are largely determined by the electronic structure (e.g. density of states and electronic occupation) at the electrode/electrolyte interface. We have developed a back-gated electrode structure that utilizes electrostatic charging (induced by a gate bias) to control electrochemical kinetics on ultrathin or 2D materials (5-nm-thick ZnO, monolayer MoS₂ and graphene).^{1,2} Such back-gated electrodes are fabricated with nanometer-thick semiconductors on SiO₂/degenerate Si substrates, analogous to the metal-oxide-semiconductor stack in the CMOS technology. Due to the extreme thinness of the electrode materials, the alignment of electronic bands as well as the electronic occupation, at the electrode/electrolyte interface, can be dramatically altered by the gate-induced charge carriers. Thus, real-time, continuous and efficient modulation of reaction kinetics can be achieved on 2D materials by varying the gate bias. In this presentation, we will use back-gated monolayer MoS₂ as an example to demonstrate how the applied gate bias affects the kinetics of heterogeneous charge transfer and surface binding processes. Specifically, the standard charge transfer rate constant between MoS₂ and ferrocene/ferrocenium redox couple can be tuned by over two orders of magnitude and the catalytic overpotential of hydrogen evolution reaction on 2H-MoS₂ can be reduced by more than 150 mV. Overall, the approach introduced here is generally applicable to investigation and optimization of interfacial electrochemical phenomena in a wide range of electrochemical systems. With the ability to control the band alignment and electronic occupation independent of the electrode potential, the back-gated 2D electrodes will provide new insights to rational design of electrode materials.

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(2) Wang, Y.; Kim, C.-H.; Yoo, Y.; Johns, J. E.; Frisbie, C. D. Field Effect Modulation of Heterogeneous Charge Transfer Kinetics at Back-Gated Two-Dimensional MoS₂ Electrodes. *Nano Lett.* **2017**, *17* (12), 7586–7592.

3:45 PM ET03.02.06

Nanoscale Characterization of Interfacial Phenomena in Battery Materials—New Insights from Correlative Electron Microscopy and Secondary Ion Mass Spectrometry Imaging Santhana Eswara¹, Alisa Pshenova¹, Venkata Siva Varun Sarbada², Lluís Yedra¹, Andrew Kercher³, Kenneth Takeuchi^{4,5}, Amy C. Marschilok^{4,5,6}, Esther Takeuchi^{4,5,6}, Nancy J. Dudney³, Tom Wirtz¹ and Robert Hull²; ¹Advanced Instrumentation for Ion Nano-Analytics (AINA), MRT Department, Luxembourg Institute of Science and Technology, Belvaux, Luxembourg; ²Dept. of Materials Science and Engineering, Rensselaer Polytechnic Institute, Troy, New York, United States; ³Materials Science & Technology Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States; ⁴Dept. of Materials Science and Chemical Engineering, Stony Brook University, The State University of New York, Stony Brook, New York, United States; ⁵Dept. of Chemistry, Stony Brook University, The State University of New York, Stony Brook, New York, United States; ⁶Energy Sciences Directorate, Brookhaven National Laboratory, Upton, New York, United States.

The performance of electrochemical energy materials depends crucially on the underlying nanoscale processes. The charge-discharge cycles of batteries result in gradual changes in nanoscale structure and chemistry of the different electrode layers with often detrimental consequences for the electrochemical properties [1]. To understand the nanoscale mechanisms causing the degradation of the battery materials and to develop strategies to counteract, high resolution imaging and analysis techniques are indispensable. While high-resolution Transmission Electron Microscopy (TEM) enables imaging of the nanostructures down to atomic resolution, analysis of light elements ($Z < 6$) and low concentrations (< 0.1 at. %) are difficult using typing analytical tools in a TEM such as Energy Dispersive X-ray Spectroscopy. In comparison, Secondary Ion Mass Spectrometry (SIMS) has an excellent sensitivity (can be as low as ppm range) and all the elements (including isotopes) of the periodic table can be analysed. However, the SIMS image resolution is limited to ~ 50 nm in most commercial SIMS instruments (except some new developments [2] where resolution < 20 nm has been demonstrated). Nevertheless, the resolution is still more than 2 orders of magnitude poorer than TEM imaging. To complement the strengths of TEM and SIMS in the same instrument, we developed an in-situ correlative microscopy technique combining TEM-SIMS [3, 4]. In this presentation, we will demonstrate the application of this new nanoscale characterization technique to elucidate the structural and chemical changes occurring in Li ion battery cathodes containing LiV₃O₈ thin film with different initial microstructures obtained by thermal annealing. Bright-Field TEM and corresponding SIMS images (e.g. Li⁺ and V⁺ maps) from uncycled and cycled samples were obtained to investigate the underlying materials phenomena (such as vanadium dissolution) in the cycled cathodes and to correlate the nanoscale processes with macroscopic electrochemical performance [5].

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4:00 PM ET03.02.07

Simulation of Charge Transfer Reactions at Graphite and Electrolyte Solution Interfaces with Density Functional and Implicit Solvation Theory Jun Haruyama and Minoru Otani; National Institute of Advanced Industrial Science and Technology, Tsukuba, Japan.

Development of a stable energy-storage device is a fundamental approach to solve energy-related issues. Lithium-ion batteries (LIBs) are one of the most promising candidates because of their high energy density and long cycle life. From electrochemical impedance spectroscopic measurements, the cell resistance of conventional LIB is dominated by charge transfer resistance at electrode/electrolyte interfaces. [1,2] Therefore, we investigate the charge transfer process, i.e. Li insertion/desorption process, at the interface between a graphite anode and 1 M LiPF₆EC electrolyte. The density functional theory (DFT) with effective screening medium (ESM) method [3] combined with the reference interaction site model (RISM), called ESM-RISM, is employed to

simulate the Li insertion/desorption process. [4] In this method, the graphite surface (Li_xC_6 slab and additional Li^+) and liquid solution (1 M LiPF_6EC) are represented as quantum mechanical and implicit classical solvation, respectively. The energy landscapes of reaction are revealed under constant electron chemical potential conditions at the interface. Across the transition state where the Li forms a half solvation shell, the reacting Li inside the electrode changes to a full solvation structure in the solution accompanied by electron transfer. The activation energies at the equilibrium potentials of the charge transfer reaction are approximately 0.6 eV, [5] which is consistent with the electrochemical impedance spectroscopy measurements. In the presentation, we explain the details of the ESM-RISM simulation and introduce the energy profiles of the Li insertion/desorption path at the $\text{LiC}_6/\text{EC LiPF}_6$ interface.

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4:15 PM ET03.02.08

Measurement of Mechanical Properties and Assessment of Mechanical Degradation of Solid Electrolyte Interphase (SEI) Formed with Carbonate-Based Electrolytes Insun Yoon; Brown University, Providence, Rhode Island, United States.

Rapidly increasing demand for low-cost, high energy density energy storage motivates researchers to develop advanced and reliable anode materials. Lithium alloying anodes such as Si, Sn, or Ge has three to ten times of charge capacity compared to the traditional graphite electrodes, and thus gathered enormous research interest. One of the major challenges associated with the lithium alloying anodes originates from de/lithiation-induced large volume change (~300%). Such volume change applies excessive cyclic strain on solid electrolyte interphase (SEI) to cause its mechanical failure and continued formation, resulting in poor cycle life. Several electrolyte additives such as fluoroethylene carbonate (FEC) or vinylene carbonate (VC) have been investigated and demonstrated to improve cyclic performance of Si electrodes. However, quantitative evaluation on influence of the additives on mechanical properties of SEI is still challenged.

With this background, we have developed an experimental approach to characterize elastic modulus, yield stress, inelastic deformation behavior, and crack density evolution of SEI formed with carbonate-based electrolytes. An SEI (~100nm) is prepared by lithium thin film - electrolyte (1.2M LiPF_6 in ethylene carbonate) reactions on a rectangular free-standing polydimethylsiloxane (PDMS) membrane (~300 - 400nm in thickness). The prepared sample is subjected to bulge testing in an inert environment; various level of controlled pressure is applied to the SEI/PDMS membrane and the corresponding deflection is measured by the atomic force microscopy (AFM). The plane strain elastic modulus and the yield stress of SEI are evaluated from the pressure-deflection relation from the bulge testing. Moreover, a careful observation of SEI surface topography yields the evolution of crack density as a function of applied strain. The experiment is repeated using FEC added electrolytes to investigate the influence of the FEC additive on mechanical stability of SEI.

4:30 PM ET03.02.09

Developing an Understanding of Solid-Electrolyte Interphase Formation in Multivalent Ion Batteries Using First Principles Calculations Joshua Young and Manuel Smeu; Physics, Binghamton University, Binghamton, New York, United States.

Multivalent ion batteries (MVIB), or those utilizing Mg, Ca, Zn, and Al, are garnering increasing attention as alternatives to Li-ion batteries in applications where portability is not an issue owing to their high energy density, cost efficiency, and abundance. However, the lack of suitable electrolytes allowing for the reversible plating of metallic anodes has limited the development of MVIBs, especially those involving Ca. This is primarily due to the fact that the solid-electrolyte interphase (SEI), a passivating layer which forms between the electrolyte and anode, often does not allow for the migration of ions in MVIBs. [1,2] In this work, we develop an understanding of the SEI in MVIB systems using a computational approach combining density functional theory (DFT) and *ab initio* molecular dynamics (AIMD) simulations. [3] We first identify the principle components of the SEI by studying the decomposition of the solvents and salts comprising various electrolytes on Li, Ca, and Al surfaces using AIMD. Following this, we identify electrolytes which can be used with a Ca metal anode by investigating the diffusion of Ca ions through the likely inorganic compounds produced using DFT. Finally, we investigate the decomposition of these electrolytes in the presence of external electric fields to more fully understand these reactions in electrochemical systems. We anticipate the promising new electrolytes proposed in this work will help guide experimentalists in the development of rechargeable MVIBs.

J.Y. and M.S. were supported by funds from Binghamton University. DFT calculations were performed on the Spiedie cluster at Binghamton University, as well as the Extreme Science and Engineering Discovery Environment (XSEDE), which is supported by NSF Grant No. ACI-1053575, under allocations TG-DMR170127 and TG-DMR180009.

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4:45 PM ET03.02.10

Structure of Room Temperature Ionic Liquids from X-Ray Scattering and *Ab Initio* Molecular Dynamics Simulations Tuan Anh Pham¹, Riley Coulthard², Mirijam Zobel³, Steven F. Buchsbaum¹, Desiree Plata², Brandon C. Wood¹, Francesco Fornasiero¹ and Eric R. Meshot¹; ¹Lawrence Livermore National Laboratory, Livermore, California, United States; ²Department of Chemical and Environmental Engineering, Yale University, New Haven, Connecticut, United States; ³Faculty of Biology, Chemistry & Earth Sciences, University of Bayreuth, Bayreuth, Germany.

Room temperature ionic liquids (ILs) have recently emerged as highly promising electrolytes for a wide range of emerging energy technologies, including next-generation supercapacitors and ion-batteries, due to their high thermal stability, ionic conductivity and wide electrochemical windows. The chemical and structural diversity of ILs creates a vast design space that could be exploited to optimize the device performance and stability. However, many mechanistic details remain enigmatic, including the fundamental nature of the cation-anion interactions and their relevance in determining structural and electronic properties of the liquids. Having this detailed information for the bulk liquid is a prerequisite for eventually deciphering the complexity the arises at nanostructured electrode interfaces, which are ubiquitous among energy storage devices. In this presentation, we combine high-level first-principles simulations and synchrotron X-ray characterization experiments to unravel the key structural, chemical and electronic properties of several archetypal ILs comprised of imidazolium-based ILs. In particular, we utilize extensive *ab initio* molecular dynamics simulations to probe the local density distribution and medium-range order of the ILs, which can be directly compared and validated by X-ray scattering measurements. Soft and tender X-ray absorption spectroscopy at the K-edge of fluorine, phosphorus, and sulfur contained on the anion also complements the chemical and electronic picture from the simulations. Our integrated theoretical and experimental approach relates these structural and chemical signatures with the intrinsic cation-anion interactions, by considering ILs with anions having significant differences in the molecular geometry, chemical composition, and charge distribution.

This work was supported by the U.S. Department of Energy at the Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344.

SESSION ET03.03: Poster Session I: Electrocatalysis
Session Chairs: Bin Liu and Karthish Manthiram
Monday Afternoon, November 26, 2018
8:00 PM - 10:00 PM
Hynes, Level 1, Hall B

ET03.03.01

Enhancing Electrocatalytic CO₂ Reduction Using a System-Integrated Approach to Catalyst Discovery Thomas Burdyny and Wilson Smith; Delft University of Technology, Delft, Netherlands.

Electrocatalytic CO₂ reduction has the dual-promise of neutralizing carbon emissions in the near future, while providing a long-term pathway to create energy-dense chemicals and fuels from atmospheric CO₂. The field has advanced immensely in recent years, taking significant strides towards commercial realization. While catalyst innovations have played a pivotal role in increasing the product selectivity and activity of both C1 and C2 products, innovations at the systems level have resulted in the scaling up of CO₂ reduction processes to industrially relevant current densities. This has been achieved by using membrane-electrode assemblies, gas-diffusion electrodes and pressurized systems to provide ample CO₂ to the catalyst. The immediate gains in performance metrics offered by these system-integrated catalytic configurations, however, go beyond reduced system losses and high current densities, suggesting that different reaction pathways and improved kinetics are possible when catalysts are tested under these conditions.

In this work we discuss the underlying reasons for the observed changes in catalytic activity between low and high current density studies. In particular, nanoscale transport phenomena is combined with experimental observations to show that the local reaction environment around a CO₂ reduction catalyst is substantially different at low current densities (<20 mA/cm²) from those at practical applied current densities (>200 mA/cm²). Specifically, the combined requirements for both CO₂ and protons (H⁺) at a catalyst's surface in CO₂ reduction leads to substantial cation, anion and pH gradients at the surface. At substantial current densities this results in alkaline reaction conditions at the catalyst's surface regardless of the chosen material, configuration or electrolyte. These conditions alter the binding energy of reactants and intermediates as compared to low current operating conditions, resulting in different product distributions and reaction efficiencies than are observed in the classical H-cell testing configuration.

Further, we extend these findings to design a practical electrochemical cell configuration (e.g. large electrode areas of >100 cm² operating at current densities of 200 mA/cm²). We find that while the majority of catalytic materials are tested under ideal 'inlet' conditions (e.g. saturated CO₂, ideal electrolyte conditions, no reaction products), a catalytic material also needs to be designed to operate with high performance under the 'outlet' conditions of an electrochemical device (e.g. the segment of active catalyst area near the outlet of the cell). We discuss how the deviation between inlet and outlet conditions has large implications for the required functionality of the catalyst, and the maximum size of a CO₂ reduction unit cell.

ET03.03.02

Ni₃P and NiFeOOH Core-Shell Nanoparticles Decorated in Nitrogen-Doped Carbon for Efficient Water Oxidation Baicheng Weng, Corey R. Grice, Fenghua Xu and Yanfa Yan; The University of Toledo, Toledo, Ohio, United States.

Transition metal Ni-based catalysts are potential candidates to replace expensive and scarce noble metal-based oxygen evolution reaction (OER) catalysts such as RuO₂ and IrO₂. Herein, we report a facile and environment-friendly method to synthesize core-shell nanoparticles consisting of Ni₃P core and NiFeOOH thin shell homogeneously studded in N-doped carbon matrix (Ni₃P@NiFeOOH/C). The obtained Ni₃P@NiFeOOH/C catalyst exhibits excellent OER activity and stability in both alkaline and neutral electrolytes, and is among the most active OER electrocatalysts yet reported in literature. Ni₃P@NiFeOOH/C reaches a 10 mA cm⁻² current density at a potential of 1.49 V (vs. RHE) in alkaline electrolyte and achieves 1 mA cm⁻² at 1.56 V (vs. RHE) in neutral electrolyte, respectively, outperforming the noble metal oxide catalysts, RuO₂ and IrO₂. The superior performance can be ascribed to the synergistic effect of Ni₃P supporting catalyst, NiFeOOH shell, and N-doped carbon matrix. A two-electrode electrochemical water-splitting device combining Ni₃P@NiFeOOH/C OER catalyst with Ni₃P hydrogen evolution reaction (HER) catalyst delivers a stable current density of 10 mA cm⁻² at 1.59 V and 1.75 V for over 17 h in alkaline and neutral electrolyte, respectively. Our design and synthesis strategy offer insights for developing new highly active electrocatalysts for water splitting and CO₂ reduction.

ET03.03.03

Nitrogen/Phosphorus Co-Doped Hole-Rich Carbon Nanotubes as Non-Noble Bifunctional Catalysts for Oxygen Reduction and Oxygen Evolution Reactions Eun Yeob Choi, Somin Lee, Jeongung Nam and Chang Keun Kim; Chung-Ang University, Seoul, Korea (the Republic of).

N,P-co-doped hole-rich carbon nanotubes (N,P-HCNTs) were fabricated and exploited as bifunctional catalysts for oxygen reduction reaction (ORR) and oxygen evolution reaction (OER). The N,P-HCNTs were fabricated by reacting multi-walled carbon nanotubes (MWCNTs) with hydrogen peroxide, followed by annealing reacted MWCNTs with urea and triphenyl phosphine. The formation of N,P-HCNT was characterized by some analyses including X-ray photoelectron spectroscopy, Raman spectroscopy and high resolution transmission electron microscopy. The unique hole-rich structure and N/P moieties in N,P-HCNT provide enhanced specific surface area and electrochemical properties compared with pristine MWCNTs, resulting in having high catalytic activity toward ORR and OER. Rotating ring disk electrode (RRDE) results indicated that the ORR and OER activities of N,P-HCNTs were comparable to noble catalysts such as Pt/C and RuO₂. In addition, the N,P-HCNT showed good long-term stability in both ORR and OER conditions. Therefore, the excellent catalytic activity and durability of N,P-HCNTs make them potential materials for replacing noble catalysts in both ORR and OER.

ET03.03.04

Ionic Transports in Liquid Under Confinement Yuepeng Guan and Jin Suntivich; Materials Science and Engineering, Cornell University, Ithaca, New York, United States.

This presentation presents an ionic-transport measurement in aqueous electrolytes that are confined within the cavities of nanoporous solids. Ionic transport plays an important role in electrochemical energy storage devices. Many studies have reported high ionic transport in nanoporous materials, for example, in porous carbon and in metal-organic framework materials. However, very little is understood how the confinements affect ionic transport. In this presentation, we present our measurement of the ionic transport through different nanoporous materials with controllable pore sizes and surface charges. We use these experimental measurements to establish the ionic transport ability and the role of electrical-double layer on ionic diffusions. These results provide insights into the elusive role of the electrical-double layer on confined ionic diffusions and a design strategy of future nanoporous materials for energy storage devices.

ET03.03.05

Graphene Oxide Enhanced Performance and Durability of Proton Exchange Membrane Fuel Cells (PEMFCs) [Likun Wang](#)¹, Yuchen Zhou¹, Stoyan Bliznakov¹, Miriam Rafailovich¹, Danielle Kelly², Audrey Shine³ and Guan Hao Chen⁴; ¹Stony Brook University, Stony Brook, New York, United States; ²Friends Academy, Locust Valley, New York, United States; ³Plainview Old-Bethpage JFK High School, Plainview, New York, United States; ⁴St. Georges High School, New York, New York, United States.

Proton exchange membrane fuel cells (PEMFCs) has attracted tremendous attentions as energy conversion device due to its high energy density, low operating temperature and environmentally friendly emission. Numerous efforts have been made to explore efficient catalysts for the reaction when valuable progress brings the large-scale commercialization of PEMFCs to the table. However, durability of the PEMFCs hindered the commercialization process. Here, we reported a simple, low-cost and readily scalable method to mitigate this effect by the incorporation of graphene oxide (GO). In our study, GO is deposited on the Nafion membrane or into the catalysts layer. The maximum power output of the cell under H₂/air atmosphere showed an enhancement over 20%. More importantly, the durability of PEMFCs was significantly improved by the GO introduction. 26.1% of maximum power degradation was observed for the cell without GO while only half amount decrease obtained for the cell with GO after 30K cycles of accelerated stress test based on DOE2020 protocol. Nearly 100% enhancement for the durability of PEMFCs can be attributed to the prohibition of H₂O₂ production. The promising durability promotion effect induced from low-cost GO involvement will help to accelerate the large-scale commercialization of PEMFCs.

ET03.03.06

Effect of the Oxygen Vacancies and Concentration of Ce³⁺ Valence State on Enhanced Electrochemical Performance of One Step Solvothermally Synthesized CeO₂ Nanoparticles [Hyeong-Ho Park](#)², Manjeet Kumar¹, Joondong Kim¹ and Ju-Hyung Yun¹; ¹Incheon National University, Incheon, Korea (the Republic of); ²Korea Advanced Nano Fab Center (KANC), Suwon, Korea (the Republic of).

Environment friendly, low-cost and high performance energy storage systems have been progressively required because of the global warming which has become an imperative and unavoidable factor. The increasing environmental setbacks along with the depletion of fossil fuels necessitate the tradition of solar photovoltaic and wind power as a source of electrical energy in practice[1, 2]. But, the unavailability of power from photovoltaic systems during night time and fluctuation in wind speed of the deliverable power have directed the researchers towards the usage of energy storage devices. Moreover, to maximize the productive use of electric vehicles, it is very essential to meet up with the intermittent energy needs and variable power demands. Correspondingly, high power delivery and long cycling stability is some of the most important criterion to be fulfilled by an energy storage device.[3]. To accomplish these demands, devices which could entail huge initial power to start up and show capability of charging with quicker rate are prerequisite. Therefore, supercapacitors have been explored as an upgraded energy storage devices to replace batteries and conventional capacitors with superior features[4].

In this work, different sized CeO₂ nanoparticles were synthesized using one step low-cost solvothermal method with various reaction time. Defect states were induced due to the reduction of Ce⁴⁺ into Ce³⁺ valence state. X-ray photoelectron spectroscopy results recommend that Ce³⁺ valence states and defects in the form of oxygen vacancies be present on the surface of CeO₂ nanoparticles. Such availability of oxygen vacancies provided high specific capacitance 142.5Fg⁻¹ at a current density of 0.25Ag⁻¹ in three electrode system using 1 M Na₂SO₄ electrolyte. There is an increase in faradaic reactions taken place on the surface which is attributed to the high surface area, more oxygen vacancies, and increased diffusion rate. The highest energy density is obtained to be ~12.68 Wh/kg, and the stability result confirmed that the capacitance retention is ~75 % after 1000 cycles of operation indicating that well optimized CeO₂ is a potential candidate as electrode materials for supercapacitor applications due to their fast mutation between Ce⁴⁺ to Ce³⁺ oxidation state.

Reference

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ET03.03.07

Heteroepitaxially Activated Durable {111}_{fcc}-Faceted Nickel Nanocrystals by Suppressing NiOOH Exfoliation during the Oxygen Evolution Reaction in an Alkaline Electrolyte [Byeongyoon Kim](#)¹, Aram Oh¹, Mrinal K. Kabiraz², Sang-Il Choi² and Kwangyeol Lee¹; ¹Korea University, Seoul, Korea (the Republic of); ²Kyungpook National University, Seoul, Korea (the Republic of).

One of the best catalyst for alkaline OER anode, nickel exist in various form of nickel oxide, hydroxide and oxyhydroxide in alkaline aqueous solution. Particularly facet-controlled surface of β -NiOOH is expected to have the best heterocatalytic performance. However, due to the great stability of layered structure of hep crystal, Ni(OH)₂ or NiOOH naturally prefer sheet-shape which is fully coordinated but difficult to form uncoordinated facet enclosure. Moreover, β -NiOOH inevitably oxidize to γ -NiOOH in alkaline OER condition. Herein, we demonstrate {111}_{fcc} facet controlled Ni nanoparticles and characteristic heteroepitaxy between {111}_{fcc} facet of rock salt NiO and layered Ni(OH)₂/NiOOH during the sequential oxidation in alkaline OER. As the result, {100}_{hep} faceted β -NiOOH surface formed on Ni octahedral nanoparticles that have resistance further oxidation. β -NiOOH/Ni octahedral nanoparticles showed excellent electrocatalytic activity and stability for OER in an alkaline electrolyte, requiring an overpotential of 0.32 V at 10 mA cm⁻² after 2 h of chronopotentiometric stability test. The facet-dependent heteroepitaxy of ionic crystals is responsible for the excellent electrocatalytic activity and stability.

ET03.03.08

Size-Controllable Synthesis of Pd_{0.5}Ru_{0.5} Solid-Solution NPs for Catalytic Applications [Dongshuang Wu](#), Kohei Kusada and Hiroshi Kitagawa; Graduate School of Science, Kyoto University, Kyoto-shi, Japan.

Pd and Ru, which are two neighbouring elements of Rh, are highly attractive for their wide applications in catalysis and energy area. However, the two metals are immiscible at the atomic level in bulk state even at the melting point of Pd. Very recently, our group synthesized PdRu non-equilibrium solid-solution nanoalloys over the whole composition range and demonstrated their applications in CO oxidation, formic acid electrooxidation and Suzuki–Miyaura cross-coupling reaction.[1-3] In view of both fundamental research and practical application, the influence of particle size on catalytic performance should be an interesting and significant subject. The surface area, electronic state and adsorption/desorption energy, which are important factors in catalysis, will change with size, especially in the sub-10 nm size range. Since Pd and Ru are immiscible metals in their bulk form, it is difficult to simultaneously control the metal composition and size of the PdRu solid-solution nanoparticles. To date, there is no report on the size effect in PdRu solid-solution system. Herein, fixing the Pd/Ru molar ratio at 1:1, we successfully synthesized Pd_{0.5}Ru_{0.5} solid-solution nanoparticles from 2 to 15 nm with narrow size distribution via a simple one-pot reaction. The relationship between size and catalytic properties is discussed.

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ET03.03.09

Construction of Ternary Transition Metal Selenides Nanosheets for High-Performance Bifunctional Water Splitting Jing Yu; Harbin Engineering University, Harbin, China.

Water electrolysis by splitting H₂O into hydrogen and oxygen is currently recognized as an attractive approach for developing regenerative hydrogen energy, which could in turn help to resolve the energy crisis and environmental pollution caused by overreliance on fossil fuels. The exploration of efficient electrocatalysts is highly desirable for reducing the energy barrier and accelerating the reaction kinetic. Transition metal selenides have drawn intense attention because of their outstanding electrocatalytic activity. However, the performance is not comparable favorably with costly noble-metal-based catalysts. Adding another metal element to binary selenides provides the opportunity to tune their crystalline and electronic structures and thus their electrocatalytic properties. In this work, we developed ternary NiCoSe₂ nanosheets configuration via an electrodeposition technique. The loose accumulation of crimped nanosheets on carbon cloth creates a porous structure with large surface area, which could provide abundant active sites for electrocatalysis and good diffusion of charge and electrolyte. The interaction between bimetallic atoms leads to significant enhancement of the catalytic performance. Density functional theory (DFT) calculation reveals the intrinsically metallic behaviour of NiCoSe₂, confirming good electronic conductivity. The prepared NiCoSe₂ exhibited superior and durable activities toward hydrogen evolution reaction (HER) and oxygen evolution reaction (OER), as well as full water splitting. The ternary metal selenides with tunable compositions provide a novel platform to develop low-cost and high-active catalysts for clean energy strategy.

ET03.03.10

Modifying Commercial Carbon with Trace Amounts of ZIF to Prepare Derivatives with Superior ORR Activities Bing Ni, Chen Ouyang and Xun Wang; Tsinghua University, Beijing, China.

Efficient electro-catalysts are highly demanded in many energy conversion devices, such as proton exchange membrane fuel cell, rechargeable batteries, water splitting devices, etc. Electrocatalytic process can be seen in this way¹: electrons are transported to (or removed from) the catalysts under external voltage, then catalysts deliver electrons to (or attract from) the surface active sites and then to the reactants, the reactants receive (or donate) electrons and proceed the catalytic reactions. Thus the methods to enhance electrochemical activities mainly rely on four aspects: (1) enhancing the conductivity of catalysts; (2) increasing the intrinsic activities of active centers; (3) augmenting the amount or concentration of active centers; (4) optimizing the mass transfer during the reaction. Tuning one or multiple factors in these four could help to enhance the electrocatalytic activities.

On the other hand, reducing costs while maintaining high activity and stability of the catalysts is also vital to applications. Guiding by the aforementioned aspects, we combined the virtue of zeolitic imidazolate frameworks (ZIFs, potential active centers) and commercial carbon black (CB, good conductor) to realize efficient and cheap oxygen reduction reaction (ORR) catalysts in alkali solution^{2,3}. The modified CB (MCB) was prepared by sequentially soaking the CB in cations (Co²⁺ and/or Zn²⁺) and ligand (2-methylimidazole) solutions, which was followed by a pyrolysis process. The sequential soaking process enabled a thin-layer coating of ZIF on the CB, and the amounts of ZIF were trace which could contribute to the great reduction of the costs (the total costs of the catalysts were less than 70RMB/kg). After the pyrolysis process, the obtained MCB showed large diffusion-limited current density (6.18mA/cm²), half-wave potential (0.858V vs RHE), and no obvious decay after 20000 cyclic voltammetry cycles. The MCB also displayed high resistance to methanol poison.

The combined experimental and theoretical studies illustrated that the C-O bond formed on the CB surface by the modification process was the main reason for the high activity, but not single-atom implanted carbon structures or metal oxides. The pristine CB surface had a large content of C=C double bonds or sp² carbon, while the MCB had a larger content of C-O bonds which are more active in ORR, and the activity increased with the increasing content of C-O bonds. On the other hand, when this kind of materials is in acidic conditions, the C-O active sites would be protonated and lose activity.

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ET03.03.11

Zr-Doped TiO₂ Nanotubes with Rich Ti³⁺ Species for Electrochemical N₂ Fixation Na Cao and Gengfeng Zheng; Fudan University, Shanghai, China.

The production of ammonia (NH₃) by the well-known Haber-Bosch process from N₂ and H₂ has marked over a century success for providing > 80% nitrogen source for fertilizer and an alternative energy carrier with large energy density. In spite of the natural abundance of N₂, the high bond energy of N≡N (940.95 kJ mol⁻¹) prevents it as a reactive form and thus requires a significant amount of the global energy cost annually. In addition, the use of fossil fuels to produce H₂ reactant also leads to a significant level of CO₂ release. The electrochemical N₂ reduction reaction (NRR) can be processed in ambient conditions and use inexpensive aqueous electrolytes as proton source, and thus is regarded as a promising approach. However, the development of high selective electrocatalysts for simultaneously producing NH₃ rather than the competing hydrogen evolution reaction (HER), is still challenging. Herein, combined with activity of Ti³⁺ species of titanium oxides, and more strong N-adatoms binding strength than H-adatoms on the surface of Ti and Zr, we developed a type of hybrid oxide Zr-doped TiO₂ nanotubes via a facile wet-chemical process towards a NRR catalyst. N₂ and water were used as nitrogen and protons sources, respectively. The replacement of Ti⁴⁺ with larger diameter of Zr⁴⁺ leads to the formation of adjacent oxygen vacancies and the increase of Ti³⁺ concentration. In contrast, further increase of the dopant size (such as Ce⁴⁺) is not capable of incorporating dopants into the original TiO₂ lattice structure. As a result, the Zr-doped TiO₂ NTs exhibited excellent catalytic ammonia synthesis performances (NH₃ yield: 9.07 μg h⁻¹ cm⁻²cat., Faradaic efficiency: 4.83%) at -0.45 V vs. reversible hydrogen electrode (RHE) in 0.1 M KOH electrolyte at under ambient conditions. This size-dependent doping strategy suggests an attractive means in tuning the active catalytic centers of electrocatalysts.

ET03.03.12

The Gate-Opening Behavior of Water Insertion Toward Heterogeneous Catalysis Chia-Shuo Hsu; Chemistry, National Taiwan University, Taipei, Taiwan.

For heterogeneous catalyst, the behavior of interphase between liquid and solid is the key for the activity of catalysis. The phase-transition step have been reported as the necessary one to improve the reaction. However, this behavior happened represent the catalyst have the interaction not only on the surface. The water should insert several layers of the structure. For the insertion undergoing, the structure need to open first and let the space enough to have water inside. But this gate-open behavior might not only happen toward the phase-transition. It would occur when the voltage applied. Therefore, We used three different kind of samples, Fe₃O₄, CoFe₂O₄, and NiFe₂O₄. In previous work, it have realized that the phase-transition occur in CoFe₂O₄ and NiFe₂O₄, Fe₃O₄ kept the original phase. By in-situ XRD, the gate-open can be observe and relate to the applied voltage. And three samples showed the same behavior. Furthermore, in-situ partial fluoresce yield can describe the change of structure during the gate-open. And by in-situ TEM, the amount of water

capacity can be calculated. According to these in-situ technologies, this detail of this behavior can be seen. And this behavior should be considered to every heterogeneous catalysis between liquid and solid.

ET03.03.13

Open Hollow Co-Pt Clusters Embedded in Carbon Nanoflake Arrays for Highly Efficient Alkaline Water Splitting [Hong Zhang](#)¹, Yanyu Liu², Haijun Wu¹, Zongkui Kou¹, Wei Zhou³, Wenjie Zang¹, Stephen John Pennycook¹, Jianping Xie¹, Cao Guan¹ and John Wang¹; ¹National University of Singapore, Singapore, Singapore; ²Beijing Institute of Technology, Beijing, China; ³Tianjin University, Tianjin, China.

Water splitting provides a clean and renewable way to produce high-purity hydrogen, but the slow kinetics and poor stability of electrocatalysts limit its practical application. Here we report a class of open hollow Co-Pt nanoclusters embedded in N-doped carbon nanoflake arrays aligned on carbon cloth (Co-Pt/C NAs, 2.5 wt% Pt), which display low overpotentials (50mV for hydrogen evolution, 320 mV for oxygen evolution, vs RHE) in alkaline media. The high performance arises from the unique nanostructure and the synergy of Co-Pt promoting water dissociation demonstrated by density functional theory (DFT) calculation results. It can be directly utilized as a highly efficient bifunctional electrocatalyst for overall alkaline water splitting and outperform noble-metal-based materials in terms of much lower operation voltage (1.54 V at 10 mA cm⁻²) and higher stability (no degradation at constant current or voltage up to 120 hrs.), representing a highly promising electrode for electrochemical energy conversion.

ET03.03.14

Gas-Phase Etched Platinum-Nickel Nanoframes and Their Extraordinary Activity Towards Methanol Electro-Oxidation [Yiliang Luan](#)¹, Can Li¹, Shaohui Yan¹, Bo Zhao², Amar Kumbhar³, Chenyu Wang¹ and Jiye Fang¹; ¹SUNY Binghamton, Binghamton, New York, United States; ²Texas Tech University, Lubbock, Texas, United States; ³University of North Carolina at Chapel Hill, Chapel Hill, North Carolina, United States.

Highly open nanoframes are a class of promising catalysts in many application fields due to their ultra large surface area and quasi-one-dimensional structure. However, the fabrication of such nanoframes is still a challenge. To date, they are usually produced by de-alloying one active component from a bimetallic precursor with an inert counterpart in a solution system, using an acidic medium such as acetic acid or even nitric acid. The drawback of this de-alloy method is that it could generate ill-defined structures with defect-rich surfaces, leading to severely deformed morphologies in the subsequent step of processing such as a substrate carbon loading process. Our recent achievement in the preparation of platinum(Pt)-nickel(Ni) tetrahedral nanoframes demonstrates that etching with carbon monoxide (CO), i.e. the Mond Process, is an efficient way to produce Pt-Ni nanoframes, in which a segregation of the Ni-component in the precursors is preferred. Herein, we disseminate a synthesis of cuboid Pt-Ni nanoframes through this CO etching approach, which has never been reported. The nanoframe precursors prepared via a colloidal synthesis presented a conventional concave cuboid profile. Our characterization indicated that there was a considerable segregation of the Ni-component on the solid concave cuboid precursors. The segregated Ni atoms could be easily removed through the Mond Process in CO atmosphere at an elevated temperature. According to TEM characterization, the resultant Pt-Ni nanoframes showed an apparently open frame structure with a solid metallic core. Further evaluation of these Pt-Ni nanoframes towards methanol electro-oxidation indicated that their surface specific activity is ~6.5-fold higher than that of the commercial Pt/C catalysts, suggesting an extraordinary performance.

ET03.03.15

Coupling Polyoxometalates and Carbon Dots for Photoelectrocatalysis [Antonino Madonia](#)¹, Fabrizio Messina², Delphine Schaming¹ and Souad Ammar¹; ¹ITODYS Laboratory, Université Paris Diderot, Paris, France; ²DiFC, Università degli Studi di Palermo, Palermo, Italy.

Nowadays the need for new energy sources required to let us overcome the intensive use of fossil fuels is more actual than ever. Some efforts have been focused on the development of a system to produce and store hydrogen in an affordable way; right now, though, this gaseous fuel is still produced by the decomposition of biomass.

A strategy then being adopted by scientists is to develop new materials capable of producing hydrogen directly from the catalytic reduction of water, a process commonly known as water splitting. Being hydrogen a very powerful combustible that only produces water when burned, giving rise to a so-called hydrogen cycle, it could be the green fuel of the future.

In the field of nanotechnologies, among some of the most interesting materials studied for this very purpose are Polyoxometalates (POM), a class of polyanionic clusters with rich redox and photochemical properties that can be opportunely tuned modifying their structure and composition [1]; despite several reports confirming their ability to catalyze water decomposition, their main drawback lies in their sensibility to light, limited only to the UV part of the spectrum. In order to make use of their appealing properties *via* the employment of the full solar radiation, several strategies have thus been approached. In this regard, many efforts have been made to obtain an effective coupling with different photosensitizers [2]; with this in mind, the recent discovery of Carbon Dots (CDs) opens completely new perspectives.

CDs are a novel class of carbon-based nanostructures, very cheap to synthesize, often non-toxic and that usually show an intense and tunable fluorescence when excited by both UV and visible light. Also, it has been reported they possess a remarkable tendency to transfer their excitation state when coupled to other species [3]. Making use of the broad distribution of molecular moieties found on CDs outer shell which allows an electrostatic interaction, we have been able to obtain a static coupling between these two species, as shown both by steady state and time resolved spectroscopy.

This nanohybrid has thus been used to prepare photoelectrodes that, studied in a common photoelectrocatalytic cell, show activity when irradiated by UV-Vis light; such a device could then be employed for the solar driven photocatalytic splitting of water, providing molecular hydrogen which could be used as a green energy source alternative to fossil fuels.

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ET03.03.17

Precision Selection Among C₂ Products from Alkenes to Alkenols in CO₂ Electro-Conversion by Carbonyl Coordination [Zheng X. Gu](#) and Gengfeng Zheng; Fudan university, Shanghai China, China.

Carbon dioxide (CO₂) is one of the main greenhouse gases accumulating from fossil fuel consumption has been caused urgent energy crisis and serious global warming problem, which represent two major challenges of the world. The electrochemical reduction of CO₂ into value-added chemicals and fuels provides both an attractive strategy for industrial-scale means and a candidate for energy storage. Copper (Cu) has been known as a unique metal catalyst in its ability of directly converting CO₂ into a high quantity of fuels from the electrochemical reduction of CO₂. However, poor selectivity and activity degradation are two remaining restraints for practical application. Upon most occasions, the CO₂ molecules obtain an electron to form CO₂⁻ intermediate has been regarded as a rate-determining step. However, the *CO intermediate is the key role to obtain deep reduction products. For instance, to formation of C₂H₄, the selectivity-determining step is the generation of the *COH intermediate by protonation of *CO and the subsequent converting into *CH₂ intermediate, which can gain ethylene through non electrochemical *CH₂ dimerization. Conversely, when the *CO intermediate is more and strongly

enough bound on the befitting facets of Cu catalyst and the adsorbed *CO species couple with each other to yield *CO dimer, which will hydrogenate with the *CO dimer that can tailored by adjusting the applied potential and the subsequent to generate ethanol. To investigate the adsorbed CO on the copper surface and discuss different reaction pathway through the *CO intermediate. We designed facile electrochemical deposition strategy to synthesize Cu nanodendrites by carbonyl coordination to expose the adsorbed CO site. Meanwhile, the adsorbed CO severely restricts hydrogen formation and the *CO intermediate adsorption strength can tailored by adjusting the applied potential.

ET03.03.18

Intercalation Na-Ion Storage in Two-Dimensional $MoS_{2-x}Se_x$ and Capacity Enhancement by Selenium Substitution Guichong Jia and Hongjin Fan; Nanyang Technological University, Singapore, Singapore.

The severe environmental pollution and the rapid development of renewable energy have stimulated the demand and research of energy storage technology in recent years. Lithium ion battery has huge demand for all kinds of electronics and energy storage devices. However, the lithium resource is rare, which will result in high cost and cannot meet the development in future. Sodium-based energy storage, as a potential alternative, has attracted enormously attention because of the abundance nature and similar storage mechanism.

Two-dimensional (2D) layered transition-metal dichalcogenides has been regarded as highly promising electrode materials for fast-rate Li-ion and Na-ion batteries. Monolayer or multilayer MoS_2 nanoflakes have been employed for metal ion batteries, but the material suffers from poor cyclic stability due to damage of the layered structure in a decomposition reaction. Herein, we judiciously synthesize ultrathin $MoS_{2-x}Se_x$ nanoflakes quasi-vertically aligned on the 3D graphene-like carbon foam backbone (the obtained material is referred to as $MoS_{2-x}Se_x/GF$). The $MoS_{2-x}Se_x/GF$ electrode with a Se concentration ($x=0.9$) exhibits enhanced rate performance with a higher reversible capacity and capacity retention compared to pure nanoflake MoS_2/GF electrodes. Quantitative analysis reveals that the improved pseudocapacitive contribution, derived from enlarged interlayer spacing by selenium substitution, is the origin of good rate performance. We also investigate the decomposition reaction of $MoS_{2-x}Se_x$ with in-situ Raman and ex-situ XRD measurements in different potential ranges (0.01-3.0 V and 0.5-3.0 V vs. Na^+/Na), which reveals that the 2D structure in $MoS_{2-x}Se_x$ can be preserved due to Na-ion intercalation process in the potential range above 0.5 V. Discharge to 0.01 V leads to damage of the 2D structure and aggregation. So we can maintain the 2D layered structure and thus significantly improve the capacity retention by choosing appropriate potential ranges. This study sheds new light on better understanding of the metal ion storage mechanism of 2D transition metal chalcogenides that are being widely investigated.

ET03.03.19

Surface Tailoring Induced by Pt Modification on Mixed-Phase Manganese-Cerium Oxides—A Promising Cathode Catalyst for Direct Methanol Fuel Cells Ammar B. Yousaf and Peter Kasak; Qatar University, Doha, Qatar.

Developing substituent of monometallic platinum (Pt) precious metal as promising cathode catalysts in direct methanol fuel cells (DMFCs) have attracted great interests underlying sustainable energy applications. Numerous strategies have been adopted to produce active Pt-based binary and ternary alloys to overcome the faced challenges in oxygen reduction reactions (ORR). To this end, we have introduced a facile strategy to develop an efficient electrocatalyst with enhanced ORR performance and negligible methanol crossover effect to maintain the overall cell voltage as a stable in DMFCs. Surface tailoring of mixed-phase manganese-cerium oxides were induced by fabrication of ultra-low and smaller sized Pt nanoparticles by capping agent free dry-chemistry reduction process. The geometry and structural analysis of as-obtained electrocatalyst were characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM), high-resolution transmission electron microscopy (HRTEM), X-ray diffraction (XRD) and X-Ray photoelectron spectroscopy (XPS). In addition, the precise surface tailoring was screened out by HAADF-STEM element mapping and atomic force microscopy (AFM). The cathode catalyst performance of Pt/Manganese-cerium oxides nanocomposite was analyzed by electro-reduction of oxygen with and without presence of methanol in alkaline medium to evaluate the negligence of methanol crossover from anode to cathode. The higher ORR performance with excellent methanol tolerance behavior compared with commercial Pt/C catalyst proved the promising nature and applications of present material in DMFCs.

ET03.03.20

Cobalt Phosphide—A Stable, Non-Precious Metal Hydrogen Evolution Catalyst in a Commercial Proton Exchange Membrane Electrolyzer McKenzie A. Hubert¹, Laurie King¹, Chris Capuano², Judith Manco², Nemanja Danilovic², Eduardo Valle¹, Thomas R. Hellstern¹, Katherine Ayers² and Thomas F. Jaramillo¹; ¹Stanford University, Stanford, California, United States; ²Proton Onsite, Wallingford, Connecticut, United States.

Proton exchange membrane (PEM) electrolyzers are a promising route to large-scale energy storage. Platinum is the state-of-the-art hydrogen evolution reaction (HER) catalyst used in commercial PEM electrolyzers today owing to its excellent activity and stability. However, the cost and scarcity of Pt motivate research into non-platinum group (NPG) electrocatalysts. For decades, electrocatalysis research has focused on developing cheaper, efficient HER catalysts to reduce the capital cost of PEM electrolyzers¹. However, a gap in this research has been demonstrating the stability of a non-platinum group (NPG) HER catalyst in a commercial-grade electrolyzer operating under conditions much different than lab-based tests².

Cobalt phosphide is among the most active NPG catalysts for HER and has been well-studied and characterized in the literature³. In this work, we develop a synthesis technique to prepare large batches of nanoparticulate CoP on a high surface area carbon support. In this form, we were able to directly integrate the nanomaterial into an 86 cm² commercial PEM membrane electrode assembly (MEA) electrolyzer without making significant changes to the fabrication process. This CoP PEM MEA demonstrated excellent stability by maintaining a nearly constant voltage for > 1500 hours of continuous operation at a current density of 1.86 A.cm⁻² and elevated temperature and pressure. To the best of our knowledge, this is the first demonstration of a stable NPG HER catalyst in a commercial PEM MEA electrolyzer.

For the purpose of energy storage, PEM electrolyzers will likely operate intermittently, following the flux in renewable power generation. We therefore also investigate lab-based accelerated stress tests (ASTs) to probe degradation of CoP to better understand failure mechanisms and predict catalyst performance when translated from the lab to a commercial device. Pre- and post-test characterization techniques such as x-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM), and inductively coupled plasma mass spectrometry (ICP-MS) were used to observe and quantify degradation. Establishing standard lab-scale ASTs for HER catalysts is essential for benchmarking stability across a wide range of materials.

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ET03.03.21

Vertically Aligned Nanoplatelets of Sputtered Iridium Oxide for the Oxygen Evolution Reaction David Baker, Milena B. Graziano and Brendan Hanrahan; Sensors and Electron Devices Directorate, U.S. Army Research Laboratory, Adelphi, Maryland, United States.

The key to efficient water electrolysis is finding a durable oxidation catalyst with a low overpotential for the four-electron oxygen evolution reaction (OER). Among known catalysts, iridium oxide (IrO₂) is often recognized as having one of the lowest overpotentials for the OER, and is found to be stable in a wide range of aqueous media [1]. IrO₂ electrodes are readily deposited by reactive sputtering, a method that can reproducibly control the resulting thickness, chemistry, and morphology of the IrO₂ films by changing the sputtering growth parameters [2]. Under low deposition temperatures and high O₂ flowrates, IrO₂ grains become vertically aligned nanoplatelets with a rutile crystal structure [3]. Due to their vertical orientation the IrO₂ nanoplatelets exhibit exceptional antireflective properties not seen with other sputtered IrO₂ morphologies, and can be electrochemically probed for their performance as OER catalysts when deposited onto electrodes. The nanoplatelet IrO₂ electrodes demonstrate high activity and good durability compared with sputtered IrO₂ exhibiting planar surface morphologies. Tafel analysis shows that the structure of the nanoplatelets is also found to have a large impact on the OER kinetics beyond simply increasing the surface area. These electrodes also exhibit comparable performance in a wide range of media, ranging in pH values from 1 to 12. Anti-reflective, nanoplatelet IrO₂ coatings are high performance catalysts for solar water splitting, without the need for damaging treatments to make antireflective patterns out of highly specialized semiconductor light absorbers.

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ET03.03.22

Magnetic Hierarchical Hollow Sub-Microwires Composed of NiFe Nanoparticles with Enhanced Electrocatalytic Activity Towards Oxygen Evolution Yang Wang, Huanting Wang and Cordelia Selomulya; Monash University, Clayton, Victoria, Australia.

Currently considerable efforts are made to develop renewable ways to replace the fossil-based route for producing hydrogen. As a well-studied option, water photoelectrolysis is restricted by its low energy efficiency and low output. Water electrolyzers are promising for producing renewable hydrogen based on acidic proton-exchange membranes (PEMs) or alkaline water electrolyzer. However, the electrode materials of the PEM electrolyzers contain platinum group metals (PGMs), which are relatively scarce and expensive thus hindering mass commercialization. By contrast, both cathode and anode materials for alkaline water electrolyzers can be produced from non-noble transition metal compounds, suitable for large scale production. However, the oxygen evolution reaction (OER) in alkaline solution is still sluggish and needs a high overpotential (>350 mV) to reach a current density of 10 mA cm⁻². Developing the right materials with favorable structures and properties can help improve the OER performance of catalysts in alkaline solutions.

As reported by Chatenet group¹, magnetic nanoparticles generate magnetic heating under high-frequency alternating magnetic fields. The localized heating to the catalysts in an electrolyzer can considerably reduce the overpotential for OER. Besides, introducing Fe into Ni-based materials may improve its conductivity and lead to an activation effect on Ni, resulting in a dramatically enhancement of the OER performance.² In addition, hierarchical structures could facilitate the electrochemical catalysis process, with active sites locating at the micro- and mesopores (nanopores) and the macropores promoting facile diffusion of species towards these active sites.³

Here we report a synthesis method that Fe was introduced into the oxide precursor (NiMoO₄) by an ion exchange method to form Prussian blue analogues (PBA, KNiFe(CN)₆) which was further transformed into hierarchical hollow sub-microwires composed of NiFe metal nanoparticles without the need for hydrogen post-treatment. The obtained hierarchical NiFe hollow sub-microwires, with a diameter of ~200 nm, had a high specific surface area (53 m² g⁻¹) which provided lots of active sites. These sub-units--NiFe nanoparticles, with a size of 3-5 nm, acted as precursors and experienced activation to form NiFe oxide *in situ* on the surface, favorable to OER.

This work introduces a facile and versatile way to introduce Fe into the precursor by an ion exchange method from different transition metal oxides, and also opened up new routes for synthesizing magnetic hierarchical hollow sub-microwires based on metal nanoparticles by directly annealing from their corresponding PBA precursors without introducing explosive hydrogen for heat-treatment.

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ET03.03.23

Computational Design of Core/shell Nanostructured Materials for Energy Conversion and Storage Liang Zhang, Abhinav S. Raman and Aleksandra Vojvodic; University of Pennsylvania, Philadelphia, Pennsylvania, United States.

Given the crucial role of catalysis science in our society, understanding how to design catalyst structures for desired catalytic activity and selectivity becomes a grand challenge. Core-shell nanostructured materials hold the promise of being active, cost-effective, and stable catalysts. I will demonstrate how we understand the structure-performance correlation at the atomic-scale level through a set of computational approaches and apply it to address the catalyst challenge in the fields of energy conversion and storages. Computationally, we designed heterostructured perovskites for electrochemical water splitting, which were experimentally synthesized, characterized and validated.¹ This sets the stage for the future design of core-shell oxide nanoparticles and their use for chemical reactions under harsh chemical environments. I will provide an understanding of the activation mechanism of the heterostructures based on first principle simulations.² Finally, I will bridge core-shell architected oxide and transition metal systems and discuss our vision of potential design strategies.

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Tuesday Morning, November 27, 2018
Hynes, Level 3, Room 302

8:00 AM ET03.04.01

A Rationally-Designed Ultrastrong Double-Layer Nanodiamond Interface for Stable Lithium Metal Anodes Yayuan Liu, Yan-Kai Tzeng, Steven Chu and Yi Cui; Stanford University, Stanford, California, United States.

Effective surface protection of lithium metal anode is the enabling factor for next-generation high-energy batteries. However, the exacting requirements on the stability, mechanical properties and homogeneities of the protection layer hinder the realization of an ideal artificial interface. Among all the material choices, diamond with its renowned mechanical strength and exceptional electrochemical inertness is a prime candidate for lithium metal stabilization. Herein, by special synthetic techniques and rational design, we successfully rendered this desirable material compatible as lithium metal interface, which could strictly satisfy all the critical requirements. By fabricating high-quality nanodiamond film with long-range homogeneity but weak adhesion to the current collector, lithium can be electroplated solely underneath the film and effectively protected from parasitic reactions with liquid electrolyte. Notably, the nanodiamond interface possessed the highest modulus of all the lithium metal interfaces reported so far (>200 GPa), which can effectively arrest dendrite propagation to afford a dense deposition morphology. And the good flexibility of the thin film can accommodate the volume change of electrode during cycling. Importantly, since pinholes and mechanical damages during cycling are the main failure mechanisms of the artificial coatings developed so far, a unique double-layer nanodiamond design was proposed for the first time to enhance the defect tolerance of the nanodiamond interface, which enabled more uniform ion flux and mechanical properties as confirmed by both simulation and experimental results. Thanks to the multifold advantages of the double-layer nanodiamond interface, high Coulombic efficiency of over 99.4% can be obtained at a current density of 1 mA cm^{-2} and an areal capacity of 2 mAh cm^{-2} . Moreover, with $\sim 250\%$ excess Li, more than 400 stable cycles can be realized in prototypical lithium-sulfur cells at a current density of 1.25 mA cm^{-2} , corresponding to an average anode Coulombic efficiency of above 99%.

8:15 AM ET03.04.02

Highly Stable Sodium Metal Anodes Enabled by Tuning the Thickness of Ultrathin Graphene Films Huan Wang, Chuanlong Wang and Weiyang Li; Dartmouth College, Hanover, New Hampshire, United States.

Sodium (Na) is most appealing as a replacement for Li batteries owing to its high similarity in chemical and physical properties as Li, low cost, high natural abundance and accessibility. However, the extremely high reactivity of Na metal with organic electrolyte leads to the formation of unstable solid electrolyte interphase (SEI) and growth of Na dendrites upon repeated electrochemical stripping/plating, resulting in poor cycling performance and serious safety issues. Here in this paper, highly stable and dendrite-free Na metal anodes over a wide current range and long-term cycling were presented by employing free-standing graphene films with tunable thickness (through controlling the number of graphene layers) on Na metal surface. To reveal the critical role of graphene thickness in detail, we systematically investigated the dependence of Na anode stability on the graphene thickness at different current densities and capacities. We discovered that the optimal cycling performance of Na anode highly depends on the thickness of the graphene film on Na surface: a thickness difference in only a few nanometers ($\sim 2\text{-}3 \text{ nm}$) can have decisive influence on the stability and rate capability of Na anode. We demonstrate that with a multi-layer graphene film ($\sim 5 \text{ nm}$ in thickness) as a protective layer on Na metal surface, a stable Na cycling behavior was first achieved in carbonate electrolyte without any additives over 300 hours at a relatively high current density of 2 mA cm^{-2} with a high cycling capacity of 3 mAh cm^{-2} . We believe that our facile and cost-effective method could be a viable route towards high-energy Na battery systems, and can provide valuable insights into the Li batteries as well.

8:30 AM *ET03.04.03

Design Li-/Na-Ion Battery Anode Materials at Nanoscale Xiaolin Li, Haiping Jia, Ji-Guang Zhang, Junhua Song, Biwei Xiao, David M. Reed and Vincent L. Sprenkle; Pacific Northwest National Laboratory, Richland, Washington, United States.

Nanostructured materials have been found to be critical in promoting the performance of energy storage and conversion devices, such as batteries. Here, Si anodes for Li-ion batteries (LIBs) and high capacity alloy anodes for Na-ion batteries (SIBs) are discussed as examples for the importance of design electrode materials at nanoscale.

For LIBs, we designed porous structured Si-C composite materials as high performance anodes. In one effort, the large mesoporous silicon sponge of tens of microns prepared have controlled porosity and pore size, which can limit the particle volume expansion at full lithiation to $\sim 30\%$ and prevent pulverization of bulk particles. The electrodes with the loading of 1.5 mAh per cm^2 demonstrated $\sim 92\%$ capacity retention over 300 cycles. The composite electrodes of porous Si and graphite ($\sim 3 \text{ mAh per cm}^2$ loading) with a specific capacity of $\sim 650 \text{ mAh per gram}$ demonstrate $\sim 82\%$ capacity retention over 450 cycles. In another effort, hierarchical structured Si-MWNT microspheres developed not only have good porous structure to accommodate the volume expansion and achieve $\sim 30\%$ apparent particle swell at full lithiation, but also demonstrate good mechanical integrity with the structure sustained up to $\sim 220 \text{ MPa}$ pressure. The anodes deliver a high specific capacity of $\sim 1500 \text{ mAh per gram}$ and 85% capacity retention over 200 cycles at the areal loading of $\sim 3 \text{ mAh per cm}^2$.

For SIBs, yolk-shell structured Sb@C particles and pomegranate microspheres have been prepared as high capacity anodes. With well-controlled nanostructure, these materials render stable cycling performance. The Sb@C yolk-shell structure prepared by controlled reduction and selective removal of Sb_2O_3 from carbon coated Sb_2O_3 nanoparticles can accommodate the Sb swelling upon sodiation and improve the structural/electrical integrity against pulverization. It delivers a high specific capacity of $\sim 554 \text{ mAh per gram}$ and long cyclability with 92% capacity retention over 200 cycles. Sb@C yolk-shell microspheres by the emulsion method further improved the packing density and the cycling stability with $\sim 99\%$ capacity retention over 200 cycles.

9:00 AM *ET03.04.04

Towards Better Electrochemical Devices—Building Effective Transport Networks for Electrons and Ions Yunfeng Lu; Department of Chemical and Biomolecular Engineering, University of California, Los Angeles, Los Angeles, California, United States.

Electrochemical devices, such as batteries and fuel cells, are commonly used for energy storage and conversion. Generally, such devices are operated through the separation, translocation, and recombination of electrons and ions (e.g., protons and lithium ions) between the electrodes. Building devices with robust and effective transport pathways is the key towards high power performance and long cycling life. In this context, this presentation will discuss the design and synthesis of materials, as well as the engineering of electrode structure, towards electrochemical devices with improved performance. Three main topics will be covered, including 1) the design and synthesis of anode and cathode materials, 2) novel solid electrolytes and functional separators, and 3) novel hydrogen fuel cells with multifunctional anodes for enhanced transient power and prolonged lifetime.

9:30 AM *ET03.04.05

Multi-Functional Few Layered Black Phosphorus Composite Qingyu Yan; Nanyang Technological University, Singapore, Singapore.

Delamination of black phosphorus (BP) into monolayer or few-layer, dubbed phosphorene, and manipulation of its newly discovered properties that are unattainable by its bulk structure have been a recent scientific breakthrough. As an elemental analogue of graphene, researchers intended to exploit its structural similarity to substitute graphene as anode for lithium ion batteries (LIBs) as one of the dominant power sources for portable electronic devices. In addition, for thermoelectric applications, theoretical studies have revealed that very high ZT values can be possibly achieved in BP with controlled charge carrier concentration.

We will present our recent activities on synthesis of few layered black phosphorus nanosheets through different methods and study their properties in Li/Na storage applications. We try to improve the chemical stability of phosphorene based composite by forming composite structures with the aid of spark plasma sintering (SPS) process. It shows that excellent air stability of SPS-processed black phosphorus can be achieved over the 60 days observation in maintaining its high Li storage properties. We also developed 0D-1D hybrid phosphorene-Ni₂P structures to show enhanced Li storage properties.

10:00 AM BREAK

10:30 AM *ET03.04.06

The Design of Nanomaterials for Pseudocapacitive Energy Storage Bruce S. Dunn; University of California, Los Angeles, Los Angeles, California, United States.

Battery materials exhibit high energy density by utilizing reversible redox reactions, but their slow ionic diffusion leads to long charging times. Electrochemical double layer capacitors (ELDCs) offer some advantages over batteries, including fast charging times (<1 minute) and long lifetimes (<500,000 cycles). However, ELDCs do not involve redox reactions and as a result they have lower energy densities compared to batteries. For this reason, there is widespread interest in pseudocapacitance, a faradaic process involving surface or near-surface redox reactions, that can lead to high energy density at high charge-discharge rates. In recent work, we have suggested that pseudocapacitive materials can be classified as extrinsic or intrinsic; in the latter case, pseudocapacitive behavior is dependent on particle size, as fundamental changes in redox reactions may occur in finite sized systems. This paper will review our work on identifying Li⁺ conducting nanoscale materials which exhibit pseudocapacitive behavior. One key feature associated with pseudocapacitance is that the rate of charge storage is determined by surface-like kinetics rather than semi-infinite diffusion as occurs with battery materials. In this regard, the presence of two-dimensional pathways in the structure of the oxide or sulfide material seems to be favorable for obtaining a pseudocapacitive response. In addition, when materials are reduced to nanoscale dimensions, they may begin to exhibit pseudocapacitive characteristics because of the large number of surface sites or because phase transitions which occur in the corresponding bulk materials are suppressed. MoO₂ is a good example of this behavior as micron-sized particles exhibit battery-like properties while nanosized materials exhibit pseudocapacitive responses and operate at high charge/discharge rates without decreasing the level of charge storage. Morphology is another parameter that has been used to develop pseudocapacitive responses in a variety of systems. Mesoporous materials, which possess an interconnected pore network that provides electrolyte access to thin (<15 nm) redox-active walls, lead to a pseudocapacitive response while two-dimensional nanosheets of transition metal oxides exhibit surface-controlled kinetics indicative of pseudocapacitive behavior. The ensemble of these results suggests that we can expect an increasing number of nanoscale materials to be developed that retain high energy density at charge/discharge rates which are well above those of battery materials.

11:00 AM ET03.04.07

In Situ Formation of Sulfide Solid-State Electrolyte Protection Layer on the Surface of Metallic Li for High Performance Li Batteries Jianwen Liang, Xiaona Li and Xueliang A. Sun; University of Western Ontario, London, Ontario, Canada.

Metallic lithium (Li) has attracted extensive attentions for Li-S, Li-air and solid-state Li batteries, due to its high theoretical capacity and low redox potential [1-3]. However, several challenges substantially hinder the real application of Li anodes, such as dendrite formation and unfavorable reaction between Li and electrolyte. In fact, the real problem is originated from the unavoidably reacts of Li with electrolyte and the non-uniform distribution of electrochemical active sites for Li plating/stripping during cycling.

Formation of a thin and stable protection layer with uniform and high Li ion flux on the surface of Li metal may address all of the main problems of Li anode. Sulfide-based solid-state electrolyte possesses reasonably high ionic conductivity (especially for nanostructured layer, which can achieve ionic conductivities higher than 10 mS cm⁻¹ at room temperature), which is a good choice for the materials of Li metal protection layer. While, the formation of a thin sulfide-based solid-state electrolyte layer, especially for *in-situ* or adjustable layer with nanosize and different thickness, on the surface of Li metal is still a challenge due to the high chemical active of metallic Li and the difficult synthesized conditions of sulfide-based solid-state electrolyte.

Here, we show an *in-situ* depositional strategy to form a sulfide solid-state electrolyte protection layer on the surface of metallic Li to address the dynamic Li plating/stripping process. Taking adjustable Li₃PS₄ solid-state electrolyte layer as an example, due to the high ionic conductivity and low electrochemical activity of Li₃PS₄, the intimate protection layer of Li₃PS₄ between Li metal and liquid organic electrolyte can not only restrain the formation of Li dendrite, but also reduce the SEI formation and prevent further corrosion of Li metal during battery cycling. Thus, excellent electrochemical performance has been achieved: (1) Symmetric cells with the Li₃PS₄ protection layer can deliver stable Li plating/stripping for 2000 h with voltage hysteresis as low as ~10 mV; (2) Full cells assembled with the Li₃PS₄-protected Li exhibit two times higher capacity retention in Li-S batteries (~800 mAh g⁻¹) at 5 A g⁻¹ for over 400 cycles compared to their bare Li counterparts; (3) High rate performances can be achieved with Li-Li₃PS₄/LiCoO₂ cells, which are capable of cycling at rates as high as 20 C.[4]

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11:15 AM ET03.04.08

Graphene Pliable Pockets Remediating Nanocrystalline Metal Anode for Full Cell Lithium-Ion Batteries and Capacitors in an Expedient and Scalable Way Jong Ho Won^{1,2} and Jeung Ku Kang²; ¹Applied Science Research Institute, Korea Advanced Institute of Science and Technology, Daejeon, Korea (the Republic of); ²Graduate school of EEWS, Korea Advanced Institute of Science and Technology, Daejeon, Korea (the Republic of).

In essence, nanocrystalline metals are promising building units to realize high-capacity anodes are enabling ever-increasing gravimetric and volumetric energy densities in lithium-ion batteries (LIBs), but their fading capacities upon both pulverization and electrical disconnection caused by large volume changes during repetitive lithiation/delithiation reactions must be remedied. Another challenge is the lack of a fast and scalable process to fabricate nanocrystalline metals into real electrodes. Herein, we report graphene pliable pockets (GPPs) remediating the limitations of nanocrystalline metals for high-performance LIBs, and Metal-encapsulated GPPs (M-GPPs) can be fabricated via the ultrafast dynamic polymerization and evaporation of specific polymers on nanocrystalline metals. This process is also shown to enable scalable mass production upon increasing the batch size.

We applied the GPP structure to silicon, a most promising but also difficult to handle electrode material. Utilizing Si₂ GPPs with high tap densities exhibits excellent rate capability and robust cycle life. We discover that the inner graphene pliable layers allow electrical conductance to Si and the outer GPP controls formation of solid-electrolyte interface (SEI) layers, while both of them provide pliable compartments to prevent volume expansion and pulverization of Si nanocrystals during repeated lithiation/delithiation cycles. Full-cell LIBs of the Si₂ GPP electrodes assembled with representative cathodes of LiCoO₂ (LCO), LiMnO₂ (LMO), and LiFePO₄ (LFP) demonstrate remarkably high gravimetric and volumetric energy densities. Moreover, Si₂ GPPs can be used as the battery-type electrodes for lithium-ion capacitors (LIC), such an attempt lead to a result in much faster charging/discharging and strikingly longer life performance while maintaining high energy densities. GPP structures are superior and feasible than other promising anode structures, thereby applicable to industries and attainable shortly.

11:30 AM ET03.04.09

Fracture Formation and Mitigation for Silicon Electrodes Taeho Yoon, Chuanxiao Xiao, Jun Liu, Seoung-Bum Son and Chunmei Ban; National Renewable Energy Laboratory, Lakewood, Colorado, United States.

Many efforts have been made to commercialize silicon-based anodes, due to its super high capacity and potentially low cost. However, Mechanical deformation associated with volume changes during lithiation/delithiation causes fracture and pulverization of electrodes, which hampers silicon's performance as a lithium-ion battery anode. This work investigates morphological evolution of Si (100) wafer during lithiation and delithiation, and the role of capping materials on the mechanical deformation. As the wafer is lithiated forming a Li_xSi regime on top of the Si wafer, compressive stress develops in the Li_xSi regime, creating <110>-oriented buckles on the surface. In contrast, Li_xSi is under tensile stress in the delithiation period, and cracks are initiated on the buckled-area where the surface is deformed severely during lithiation. While the cracks propagate along <110> direction on the buckled-area, it changes the direction to <100> when reaching to the flat surface where geological deformations are not significant upon lithiation. Furthermore, this presentation will discuss effects of capping layers on cracking behavior of silicon electrode and provide mechanistic insight into cracking formation to prevent deformations on Si electrode.

11:45 AM ET03.04.10

Isotropic and Ultrafast Sodiation Behavior of Sn Crystals Young-Woon Byeon^{2, 1}, Yong-Seok Choi², Jaepyoung Ahn¹ and Jae-Chul Lee²; ¹Advanced Analysis Center, Korea Institute of Science and Technology, Seoul, Korea (the Republic of); ²Department of Material Science and Engineering, Korea University, Seoul, Korea (the Republic of).

In situ sodiation experiments were performed on the Na-Sn system to evaluate the rate capability and cycle stability of the anode material. Experiments showed that the sodiation rate of crystalline Sn (c-Sn) is 2-3 orders of magnitude faster than the lithiation rate of c-Si with the same diameters. Furthermore, the observed rates were nearly the same regardless of the orientation of c-Sn, causing the Sn anode to swell in an isotropic manner and thus mitigating pulverization. Here, using atomic simulations and advanced analysis techniques, we elucidated the mechanistic origins responsible for the ultrafast sodiation and isotropic swelling observed from for the Sn anode by clarifying the diffusion kinetics at the Na-Sn diffusion couple. It was found that both the crystalline-to-amorphous phase transformation at thin layers of c-Sn near the propagating interface and pipe diffusion through sodiation-induced dislocations are the two dominant structural features occurring during sodiation. These sodiation behaviors observed from the Na/Sn interface alleviate the rate-limiting behavior of the propagating interface, while nullifying the orientation effect of diffusion in c-Sn. This promotes the Na diffusion to c-Sn at unprecedented rates and enables isotropic swelling of c-Sn. The observed phenomena provide insight into the design of anode materials for realizing batteries with high rate performance and cycle stability.

SESSION ET03.05: Fuel Cells and Electrosynthesis

Session Chairs: Bin Liu and Karthish Manthiram

Tuesday Afternoon, November 27, 2018

Hynes, Level 3, Room 302

1:30 PM *ET03.05.01

Recent Developments in the Design and Synthesis of Platinum-Based Catalysts for Fuel Cell Application Younan Xia; Georgia Institute of Technology, Atlanta, Georgia, United States.

Platinum (Pt) is by far the best catalyst for the oxygen reduction reaction (ORR) occurring on the cathode of a proton exchange membrane fuel cell (PEMFC). Its low abundance, limited supply, and ever-increasing price have kept motivating researchers to minimize the loading of this precious metal in the catalyst. In this talk, I will discuss a number of strategies for greatly increasing the mass activity and durability of Pt-based ORR catalysts, including facet-controlled synthesis, increase of dispersion by forming a core-shell or hollow structure, manipulation of surface strain, electronic coupling through the incorporation of a second metal, and use of particles with an uniform, optimal size. These strategies have resulted in the development of advanced ORR catalysts, enabling the society to achieve a sustainable use of precious metals such as Pt in energy conversion, industrial catalysis, and related applications

2:00 PM *ET03.05.02

Extending the Limits of Pt/C Catalysts with Passivation-Gas-Incorporated Atomic Layer Deposition Shicheng (John) Xu¹, Yongmin Kim¹, Joonsuk Park², Drew Higgins³, Shih-Jia Shen⁴, Peter Schindler⁵, Dickson Thian⁶, J. Provine⁵, Jan Torgersen^{1, 7}, Tanja Graf⁸, Thomas D. Schladt⁸, Marat Orazov³, Bernard Haochih Liu⁴, Thomas F. Jaramillo³ and Fritz Prinz¹; ¹Department of Mechanical Engineering, Stanford University, Stanford, California, United States; ²Department of Material Science and Engineering, Stanford University, Stanford, California, United States; ³Department of Chemical Engineering, Stanford University, Stanford, California, United States; ⁴Department of Materials Science and Engineering, National Cheng Kung University, Tainan, Taiwan; ⁵Department of Electrical Engineering, Stanford University, Stanford, California, United States; ⁶Department of Applied Physics, Stanford University, Stanford, California, United States; ⁷Department of Mechanical and Industrial Engineering, Norwegian University of Science and Technology, Trondheim, Norway; ⁸Volkswagen Group Research, Wolfsburg, Germany.

Cost and life-time are key factors in limiting the broad adoption of polymer electrolyte fuel cells for cars. In response, we have been investigating the morphology of noble metal nanoparticles during surface deposition. In particular, we explored the influence of precursor-substrate and precursor-deposit interactions. Depositions can be improved through a variety of means, including tailoring the surface energy of a substrate to improve precursor wettability, or by modifying the surface energy of the deposits themselves. Here, we show that carbon monoxide can be used as a passivation gas during atomic layer deposition to modify the surface energy of already deposited Pt nanoparticles to assist direct deposition onto a carbon catalyst support. The passivation process promotes two-dimensional growth leading to Pt nanoparticles with suppressed thicknesses and a more than 40% improvement in Pt surface-to-

volume ratio. This approach to synthesizing nanoparticulate Pt/C catalysts achieved high Pt mass activities for the oxygen reduction reaction (ORR), along with excellent stability likely facilitated by strong catalyst-support interactions afforded by this synthetic technique.

2:30 PM ET03.05.03

High-Productivity Electrochemistry with Flow-Through Nanowire Electrodes Myung Jun Kim, Feichen Yang and Benjamin Wiley; Duke University, Durham, North Carolina, United States.

The high surface area per unit volume and large mass-transfer rates offered by porous, flow-through electrodes have resulted in their use in a wide variety of electrochemical processes, including organic electrosynthesis, water electrolysis, water treatment, fuel cells, and redox flow batteries. Many types of porous electrodes are commercially available, including carbon paper, graphite felt, reticulated vitreous carbon (RVC), metal mesh, and metal foam. Metal foam offers relatively high conductivity but a low surface area, whereas carbon paper has one of the highest surface areas but lower conductivity.

This presentation will describe the characteristics of a Cu nanowire flow-through electrode that has 15 times more surface area and is 32 times more conductive than carbon paper. The improvement in surface area is due to the small diameter of the nanowires relative to carbon fibers. The higher conductivity is due to the intrinsically higher conductivity of Cu, and the fact that the metal nanowires can be sintered together. The nanowire electrode has a porosity of 94%, but its hydraulic permeability was 89 times lower than carbon paper. For Cu ion reduction, the Cu nanowire electrode can achieve the same single-pass conversion as carbon paper at flow rates 300 times greater under mass transport-limited conditions, and 10 times greater under kinetically limited conditions. We will also report the performance of the flow-through nanowire electrodes for organic electrosynthesis and for water splitting. The high-conductivity, high surface area, and high porosity that can be achieved with metal nanowire electrodes create new opportunities for improving the performance of electrochemical systems for energy storage, hydrogen production, water treatment and the production of fine chemicals.

2:45 PM ET03.05.04

Quasi-2D PdPt Alloy Nanoclams for CO₂ Reduction and Proposed Application in Tandem with Microbial Communities Andrew B. Wong¹, Joseph A. Gauthier¹, Frauke Kracke², Antaeres Antoniuk-Pablant¹, Christopher Hahn^{1,3}, Karen Chan^{1,3}, Alfred Spormann^{2,4} and Thomas F. Jaramillo^{4,1,3}; ¹SUNCAT Center for Interface Science and Catalysis, Department of Chemical Engineering, Stanford University, Stanford, California, United States; ²Civil and Environmental Engineering, Stanford University, Stanford, California, United States; ³SUNCAT Center for Interface Science and Catalysis, SLAC National Accelerator Laboratory, Menlo Park, California, United States; ⁴Chemical Engineering, Stanford University, Stanford, California, United States.

Improving the performance of cathodes for the electrochemical CO₂ reduction reaction (CO₂RR) will benefit from the discovery of new materials as well as the introduction of new paradigms. This presentation focuses on the synthesis and systematic study of the CO₂ reduction activity of a novel quasi-2D PdPt bimetallic 'nanoclams' catalyst synthesized on carbon cloth electrodes via a pulsed electrodeposition technique. These results highlight the importance of nanostructuring to improve selectivity and geometric activity for CO₂ reduction in this system through the comparison of the bulk and nanostructured PdPt. In addition, we also propose that the high activity of this catalyst at low overpotential is ideal for paring with biological systems to realize a hybrid system for CO₂ reduction.

The PdPt nanoclams have a unique tapered morphology that combines high surface area with exposure of numerous undercoordinated sites for CO₂ reduction with activity exceeding that of either Pd or Pt for CO₂ reduction to formate at 0.2 V vs RHE, which is a provocative result. In comparison with bulk Pd, PdPt, and Pt systems, we find that the interplay of multiple trends affects selectivity and activity:

1. Increasing Pt content shifts selectivity from formation of formate to hydrogen evolution in the bulk
2. Increasing Pt content increases overall activity and prevents catalyst deactivation by changing the energetics of hydride intercalation into PdPt
3. Nanostructured morphology of PdPt nanoclams increases selectivity to formate in PdPt nanoclams vs in bulk, planar PdPt.

In addition to this understanding, we report our initial results on the creation of a hybrid electrochemical-biological CO₂ reduction system in which formate and hydrogen are produced through electrochemical CO₂ reduction by PdPt nanoclams. These products are metabolized by methanogens in combination with CO₂ to yield ~100% faradaic efficiency to methane. Going forward, the integration of microbial communities with these nanostructured PdPt catalysts has the potential to combine the best-of-both-worlds from electrochemical and biological systems to achieve a regenerative catalytic system with high-selectivity, high activity, and low overpotential.

3:00 PM BREAK

3:30 PM DISCUSSION TIME

3:45 PM ET03.05.06

Rational Design of Electrode-Electrolyte System for Highly Efficient Electrochemical Nitrogen Reduction Reaction Bryan H. Suryanto², Colin S. Kang¹, Dabin Wang¹, Luis M. Azofra³, Luigi Cavallo³, Fengling Zhou², Xinyi Zhang² and Douglas R. MacFarlane²; ¹Monash University, Clayton, Victoria, Australia; ²School of Chemistry, Monash University, Clayton, Victoria, Australia; ³King Abdullah University of Science and Technology, Thuwal, Saudi Arabia.

Ammonia is one of the most important chemicals used in the modern society. As an essential precursor used in the fertilizer production, the supply of ammonia is strongly associated to food furnishing.¹ Without ammonia, it is predicted that more than half of the world population would starve. However, the synthesis of ammonia is extremely challenging due to the great thermodynamic stability of the nitrogen triple bond. Currently, more than 90% of the global ammonia commodity is produced by the Haber-Bosch process which is responsible for the release of ~12 Gt (1.5% of global total greenhouse gas emissions) of CO₂ into the atmosphere, annually.² Therefore, the synthesis of ammonia from atmospheric N₂ utilizing renewable energy sources with zero carbon footprint will become an important process in moving forward.³

Electrochemistry provides a direct pathway for N₂ conversion into NH₃ utilizing renewable electricity. Hitherto, the NH₃ electrosynthesis suffers from the drawbacks of low yield rate and selectivity (<10%), mainly due to the predominating hydrogen evolution reaction (HER).⁴ In this work, an electrochemical nitrogen reduction reaction (NRR) with a significantly enhanced selectivity and yield rate of NH₃ have been obtained via both electrode and electrolyte engineering. Surface area enhanced α -Fe@Fe₃O₄ nanorods were employed as the NRR cathode in an aprotic solvent – ionic liquid mixed electrolyte. Remarkably, a NH₃ yield rate of $\sim 2.35 \times 10^{-11}$ mol s⁻¹ cm⁻² with a high selectivity of ~32% was achieved. This work reveals that the abilities to both regulate the proton availability and enhance the N₂ solubility in the engineered electrolyte are imperative in achieving highly efficient NRR at room temperature and pressure.

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4:00 PM ET03.05.07

Nitrogen Fixation via Electrochemical Biosynthesis Under Ambient Atmospheric Environment [Shengtao Lu](#), Xun Guan and Chong Liu; Division of Chemistry, University of California, Los Angeles, Los Angeles, California, United States.

The hybridization of electrochemical interface and microbiological synthesis combines the high efficiency of electrochemical reactions and the catalytic capability of microbes to produce valuable chemicals. Such hybrid can be used for nitrogen fixation, which consumes renewable energy such as solar electricity, and enables distributed production of environmental-friendly fixed nitrogen species. However, a fundamental contradiction occurs as the crucial nitrogen fixing enzyme, nitrogenase, is incompatible with oxygen. This prevents nitrogen fixation via nitrogenase in air, the most abundant nitrogen source. Here we report a micro-structured electrochemical interface that solves this problem. Our design enables successful nitrogen fixation under ambient atmospheric conditions. We also prove that such interface is scalable, which enables potential applications.

4:15 PM ET03.05.08

The INCA (Ionomer Nc Analysis) Method, a New Approach to Study Perfluorinated Ionomers [Riccardo Narducci](#)^{1,2} and Maria Luisa Di Vona^{1,2}; ¹University of Rome tor Vergata, Roma, Italy; ²LIA, Roma, Italy.

Both the impelling need for a constant reduction of pollution in large cities and carbon dioxide in the atmosphere, as well as the continuous increase in petrol cost, have reinforced the interest in more efficient, clean, and sustainable systems such as fuel cells (FCs) for the conversion of electrical energy. However, the present FC technology does not give till now the wished performances and the complete assurance for a long durability in all climatic conditions. The proton conducting separators preferred by cars producers are perfluorosulfonic acid (PFSA) membranes at temperatures of about 80 °C. The main target of the use of the INCA Method (Ionomer Nc Analysis) is the study and the understanding of ionomers in the conditions of use and the improvement of ionomeric membranes under operating conditions. In this presentation we will illustrate the results obtained comparing pristine Nafion 1100, oriented Nafion 1100 prepared in our laboratory, and stabilized (crystalline) Nafion 1100 membranes treated with special annealing agents. We will propose the best tailor made annealing in order to avoid critical degradations of mechanical properties and ionic conductivity due to the formation of layered morphologies, prevalently oriented in the direction parallel to the membrane surface. Hence commercial Nafion 1100 membranes were treated with dimethylsulfoxide (DMSO) for 7 days at 140 °C, to increase the thermal stability because of the formation of semi-crystalline phase (physical crosslinking), followed by hydrothermal annealing in liquid water to obtain a suitable water Uptake (WU). The results obtained with the INCA Method will be compared with the Dynamic Mechanical Analysis (DMA) and tensile stress measurements. The INCA analysis was also used to study the effect of the presence of H-bond and/or crystallinity in un-crystallized Nafion 1100 prepared from the solution. This material, prevalently amorphous, has a melting temperature (Tm) lower of about 50 °C respect to commercial Nafion 1100, but presents a high WU in the same condition of temperature and relative humidity. At the same time we will present the effect of the variation of the equivalent weight (EW) on the Tm: the lowering of EW causes a decrease in Tm of 10 °C. The knowledge of this effect on Tm is fundamental for Aquivion membranes, which have a wide range of EW. The INCA method allowed us to evaluate the behavior of Aquivion membranes in fuel cell conditions and compare them with Nafion membranes. The results permit to suggest the most appropriate thermal/hydrothermal treatments to stabilized these ionomers, where the mechanical stability play a fundamental role.

4:30 PM ET03.05.09

Unveiling the Effect of Pt-Based L1₀ FCT Core in Core/Shell Nanoparticles for Oxygen Reduction Reaction [Mingjie Liu](#), Huolin L. Xin and Qin Wu; Brookhaven National Laboratory, Upton, New York, United States.

Rational design of active, durable and low-cost catalysts for oxygen reduction reaction (ORR) is highly desirable in fuel cell research. Nanoparticles with a core (Pt-based alloy)/shell (few layers of Pt skin) structure have attracted much attention due to their lower cost than pure Pt and potential benefits of activity tuning afforded by careful configuration of the core alloys. Previous theoretical work studying the enhancement effects has primarily focused on core alloys with cubic structures, i.e. disordered alloy or L1₂ ordered structure. In this work, using *ab initio* calculations, we have systematically investigated the structure-activity relationship of a new class of Pt_{0.5}M_{0.5} (M=V, Cr, Fe, Co, Ni, and Cu) core alloy that has a low-temperature tetragonal L1₀ intermetallic structure. We have calculated the adsorption energies of O, OH, and OOH on various Pt skins and the underlying tetragonal structured alloys. We comprehensively explore the interaction between Pt layers and host materials to acquire the best Pt thickness associated with certain host material, tuning the ORR activity toward the peak of the ORR volcano plot. We further decompose the enhancement factor into ligand, normal and shear strain effects in these systems and clarify the origin of the improved activity of this class of catalysts. Our results could facilitate future design of ordered intermetallic FCT structure in ORR applications.

4:45 PM ET03.05.10

Oxide Nanoparticles as High Performance Bifunctional Catalyst [Hongmei Luo](#), [Meng Zhou](#) and [Litao Yan](#); New Mexico State University, Las Cruces, New Mexico, United States.

Developing efficient electrocatalysts for oxygen evolution reaction (OER) and oxygen reduction reaction (ORR) are vital to the new generation of electrochemical storage and conversion devices such as electrolyzer, metal-air batteries, and fuel cells. For the demand of reversible fuel cells and rechargeable metal-air batteries, the bifunctional catalyst that can be used for both ORR and OER is gathering attention. In order to address the longstanding problems with high cost and poor stability of noble metal electrocatalysts, perovskite (ABO₃ formula, where A is rare-earth or alkaline metal and B is transition metal) with low cost, high versatility in structure and potential as bifunctional catalyst is of special interest. Applying our successful and novel polymer-assisted chemical solution (PACS) method, we will present the controlled synthesis of (La_{0.8}Sr_{0.2})_x(Mn_{1-y}B_y)O₃ (B: Ir and Co, x=0-0.1, y=0-0.2) nanoparticles with different particle sizes, A-site nonstoichiometry, B-site doping, and oxygen vacancy, and epitaxial thin films with different crystal orientations. Structural characterizations and electrochemical analysis are utilized to investigate the correlation between their compositions, structures, and electrochemical properties.

ET03.06.01

Nanoscale Three-Dimensional Resistivity Mapping of the Lithium-Ion Battery Solid Electrolyte Interphase on Silicon Anodes Caleb Stetson^{1,2}, Taeho Yoon², Yanli Yin², Steve Harvey², Andrew Norman², Chunmei Ban², Chunsheng Jiang², Steven DeCaluwe¹ and Mowafak Al-Jassim²; ¹Colorado School of Mines, Golden, Colorado, United States; ²National Renewable Energy Laboratory, Golden, Colorado, United States.

In lithium-ion batteries, the solid electrolyte interphase (SEI) is an important passivating layer formed on the anode from electrolyte decomposition products. On silicon anodes, the SEI is believed to be critical to battery reliability and performance. SEI must be both electronically insulating to prevent further electrolyte decomposition and ionically conductive to permit the flow of lithium ions. While electronic resistivity is a critical intrinsic property of SEI, characterization tools to investigate the electronic properties of this thin, reactive layer have been limited.

To advance understanding of the electronic properties of SEI, our group has developed an instrumental approach utilizing scanning spreading resistance microscopy (SSRM) to characterize electronic properties in three dimensions in the nanoscale. Resistivity vs. depth profiling results originating from this technique have shown that electronic resistivity decreases from the surface of SEI moving towards the SEI/Si interface. Moreover, total SEI thickness is readily calculated by the identification of electronically conductive silicon beneath the insulating SEI. Thickness of SEI is highly variable based on the electrolyte and the cycling conditions utilized. Additionally, two-dimensional mapping of electronic resistivity at varied depths within the SEI gives quantitative and qualitative data regarding the heterogeneity of SEI structures in the nanometer regime.

Investigation of reference materials with known electronic properties has allowed for determination of instrumental resolution. Characterization of model SEI systems with SSRM alongside transmission electron microscopy (TEM), X-ray photoelectron microscopy (XPS), and time-of-flight secondary ion mass spectrometry (ToF-SIMS) permits the association of electronic properties with specific SEI chemical components.

ET03.06.02

Muon Spin Spectroscopy as a Nanoscale Probe for Studying Ionic Diffusion in Electrode Materials Beth I. Johnston¹, Peter Baker² and Serena Corr¹; ¹University of Glasgow, Glasgow, United Kingdom; ²ISIS Pulsed Neutron and Muon Source, Didcot, United Kingdom.

Lithium ion batteries are ubiquitous in today's technology: they power our phones, laptops and are finding greater use for larger scale applications such as electric vehicles. Developments in sodium ion batteries are also of great current interest for use in stationary energy storage technologies such as grid storage for renewable energy sources.¹ The movement of Li⁺ or Na⁺ ions through the active electrode material in a battery is crucial for its electrochemical performance, yet quantifying this behaviour can be very technique dependant. For example, macroscopic ionic diffusion measurements can indicate greater activation energies for ion diffusion due to the extra impedance imparted by macroscopic grain boundaries. Here, we demonstrate the use of muon spin relaxation spectroscopy (μ^+ -SR) as a valuable local tool to probe the Li⁺ and Na⁺ diffusion dynamics in battery electrode materials. The μ^+ -SR method allows one to probe the nanoscale diffusion of ions via the muon spin perturbation due to diffusing ions nearby.² Developing a clearer understanding of these diffusion processes at a local scale can provide us insights into electrochemical behaviour and the opportunity to optimise and tailor performance.

We present the investigation of local ion diffusion in the polyanionic positive insertion electrode materials LiFeSO₄F and Na₂FePO₄F using μ^+ -SR for the first time. It is predicted that these structures possess multi-dimensional ionic diffusion pathways, suggesting facile ion diffusion.^{3,4} In addition to enhanced ionic diffusion, these compounds display high energy densities driven by the inductive effect where the presence of electronegative species such as fluoride changes the ionic-covalent nature of bonds. The results obtained from these μ^+ -SR studies indicate lower activation energies and larger diffusion coefficients at room temperature compared to values obtained by computational and bulk characterisation means. This indicates intrinsically favourable diffusion dynamics which could be accessed by improvements in, for example, engineering of materials to reduce impedance effects from grain boundaries.

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ET03.06.03

In Situ Electrochemical Dilatometry Study of Capacity Fading in Nanoporous Ge-Based Na-Ion Battery Anode During Sodiation-Desodiation Cycles Manni Li^{1,2} and Eric Detsi¹; ¹Materials Science & Engineering, University of Pennsylvania, Philadelphia, Pennsylvania, United States; ²Materials Science & Engineering, Harbin Institute of Technology, Harbin, China.

Although the rechargeable battery industry is currently dominated by lithium-ion battery technology, sodium-ion batteries are expected to play a key role in the near future, owing to the high abundance of raw sodium resources. Achieving high energy densities in sodium-ion batteries equal to, or exceeding lithium-ion batteries requires alloy-type high-capacity anode materials such as Sb, Sn, P, Ge [1]. However, alloying reaction of sodium with these materials result in significant phase transformation-induced stresses and volume changes, which ultimately cause a rapid capacity fading. In this work, nanoporous germanium was made by selective alloy corrosion and used to prepare sodium-ion battery composite slurry anodes. The performance of this composite electrode for reversible sodium storage was investigated by *in situ* electrochemical dilatometry, during which the (de)sodiation-induced macroscopic dimensional changes were recorded simultaneously during (dis)charging cycles, and for the first 200 cycles. (De)sodiation-induced dimensional changes and capacity fading were found to be proportional [2].

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ET03.06.04

Theoretical Investigations on the Structural and Electrochemical Properties of Silicon Nano-Particle Anode Material for Lithium-Ion Batteries Seung Eun S. Lee¹, Hyung Kyu Lim² and Sangheon Lee¹; ¹Chemical Engineering and Materials Science, Ewha Womans University, Seoul, Korea (the Republic of); ²Chemical Engineering, Kangwon National University, Seoul, Korea (the Republic of).

Lithium-Ion batteries (LIBs) are one of the most predominant energy storage systems for portable to stationary electronic devices. The LIBs are

indispensable to laptops, mobile phones, and electric vehicles due to their high energy/power density and long cycle life. Accordingly, there is a continuing increase in the technical demand for developing higher capacity/power LIBs. Especially, silicon (Si) has been intensively pursued as the most promising anode material for its high specific capacity (> 3500 mAh/g) and abundance. Despite its high capacity, Si suffers from fast capacity loss caused by its large volume change (> 300%), unstable solid electrolyte interphase (SEI) and physical disintegration (cracking and crumbling) of the electrode structure during lithiation/delithiation processes. Therefore, there are various research activities to control the physico-chemical stabilities of Si anode material. Currently, Si nanostructures such as nanowires and nanoparticle carbon composites are proved to be effective methods for improving capacity and cycling stability, since nano-sized Si can alleviate mechanical fractures during volume changes. In this work, we conducted a series of computational simulations to understand how the physico-chemical stabilities of nanostructured Si anodes are associated with the high surface ratio of Si nanostructures. Using Monte Carlo simulations within the first-principles based reactive force-field (ReaxFF) framework, we determined atomic structures of Si nanoparticles in terms of particle size and lithiation ratio. Then, we elucidated a unique relationship between the structure of Si nanoparticle anodes and their physico-chemical properties such as theoretical charge/discharge potentials, by using the density-functional theory (DFT) calculations. Our theoretical findings will provide future guidance for developing next-generation Si nanomaterials, which can be successfully applied to commercialization of Si anode materials.

ET03.06.05

Porous Paper Electrodes Using Layer-by-Layer Assembled Silver Nanoparticles with Room-Temperature Metallic Fusion Yongkwon Song, Seunghui Woo, Junsang Yun and Jinhan Cho; Department of Chemical and Biological Engineering, Korea University, Seoul, Korea (the Republic of).

The development of flexible and conductive electrodes is crucial for rapidly evolving flexible/wearable electronic applications. For this purpose, various Ag nanomaterials with high electrical conductivity, such as nanoparticles and nanowires, have been physically deposited onto flexible substrates, but the electrical conductivity and mechanical stability of these electrodes are still restricted. Including Ag nanomaterials, commercially available cellulose papers have received great attention as promising substrates for next-generation flexible electrodes due to their high flexibility, large specific surface area, lightweight and low cost. Herein, we introduce a highly porous paper electrode with bulk metal-like electrical conductivity using room-temperature metallic fusion-assisted layer-by-layer (LbL) assembly. The newly synthesized tetraoctylammonium thiosulfate (TOAS) stabilized-Ag NPs were LbL-assembled with tris(2-aminoethyl) amine (TAA), allowing the almost perfect ligand exchange reaction between bulky/insulating TOAS ligands and small TAA molecules. The introduced small TAA molecules connect between neighboring Ag NPs, significantly decreasing the interparticle distance of Ag-Ag NPs. In addition to the minimized interparticle distance of Ag-Ag NPs, the low cohesive energy of Ag NPs strongly induces metallic fusion between closely packed Ag NPs at room temperature without any additional treatments. The resultant multilayers of (TOAS-Ag NP/TAA)_n exhibits the bulk metal-like electrical conductivity of $\sim 1.60 \times 10^5 \text{ S cm}^{-1}$. When depositing the Ag NPs onto cellulose papers through our approach, the insulating papers can be converted to flexible and bulk metal-like conductive papers that can be used as 3D current collectors for high-performance energy storage devices.

ET03.06.06

Electron-Dense Ligands and Their Optoelectronic Effects on PbS Quantum Dot Photovoltaics Daniel Gregory, Hazel Assender and Andrew Watt; University of Oxford, Oxford, United Kingdom.

Quantum dot solar cells offer a low-cost route to flexible photovoltaics, with additional effects such as the relative ease of multiple exciton generation (MEG) offering tantalising possibilities of breaking the shockley-queisser limit in the future. However, bottlenecks in device design and fabrication currently limit this technology's record efficiencies. Chief among those problems are the mobility of charges within the quantum dot layers of the device – causing a reduction in fill factor - and the need for stronger n-doping to improve open circuit voltages. One method of suppressing these problems is through ligand passivation, or combinations thereof. Current research has focused on ever-smaller ligands, down to individual halide ion passivation with dissociating organic salts, while research into the effects of substituent groups residing beyond the coordinating groups of small molecules has waned. This research begins with the introduction of novel ligand systems using electron-dense substituents outside the coordinating functional group, and follows with an exploration of the optoelectronic properties this class of ligands can provide to PbS quantum dot films, finishing with an overview of the photovoltaic performance of these systems.

ET03.06.07

Two-Dimensional Hexagonal Indium Selenide Nanosheets for Li-Ion Battery Applications Valeria Nicolosi, Chuanfang Zhang and Meiyang Liang; Trinity College Dublin, Dublin, Ireland.

Metal chalcogenides (MCs), including metal sulfides, metal selenides and metal tellurides, have attracted tremendous attention for energy storage applications and development of rechargeable lithium-ion batteries due to their unique physicochemical properties (e.g. high electrical conductivity, good thermal stability, earth abundance, etc.). Especially, MCs possess higher theoretical specific capacities for rechargeable lithium-ion batteries compared to traditional intercalation electrode materials. In addition, metal chalcogenides tend to be more electrochemically reversible as compared to metal oxide counterparts due to their faster charge transfer kinetics.

Recently, as an alternative anode material for replacing currently commercialized graphite or carbon-based anode materials, various two dimensional (2D) MCs materials, such as 2D gallium sulfide nanosheets, are investigated because of their large theoretical capacity. However, there is still a plenty of room for the development of new efficient anode materials from 2D MCs since only a few studies are carried out for this type of materials. In this work, hexagonal shape layered indium selenide (InSe) was prepared via phase-controlled synthesis method and 2D InSe nanosheets were obtained via liquid phase exfoliation approach. Then, single-wall carbon nanotube (SWCNT) was added to improve the conductivity and flexibility of the hexagonal shape 2D InSe nanosheets electrodes for lithium-ion batteries' anodes. Compared to commercially available InSe and bulk layered InSe, the hexagonal shape 2D InSe nanosheets displays the most excellent rate capability and high specific capacity (926 mAh g⁻¹ and 595 mAh g⁻¹ at 50 mA g⁻¹ and 2 A g⁻¹, respectively). In addition, it shows exotic cycling stability. The capacity of it has increased with the increase of cycling numbers (the capacity of the battery dramatically increased in the first 100 cycles and it continuously increased until 900 cycles), which means the quality of a battery will be improved when the battery is used. This work opens up vast opportunities for InSe to be scalably processed into flexible conductive composite films with a broad range of applications such as wearable electronics, optoelectronics, and other energy storage systems.

ET03.06.08

Nickel Vanadium Layered Double Hydroxides Nanostructures for High-Performance Flexible Supercapacitor Applications Ankit Tyagi and Raju Kumar Gupta; Department of Chemical Engineering, Indian Institute of Technology Kanpur, Kanpur, India.

In recent times, demand for portable electronic devices like mobile phones, cameras, and laptops, etc. is increasing day by day. Energy storage devices such as batteries and supercapacitors have significant importance because of their high energy density and high power density, respectively.¹ The supercapacitor is gaining a considerable amount of attention because it uses the less toxic material, offers high power density, excellent electrochemical stability, a wide range of operating temperatures and durability. Facile fabrication of low cost, efficient, stable, eco-friendly and earth-abundant electrode materials for supercapacitors is critical.² Layered double hydroxide (LDH) is a new class of material having positively charged hydroxalcalite-like layers, weakly bound, intercalating charge compensating anions and water molecules, has shown tremendous supercapacitive performance.³ In this work, an ionic lamellar, two-

dimensional (2D) nickel-vanadium layered double hydroxide (NV LDH) nanosheets have been synthesized via facile, cost-effective and potentially scalable hydrothermal method. The as-prepared 2D NV LDH nanosheets over carbon cloth (NVL@CC) was used as the supercapacitor electrode. The electrochemical characterization techniques such as cyclic voltammetry (CV), galvanostatic charge-discharge (GCD) and electrochemical impedance spectroscopy (EIS) were used to characterize the material for its electrochemical properties, while SEM, TEM, XRD, BET, and XPS, etc. techniques have been used for their morphological, structural and physical characterization. The high specific capacitance of $\sim 2600 \text{ F g}^{-1}$ at the current density of 1 A g^{-1} was observed in a three-electrode system using KOH as an electrolyte, which remained quite high at an increased current density of 10 A g^{-1} . This work demonstrates excellent potential for NV LDH nanosheets as an electrode material for supercapacitor applications.

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ET03.06.09

Improvement of LiCoO₂ High Voltage Cycling Stability by Nanoscale Polymer Surface Engineering via Chemical Vapor Deposition Polymerization Laisuo Su and B. Reaja Jayan; Mechanical Engineering, Carnegie Mellon University, Pittsburgh, Pennsylvania, United States.

The interface between an electrode and electrolyte is crucial to the overall performance of lithium ion batteries (LIBs). Here we demonstrate chemical vapor deposition polymerization as a novel method to improve the performance of LiCoO₂ cathode electrode for LIBs, including both rate capability and high voltage (4.5 V) cycling stability. Three polymers are utilized to engineer the surface and CR2016 coin cells are fabricated to study the effect of these polymers on LIBs electrochemical performance. The three polymers are poly(3,4-ethylenedioxythiophene) (PEDOT), poly(divinylbenzene) (PDVB) and poly(divinylbenzene-co-1H,1H,2H,2H-perfluorodecyl acrylate (P(DVB-co-PFDA)). Our results show that the PEDOT improves both the rate and the high voltage cycling performance of LiCoO₂ electrodes, the PDVB has little effect on the both performances, while the P(DVB-co-PFDA) inhibits the performances. The PEDOT coating increases 10C rate capacity by 62% (from 34 to 55 m Ah/g). The high voltage cycling number is increased by 250% (from 40 to 100 times) when the capacity decreases to 50% of its initial capacity. X-ray photoelectron spectroscopy is applied to understand the improvement of cycling stability. The results suggest that chemical or coordination bonds form between Co in LiCoO₂ and O and S in the PEDOT film, while there is no bonds formation from the PDVB or the p(DVB-co-PFDA) coatings. The bonds stabilize the surface of LiCoO₂ and thus improve the high voltage cycling performance. This work introduces chemical vapor deposition polymerization as a new research tool for surface modification and interface engineering of lithium ion battery electrodes.

ET03.06.10

Mutually Embedded MOF-Derived Uniformly Dispersed Co₃S₄ within Porous Graphitic Carbon Polyhedrons and Carbon Nanotube Sponge for Ultralong Life Lithium-Sulfur Batteries Hui Zhang; Peking University, Beijing, China.

Lithium sulfur battery represents an advanced energy storage system because of its environmental benignity, high theoretical energy density (2600 Wh kg^{-1}) and natural abundance of sulfur. However, the low conductivity of sulfur, polysulfides dissolution, and sulfur volumetric expansion during lithiation/delithiation process will decrease the reaction kinetics of polysulfides and sulfur utilization, leading to low capacity, limited rate capability and inferior cycling stability. To solve these problems, there have been intensive efforts in choosing highly conductive carbon materials to design porous or hollow structures for secure sulfur hosts. Although these materials can effectively alleviate polysulfides dissolution during short-time cycling, the weak interaction with polar polysulfides will inevitably results in increase of charge transfer and dissolution of polysulfides over long-time electrochemical reaction.

Here, we first grew ZIF-67 nanoparticles ($\sim 350 \text{ nm}$) uniformly within a three-dimensional carbon nanotube sponge, and after carbonization and sulfuration, we finally fabricated a hybrid network with numerous carbon nanotubes penetrating hierarchically porous graphitic carbon polyhedrons uniformly dispersing Co₃S₄ nanoparticles (from ZIF-67) to host sulfur. Co₃S₄ has been reported to have strong affinity to polysulfides, and can act as a catalyst to accelerate the conversion of polysulfides to Li₂S₂/Li₂S (insoluble discharged products), which are beneficial for improving battery cycling stability (polysulfide stabilization) and rate capability (increased reaction kinetics). In our system, highly dispersed Co₃S₄ nanoparticles can provide sufficient sites to trap polysulfides and catalyze the conversion reaction smoothly, additionally the outer wrapping porous graphitic carbons (physical barriers) can further protect polysulfides from dissolving into the electrolyte. Moreover, the highly three-dimensional conductive CNT and graphitic carbon hybrid network acting as a self-standing electrode can not only facilitate electrolyte infiltration and charge transport, but also improve sulfur loading and utilization. As a result, our novel 3D hybrid electrodes exhibit a much superior ultralong Li-S battery performance than previously reported MOF-based electrodes in recent literature.

ET03.06.11

Photo- and Redox-Active Eumelanin on Carbon Quantum Dot Current Collectors as Sustainable Electrode Material for Solar Batteries Abdelaziz M. Gouda¹, Francesca Soavi² and Clara Santato¹; ¹Engineering Physics, Ecole Polytechnique Montreal, Montreal, Quebec, Canada; ²Department of chemistry, University of Bologna, Bologna, Italy.

With the increase in energy demand and the booming environmental crisis, the use of renewable energy sources, such as the Sun, has become an urgent matter in our daily life. Within this context, developing efficient, stable, low-cost and environmentally friendly solutions integrating solar energy harvesting and energy storage (batteries and supercaps) is a key challenge. Among electrochemical energy storage solutions, aqueous rechargeable batteries are particularly interesting since, in principle, they are safe and do not make use of critical elements [1].

Melanin is a bio-pigment found in various classes of mammals, fishes, and different species of plants. This organic bio-pigment features unique physiochemical properties such as UV-Vis-near IR absorption, redox activity (hydroquinone-semiquinone-quinone couples), metal chelation and ionic-electronic hybrid electrical conduction [2]. The photoredox properties of melanin combined to its capability to reversibly bind cations opens the door to explore this intriguing quinone-based material as electrode for solar batteries [3].

Here we report on the use of melanin on carbon quantum dots (CQD)-based current collectors. CQDs offer high surface area to the redox active melanin and facilitate the electron transport to the back contact. Cyclic voltammetry and galvanostatic charge/discharge cycles were employed to evaluate the storage performance of the melanin-electrode materials at different pH conditions and chemical composition of the electrolyte (e.g. including cations such as H⁺, Na⁺, K⁺, Mg²⁺), under simulated solar light. We observed that the redox state of the melanin-based electrodes affects its photoresponse. Our work constitutes a relevant contribution towards (photo)electrodes for sustainable, aqueous, rechargeable solar batteries.

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ET03.06.12

Comparison of Stress Evolution in Silicon and Silicon Oxide Composite Electrodes Mok Yun Jin¹, Ravi Kumar² and Brian W. Sheldon¹; ¹Brown University, Providence, Rhode Island, United States; ²Ram Research Corporation, Tualatin, Oregon, United States.

Silicon has received much attention as a promising negative electrode material, owing to its greater theoretical capacity than state-of-the-art graphite negative electrodes. Silicon, however, undergoes internal microstructural changes and large volume changes that induce substantial compressive stresses inside of particle-based electrodes. These are believed to contribute to poor cycling performance. In the present work, in-situ stress and electrochemical measurements are monitored directly to capture stress evolution in silicon and silicon oxide composite electrodes with various particle sizes. Silicon nanoparticle electrodes reveal a stress response with notable hysteresis characterized as plastic flow. When silicon oxide(SiOx) is incorporated, the cycling performance improves and the amount of stress decreases. The stress response of electrodes based on SiOx composite particles also shows more reversible and elastic behavior compared to electrodes with silicon nano particles.

ET03.06.13

High Tap-Density and Layer-by-Layer Assembled LiFePO₄ Nanosheets as Advanced Cathode Materials used in High Power Li-Ion Batteries Haijun Zhang^{1,2}, Ben Pei^{2,1}, Lu Zhang³, Wenwu Qin², Jun Zhang^{3,1} and Jiye Fang¹; ¹SUNY Binghamton, Binghamton, New York, United States; ²Lanzhou University, Lanzhou, China; ³China University of Petroleum, East China, Qingdao, China.

As a class of outstanding cathode material for lithium ionic (Li-Ion) batteries, LiFePO₄ has an obstacle of low rate capability due to its slow Li ionic diffusion and poor electronic conductivity as well as power density issue. To improve this, one should shorten the channels of Li-ion travelling (i.e. reduce the dimension of LiFePO₄ in <010>), and enhance the particle impact on the same crystallographic orientation. According to this hypothesis, one of the proposals is to produce 2D LiFePO₄ as the building block materials by exposing their {010} facets as the termination planes, and to further pack these 2D LiFePO₄ along the <010> direction efficiently. Herein, we report a novel synthesis of ultrathin 2D LiFePO₄ nanosheets using a modified hot organic solvent approach. The structure of the resultant LiFePO₄ is precisely controlled with some unique features: the nanosheets exhibit in shape of rectangle with a thickness of as small as ~10 nm. Importantly, the exposed planes are {010}, which can maximize the channels for the travel of Li-ions. Calcination of the oleylamine/oleic acid capped LiFePO₄ nanosheets resulted in densely hierarchical structures containing Layer-by-Layer stacked assemblies with a tap density as high as 1.3 g cm⁻³. In contrast, the tap density of freestanding LiFePO₄ nanomaterials is usually less than 1.0 g cm⁻³. The in-situ generated carbon blacks from the pyrolysis of the capping ligands act as not only a medium conductor for the electrons but also a baffle to possibly prevent the nanosheets from fusing into larger particles during the calcination. With such an in-situ carbon coating evenly on every single nanosheet, the 2D LiFePO₄/C composite nanosheets self-assembled into superstructures. The electrochemical evaluations on these LiFePO₄/C assemblies show a reversible specific capacity of as high as 105 mAh g⁻¹ at 10 C, as well as an excellent rate capability and cycling performance. Both the high tap density and high-rate capability are promising for the increase of volumetric power and energy density as Li-ion cathodes. Such layer-by-layer compacted patterns, rather than an accumulation of disordered building blocks, could also effectively increase both gravimetric and volumetric power densities of LiFePO₄ electrodes, paving the way for promoting high-rate capacity and minimizing the ionic diffusion issue by shortening the length of Li-ion travelling channels.

ET03.06.14

Capacitive Performance of C₆₀-Functionalized Graphene Supercapacitors—Atomistic Origins and Implications Tuan Anh Pham¹, Cheng Zhan^{1,2}, Maira Raquel Ceron Hernandez¹, Patrick G. Campbell¹, Vedasri Vedharathinam¹, Minoru Otani³, De-en Jiang², Juergen Biener¹, Brandon C. Wood¹ and Monika Biener¹; ¹Lawrence Livermore National Laboratory, Livermore, California, United States; ²University of California, Riverside, Riverside, California, United States; ³National Institute of Advanced Industrial Science and Technology, Tsukuba, Japan.

Controlling the electrical response at the electrode-electrolyte interface is key to the development of next-generation supercapacitors and other electrochemical storage systems. In this work, we utilize first-principles calculations to elucidate the key factors that determine the performance of C₆₀-functionalized graphene as a promising carbon-based supercapacitor material. We show that, for the hybrid electrode, the surface morphology influences the electric double-layer (EDL) formation by affecting the charge localization character, which in turn significantly enhances the EDL contribution to the capacitance, in sharp contrast to pristine graphene. In addition, the electronic structure was found to govern not only the quantum capacitance but also the double-layer response. Our study highlights a complex interplay among surface morphology, electronic structure and functionality of the hybrid electrode, suggesting general improvement strategies for optimizing EDL and total capacitance in carbon-based supercapacitor materials.

ET03.06.15

Electrospun Polymer-Ceramic Composite Separator for Structural Battery Applications Wisawat Keaswejareansuk and Jianyu Liang; Worcester Polytechnic Institute, Worcester, Massachusetts, United States.

Lithium-ion battery (LIB) is widely utilized in many modern applications as energy sources. Numerous efforts have been dedicated to increasing electrochemical performances, but improvement on battery safety remains a visible challenge. While new electrode materials have been developed, advancement in new separators for LIBs has remained relatively slow. A separator is the polymeric porous material that physically separates electrodes and allows free flow of ions through its structure. It is electrochemically inactive but essential for avoiding thermal runaway conditions. Besides its crucial functions, the separator has been known as the mechanically weakest component. Structural battery is a new approach that employs a multifunctional material concept to use LIB as a load-bearing material to minimize the weight of the complete system and maximize the efficiency. Separator materials are required to have good thermal stability, battery chemistry, and mechanical performance. This work aims at creating electrospun membranes with improved thermal resistance and structural integrity as the next generation LIB separators. The electrospinning (ES) is known as a versatile and straightforward technique to fabricate continuous fibers at nano- and micro- scales. Solution and process parameters including, type of polymer and solvent system, concentration of polymer solution, acceleration voltage, and solution feed rate have been studied to achieve the desirable membrane properties. Adding various ceramic materials to the polymers have been studied for improving the thermal shrinkage, increasing ionic conductivity and, decreasing interfacial resistance of the composite separators. In this study, nanofibrous membranes are created by the electrospinning process. Graphene oxide is used due to its high storage modulus. Synthesized, non-conductive graphene oxide and titanium dioxide nanoparticles (for comparisons) are incorporated into the polymer solutions for the electrospinning. In this presentation, we will discuss the control of electrospinning process, graphene oxide synthesis and properties of composite membranes for structural battery applications.

ET03.06.16

Facile and Cost effective Synthesis of Ultrathin and Porous Nitrogen Enriched Carbon Hollow Shells for Energy Storage Application Gihwan Kim¹ and Jeung Ku Kang^{2,1}; ¹Department of Materials Science and Engineering, Korea Advanced Institute of Science and Technology, Daejeon, Korea

(the Republic of); ²Graduate School of EEWs, Korea Advanced Institute of Science and Technology, Daejeon, Korea (the Republic of).

Mesoporous carbon materials have received intensive attention due to their wide applications including energy storage/conversion, catalysis and absorption. Herein, ultrathin and porous nitrogen enriched carbon hollow shells have been synthesized by a facile and cost effective sol-gel coating method using different ratio of carbon precursor and nitrogen precursor. As-synthesized hollow shells possessed uniform size of ~120nm in diameter and ~4.5nm significantly thin, porous shells obtained from silica template that size controlled by solvent ratio. As the ratio of nitrogen precursor increased, thinner and smaller shells were synthesized. In lithium ion hybrid capacitor system, cathode electrode material is storing electrical energy through electrical double-layer capacitance mechanism of electrode surface. Based on these mechanisms, as-synthesized ultrathin and porous nitrogen enriched carbon hollow shells used as a cathode material of lithium ion hybrid capacitor. It is shown remarkable electrochemical performance, delivering a high reversible capacity (~48mAh/g in 3V~4.5V (Li/Li⁺) potential range) as well as superior rate performance for long cycles in an organic solvent system. These excellent results can be attributed to two major reasons. First, hollow and porous structures could improve the properties of surface adsorption for lithium ion capacitor by facilitating the accessibility of ions. Sites from both inside and outside of carbon shell can be accessed by PF₆⁻ ions, whereas the closed window of the pore for solid sphere can offer the sites for electrostatic adsorption only on the outside surface. Second, nitrogen contents could significantly change the interaction sites and enhance the adsorption of ion towards a carbon shell framework. These effects are also shown in capacity analysis of various synthesized samples with different amounts of nitrogen precursor. As the nitrogen content increased, the capacity tended to increase. Even in the case of carbon precursor only, the capacity is less than half of that of nitrogen contained hollow shells. This simple and cost effective strategy could be extended to synthesize tunable interior architecture mesoporous carbon composites like yolk-shell structure and core-shell structure with metal, metal oxide. Also, due to the characteristic of the nitrogen-containing material, it can be applied to various ions adsorption. By applying this phenomenon, it can be utilized not only for commercial carbon material like an electric double layer capacitor (EDLC) but also for various electrochemical energy storage and conversion application.

ET03.06.17

Electrochemical Behaviors of Room Temperature Ionic Liquids—Carbon Electrodes Interfaces Kirti Bhardwaj and Greg Swain; Michigan State University, East Lansing, Michigan, United States.

Room temperature ionic liquids (RTILs) have great potential to replace conventional organic solvent/electrolyte systems in energy storage devices because of their remarkable properties like wide electrochemical potential window (> 4V), environmentally-benign characteristics (non-volatility, non-toxicity) and excellent thermal and electrochemical stability. To optimally harness these properties and engineer RTIL-based devices, a comprehensive fundamental understanding of their electrochemical behavior is critical. Understanding the structure, distal extent, and dynamics of interfacial organization at RTIL-polarized electrodes interfaces has been the subject of both fundamental and applied research, particularly in the field of supercapacitors. Research is needed to better understand how electrode properties, like its material, microstructure, surface chemistry, affect the electrochemical behavior of RTILs. Traditional models of the electrochemical double layer based on the dilute-solution approximation may not be applicable to RTILs because of the absence of solvent, high concentration of ions (3-7 M), asymmetric charge distribution and strong interionic interactions.

In this presentation, potential dependent capacitance of carbon electrodes as a function of the RTIL type, carbon electrode type and surface wettability will be reported on. 1-alkyl-3-methylimidazolium-based RTILs were studied at hydrogen- and oxygen-terminated boron-doped-diamond and nitrogen-incorporated tetrahedral amorphous carbon thin-film electrodes. Comparison measurements were made in aqueous electrolytes. Cyclic voltammetry and electrochemical impedance spectroscopy were used to measure the interfacial capacitance. Our findings suggest that interfacial capacitance depends on the length of alkyl chain in the cationic component of RTIL. Capacitance-potential (C-E) trends on carbon electrodes are in stark contrast with theoretical models predicted for metallic electrodes. It is intriguing that heavily-doped diamond behaves as a metal with respect to faradic processes has characteristic interfacial behavior. This work highlights the unique C-E trends shown by carbon electrodes in RTILs and serves to progress the current understanding of interfacial organizations and the role of electrode-electrolyte interactions.

ET03.06.18

Freestanding 2D MXene/Polyaniline Pseudocapacitive Electrodes with High Mass loading and Ultrahigh Gravimetric and Volumetric Capacitances Armin VahidMohammadi and Majid Beidaghi; Auburn University, Auburn, Alabama, United States.

Two-dimensional (2D) MXenes (i.e. Ti₃C₂T_x) have shown fascinating performances as electrode materials for electrochemical capacitors (ECs). However, conventional methods for fabrication of freestanding MXene films results in their self-restacking, decreasing ions accessibility to their redox-active sites and limiting their rate-capability. These problems are more signified for thicker electrodes and, as a result, fabrication of MXene electrodes with thicknesses and mass loadings close to commercial EC electrodes is not feasible. Here, we demonstrate a strategy to fabricate hybrid electrodes of MXene and conductive polyaniline (PANI) with highly accessible surfaces and excellent electrochemical performance event at high mass-loadings and thicknesses. The freestanding and flexible films of Ti₃C₂T_x/PANI were fabricated through an oxidant-free *in situ* polymerization of aniline monomer on the surface of MXenes sheets. The fabricated hybrid electrodes delivered outstanding gravimetric and volumetric capacitances of 503 F g⁻¹ and 1682 F cm⁻³, respectively, at a scan rate of 2 mV s⁻¹. Even at electrode thicknesses close to commercial ECs, these hybrid electrodes could maintain their high specific capacitance. For instance, a 90-μm-thick electrode with a mass loading of 23.82 mg cm⁻² could deliver a specific capacitance of about 336 F g⁻¹ and 888 F cm⁻³ in a sulfuric acid electrolyte. The MXene /PANI hybrid electrodes also showed a long cycle life with a capacitance retention of 98.3% after 10,000 cycles.

SESSION ET03.07: Carbon Dioxide Reduction
Session Chairs: Bin Liu and Karthish Manthiram
Wednesday Morning, November 28, 2018
Hynes, Level 3, Room 302

8:00 AM ET03.07.01

A Novel Hybrid Anion Exchange Membrane with High Performance by Incorporating Quaternary Ammonium-Functionalized Covalent Organic Frameworks Jia Chen¹ and Shaokun Tang^{1, 2}; ¹School of Chemical Engineering & Technology, Tianjin University, Tianjin, China; ²Collaborative Innovation Center of Chemical Science and Engineering (Tianjin), Tianjin University, Tianjin, China.

In recent years, alkaline anion exchange membrane fuel cells (AAEMFCs) have a rapid development due to their advantages including high electrode reaction activity, free from precious metal catalysts, low fuel permeation and so on. However, anion exchange membrane (AEM), which is a crucial

component in AEMFCs, continue to perform unfavorably owing to its low conductivity and poor alkaline stability. Thus, constructing novel hydroxide-conducting materials with both high ionic conductivity and good alkaline stability for AEM has attracted wide interest. Herein, we have designed and synthesized a new hybrid membrane with high alkaline and thermal stability *via* combining quaternary ammonium (QA) functionalized covalent organic framework and brominated poly (2,6-dimethyl-1,4-phenylene oxide) (BPPO). Covalent organic framework was quaternized *via* in situ assembly of N,N,N',N'-tetramethyl-1,6-hexanediamine (TMHDA) and allyl bromide within the highly ordered pores of two-dimensional imine-linked COF-LZU1, to fabricate long-range ordered one dimensional ion channels. The obtained QA@COF-LZU1 as a novel filler was then incorporated into QAPPO to fabricate hybrid anion exchange membrane for the application in AAEMFCs. Hybrid membranes were evaluated by hydroxide conductivity, alkaline stability, thermal stability, and so forth. Remarkably, the QA@COF-LZU1/PPO hybrid membranes showed high hydroxide conductivity, and alkaline and thermal stability of QA@COF-LZU1/PPO hybrid membranes were significantly enhanced.

8:15 AM ET03.07.02

Understanding Structure-Property Relationships in Nanocatalysts by Using Cluster Expansions [Chenyang Li](#)¹, David Raciti², Yuxuan Wang², Liang Cao¹, Chao Wang² and Tim Mueller¹; ¹Materials Science and Engineering, Johns Hopkins University, Baltimore, Maryland, United States; ²Chemical and Biomolecular Engineering, Johns Hopkins University, Baltimore, Maryland, United States.

Density functional theory (DFT) is widely used to predict the structures and properties of materials, but its direct applications to nanomaterials of experimentally relevant sizes can be prohibitively expensive. It has been demonstrated that this problem can be addressed through the generation of cluster expansion models trained by DFT. In this talk, two examples of using cluster expansions to better understand structure-property relationships in nanocatalysts are given. In the first example, we compare predicted Pt-Cu nanoparticle structures with experimental characterization. We demonstrate that the best agreement is achieved by constructing a novel cluster expansion for alloy nanoparticles of varying shape and size that explicitly includes adsorbates, enabling the prediction of nanoparticle structure in an oxidizing environment. In the second example we present a study of the CO₂ reduction reaction (CO₂RR) on Au nanowires. Nanowires with the 4H structure have shown enhanced activity relative to fcc nanowires and nanoparticles. Cluster expansions are used to predict the equilibrium surface structures of fcc, 4H, and twinned nanowires. DFT calculations are then performed on the extended surfaces identified from cluster expansions to construct a free energy diagram for CO₂ reduction. The enhanced CO₂RR activity on 4H-Au nanowires is ascribed to the unique surface structure of the 4H phase, which could provide design principles for experimental research.

8:30 AM *ET03.07.03

Nanoparticle Catalysts for Electrochemical Transformation of Carbon Dioxide to Value-Added Products [Peidong Yang](#)^{1,2} and Dohyung Kim^{1,2}; ¹University of California, Berkeley, Berkeley, California, United States; ²Lawrence Berkeley National Laboratory, Berkeley, California, United States.

Electrochemical conversion of CO₂ to valuable products has gained much interest recently, as a part of the many efforts to develop sustainable practices that can support our society. Among a variety of approaches, utilizing nanoparticles as CO₂ electrocatalysts have brought significant advances to the field. Here, various structural aspects of nanoparticles used as electrocatalysts, that range from the atomic scale all the way to the macroscopic length scales, are correlated with their CO₂ electrocatalytic performances. Furthermore, the catalytic role of the dynamics of nanoparticles has been explored which can be utilized to promote their CO₂ reduction activity. The complexity originating from the larger number of structural variables associated with nanoparticles requires a deepened understanding of their combined effects to the catalytic behavior of nanoparticles. Acknowledging this complexity and a thorough consideration of its impact will lead to further improvements of nanoparticles used as CO₂ electrocatalysts.

9:00 AM *ET03.07.04

Electrochemical Synthesis of Highly Concentrated C₂ Product Streams [Matt Kanan](#); Chemistry, Stanford University, Stanford, California, United States.

Electrochemical CO₂ and CO conversions provide direct pathways to harness renewable electricity for chemical and fuel synthesis. This talk will describe our recent work to develop catalyst- and cell-design principles for electrochemical systems that generate concentrated C₂ product streams. For the catalyst, a key issue is to identify structural features that favor CO₂/CO reduction over H₂O reduction at low overpotentials. We have previously shown that grain boundaries are correlated with electrocatalytic activity for CO₂ reduction on Au and CO reduction on Cu electrodes, but not with H₂O reduction on these materials.^{1,2} I will describe our recent work to uncover the structural origin of grain boundary effects. Experimental studies combining electron diffraction grain mapping and spatially resolved (<1 μm) electrocatalytic measurements have revealed that grain boundary surface terminations are “hot spots” for electrocatalytic CO₂ reduction on coarse-grained Au electrodes.³ This phenomenon may result from the accumulation of line defects in the grain boundary vicinity, which perturb the surface structure. I will discuss our efforts to test this model with nanograined materials and extend these studies to electrochemical CO reduction on Cu. For the cell design, practical electrosynthesis must simultaneously achieve high synthesis rates and high single-pass conversions of CO₂/CO at low potentials to maximize the energy efficiency and minimize the separation costs. To this end, we have developed a gas-diffusion CO electrolysis cells that reach >100 mA cm⁻² with >70% single-pass conversion at moderate cell potentials. With optimized electrode/membrane interfaces, the cells can simultaneously produce concentrated ethylene in the gas phase and a liquid product stream that is nearly 1 M in acetate. I will discuss the design features that are critical for generating concentrated products and efforts to optimize nanostructured catalysts for high synthesis rates.

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2. Feng, X., Jiang, K., Fan, S. & Kanan, M. W. *ACS Cent. Sci.* **2**, 169-174 (2016).

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9:30 AM *ET03.07.05

Insights into the Electrocatalytic Conversion of CO₂ into CO or Ethylene/Ethanol in Alkaline Media [Paul Kenis](#); University of Illinois at Urbana-Champaign, Urbana, Illinois, United States.

Utilization of CO₂ as a feedstock for the production of intermediates for chemical or fuel production such is one of several approaches being explored to help reduce anthropogenic CO₂ emissions, while also reducing society's dependence on fossil fuel reserves. A range of active electrocatalysts for the selective reduction of CO₂ to products such as formic acid, CO, ethylene, and ethanol have been reported. We have explored both Ag- and Au-based catalyst as well as micro-structured CuAg alloy films, respectively for the selective and energy efficient reduction of CO₂ to CO [1,2] and to ethylene and ethanol [3]. Partial current densities for CO exceeding 150 mA/cm² at cell overpotentials less than 1V now can be achieved routinely at energetic efficiencies of 50-60%. Similarly, high surface area CuAg alloy films exhibit Faradaic efficiency for C₂H₄ and C₂H₅OH production of 60% and 25%, respectively, at a cathode potential of just -0.7 V vs RHE and a total current density of ~300 mA/cm², the highest levels of selectivity at high activity and low applied potential reported to date. This talk will report mechanistic insights regarding CO₂ electroreduction on these different catalysts in alkaline electrolyte. E.g., the onset cathode potentials, the kinetic isotope effect, and Tafel slopes indicate that the production of CO at low overpotentials in alkaline media is the result of a pH-independent rate-determining step (i.e., electron transfer) in contrast to a pH-dependent overall process. Also, in situ Raman and

electroanalysis studies suggest that the origin of the high selectivity toward C2 products observed with CuAg alloy films results from both the enhanced stabilization of the Cu₂O overlayer and the optimal availability of the CO intermediate due to the Ag incorporated in the alloy. The talk will also provide a summary of techno-economic feasibility of CO₂ electrolysis for the production of these different intermediates.

Gold Nanoparticles on Polymer-Wrapped Carbon Nanotubes: An Efficient and Selective Catalyst for the Electroreduction of CO₂, H.R.M. Jhong, C.E. Tornow, C. Kim, S. Verma, J. L. Oberst, P.S. Anderson, A.A. Gewirth, T. Fujigaya, N. Nakashima, P.J.A. Kenis, *ChemPhysChem*, **2017**, 18 (22), 3274-3279.

Insights into the Low Overpotential Electroreduction of CO₂ to CO on a Supported Gold Catalyst in an Alkaline Flow Electrolyzer, S. Verma, Y. Hamasaki, C. Kim, W. Huang, S. Lu, H.R.M. Jhong, A.A. Gewirth, T. Fujigaya, N. Nakashima, P.J.A. Kenis, *ACS Energy Lett.*, **2018**, 3, 193-198.
Nanoporous Copper–Silver Alloys by Additive-Controlled Electrodeposition for the Selective Electroreduction of CO₂ to Ethylene and Ethanol, T.T.H. Hoang, S. Verma, S. Ma, T.T. Fister, J. Timoshenko, A.I. Frenkel, P.J.A. Kenis, and A.A. Gewirth, *J. Am. Chem. Soc.*, **2018**, 140 (17), 5791–5797.

10:00 AM BREAK

10:30 AM ET03.07.06

Understanding and Tuning CO₂ Reduction on Copper Electrocatalysts Marcel Schreiber¹, Michael Graetzel² and Yogesh Surendranath¹; ¹Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States; ²Chemistry and Chemical Engineering, Ecole Polytechnique Federale de Lausanne, Lausanne, Switzerland.

CO₂-derived fuels, electrochemically synthesized using renewable energy, present an attractive route towards fuel formation from sustainable energy. However, insufficient understanding of the factors controlling catalytic activity and selectivity, as well as the limited availability of selective, active and inexpensive catalyst materials remain key challenges on the way to the production of renewable carbon fuels. Copper is a particularly interesting electrocatalyst for this reaction since it can reduce CO₂ to a variety of products including carbon monoxide and hydrocarbons but rational modification of its selectivity towards a single product remains challenging. In this context, we here demonstrate the successful tuning of copper electrocatalysts towards the selective production of CO from CO₂ and we present unprecedented insight into the mechanistic pathways governing the electrochemical reduction of CO to hydrocarbons on copper surfaces.

Atomic Layer Deposition (ALD) is introduced as a versatile tool for the modification of electrocatalyst selectivity. By ALD modification with thin layers of SnO₂, the wide product distribution observed from CuO-derived nanowires could be narrowed to yield predominantly CO at low overpotentials, a feat which normally requires gold catalysts. The origin of this performance modification is investigated on the basis of kinetic studies, HR-STEM and gas chemisorption analysis. Operation of the SnO₂-CuO catalyst is subsequently demonstrated in an all Earth-abundant electrolysis cell using a bipolar membrane, allowing for the separation of product gases while maintaining a sustained pH gradient. Driven by a 3-junction solar cell, this device achieved long-term solar splitting of CO₂ into CO and O₂ at an efficiency of 13.4 %, constituting the current record.

On the path to the selective production of higher order products, we investigate the reduction of CO to hydrocarbons at polycrystalline copper electrodes. By studying this process in nonaqueous electrolytes at low temperature we gain fine-tuned control of the proton donor and the CO binding strength, enabling activation-controlled kinetic studies over an extended parameter range. Our studies lead to the surprising finding that increased CO supply serves to suppress both methane and hydrogen production, while ethylene remains unaffected. These observations provide unprecedented insight into the mechanism of electrochemical CO and CO₂ reduction. Specifically, our data indicates that the rate of methane and hydrogen formation is governed by reactions among adsorbed CO and H species which compete for surface sites. We discuss the implication of these results, suggesting that simply increasing the supply of CO may not be sufficient for intrinsically enhancing CO and CO₂ reduction systems. Furthermore, we demonstrate how knowledge of this reaction mechanism can be exploited to suppress hydrogen evolution relative to CO reduction by rational tuning of the proton donor.

10:45 AM ET03.07.07

Metal Ion Cycling of Cu Foil for Selective C–C Coupling in Electrochemical CO₂ Reduction Haotian Wang; Harvard University, Cambridge, Massachusetts, United States.

Electrocatalytic CO₂ reduction to higher-value hydrocarbons beyond C₁ products is desirable for applications in energy storage, transportation and the chemical industry. Cu catalysts have shown the potential to catalyze C–C coupling for C₂₊ products, but still suffer from low selectivity in water. Here, we use density functional theory to determine the energetics of the initial C–C coupling steps on different Cu facets in CO₂ reduction, and suggest that the Cu(100) and stepped (211) facets favour C₂₊ product formation over Cu(111). To demonstrate this, we report the tuning of facet exposure on Cu foil through the metal ion battery cycling method. Compared with the polished Cu foil, our 100-cycled Cu nanocube catalyst with exposed (100) facets presents a sixfold improvement in C₂₊ to C₁ product ratio, with a highest C₂₊ Faradaic efficiency of over 60% and H₂ below 20%, and a corresponding C₂₊ current of more than 40 mA/cm²

11:00 AM ET03.07.08

Closing the Carbon Cycle by Electrochemical Reduction—Upgrading Carbon Dioxide to Engine Fuels Taotao Zhuang¹, Zhiqin Liang¹, Ali Seifitokaldani¹, Shu-Hong Yu² and Ted H. Sargent¹; ¹University of Toronto, Toronto, Alberta, Canada; ²University of Science and Technology of China, Hefei, China.

Electrocatalytic reduction of carbon dioxide (CO₂) to value-added carbon-based chemical feedstocks addresses the need for long-term storage of renewable electricity and decarbonization of the transportation sector. Liquid multi-carbon alcohols such as ethanol and n-propanol are desired as renewable transportation fuels. They offer high energy densities, ease of long-range transport, and direct drop-in usage in existing internal combustion engines.

Engineering copper-based catalysts that favor high-value alcohols is desired. In the design of catalysts, much progress has been made to target deliberately the C-C coupling step; while comparatively little effort has been expended to target post-C-C coupling reaction intermediates.

Among electrocatalysts for CO₂ reduction, Cu-based materials are the most prone to reduce CO₂ to C₂ and above products, with alkenes traditionally dominating multi-carbon product formation. To develop more efficient electrocatalysts for alcohol production, it is crucial to modify the catalyst structure to promote the desired alcohol and suppress alkene electrosynthesis. Additionally, it is vital to understand the mechanisms that underlie selectivity to enable further catalyst refinement. We reasoned that – since ethylene and ethanol share a penultimate reaction intermediate (*C₂H₃O) – we could potentially modify a catalyst's surface structure to target the hydrogenation of this intermediate, and thereby promote C₂ liquid production. Suppressing off-produced ethylene would enhance production and selectivity towards alcohols.

Here we report a class of core/shell vacancy engineering catalysts that utilize sulfur atoms in the nanoparticle core and copper vacancies in the shell to achieve efficient electrochemical CO₂ reduction to propanol and ethanol. These catalysts shift selectivity away from the competing ethylene reaction and toward liquid alcohols. We increase the ratio of alcohol-to-ethylene by over 6x compared to bare-copper nanoparticles, highlighting an alternative approach to electroproduce alcohols instead of alkenes. We achieve a C₂₊ alcohol production rate of 126 ± 5 mA cm⁻² with a selectivity of 32 ± 1% Faradaic

efficiency.

Reference: Zhuang, T.-T. et al. Steering post-C-C coupling selectivity enables high efficiency electroreduction of carbon dioxide to multi-carbon alcohols. *Nature Catalysis* **1**, 421-428 (2018).

11:15 AM ET03.07.09

Photoelectrochemical CO₂ Reduction with Nanoporous Au Electrodes Alex J. Welch, Joseph S. DuChene, Giulia Tagliabue, Artur R. Davoyan, Wen-Hui Cheng and Harry A. Atwater; California Institute of Technology, Pasadena, California, United States.

Here we report a large-area, catalytically-active and highly stable nanoporous gold (np-Au) electrode for (photo)electrocatalytic CO₂ reduction in aqueous electrolytes. A one μm thick np-Au electrode has a 27x larger electrochemical activity than a comparable planar Au film, owing to increased surface area. The np-Au structure is fabricated via electron beam co-deposition of a gold/silver (Au/Ag) alloy of tunable elemental composition (10/90 to 30/70) and variable thickness (0.1 μm to 2 μm), followed by a chemical etch of silver with nitric acid to yield a monolithic, np-Au structure. Depending on the etching temperature, we can alter the Au feature size from 10 nm to 25 nm. The np-Au also possesses near-unity absorption throughout a broad portion of the visible spectrum from 400 nm to 600 nm. Gas chromatography indicates H₂ and CO as the main CO₂ reduction products from np-Au electrodes in a 50 mM K₂CO₃ buffer. Although produced in a similar CO:H₂ product ratio vs applied potential as that obtained for planar Au electrodes, the increased surface area results in significantly higher partial current densities for CO than planar Au. Chronoamperometry measurements indicate stable np-Au electrode operation over periods exceeding 24 h at a potential of -0.5 V vs. RHE and a cathode current of -6 mA/cm². The faradaic efficiency remains similar across different thickness and etch temperatures, although the current does increase as the surface area of the np-Au layer increases. These np-Au electrodes show a photocatalytic response marked by an increase in current density of ~1 mA/cm² upon irradiation with white light at an incident power of 1.5 W/cm². Changes in the product selectivity observed from np-Au photocathodes as a function of electrolyte temperature, illumination wavelength, and incident light power will be discussed. In summary, np-Au electrodes exhibit both high electrocatalytic activity and sustained electrochemical stability, making them interesting candidates as cathodes for (photo)electrochemical CO₂ reduction.

11:30 AM ET03.07.10

Influence of Graded Mesoporosity on CO₂ Reduction Reaction on Copper Yichen Yan¹, Sarah A. Hesse¹, Ulrich Wiesner¹ and Jin Suntivich^{1,2}; ¹Cornell University, Ithaca, New York, United States; ²Kavli Institute at Cornell for Nanoscience Science, Ithaca, New York, United States.

Carbon dioxide reduction reaction (CO₂-RR) provides an environmental friendly way to convert readily available resources such as carbon dioxide and water to produce high-valued chemicals and energy-dense fuels to address the energy storage challenge. In this work, we compare the CO₂-RR on the planar copper electrode vs. mesoporous copper as a function of microstructure and pore sizes. The hypothesis is that mesoporous copper can recapture the intermediate(s) such as carbon monoxide for further reduction. We prepare the model graded mesoporous copper electrodes using electroless plating on the template formed by self-assembled triblock terpolymers and control the pore sizes by tuning the phase separation. On these copper electrodes, we quantify the CO₂-RR products over a fixed potential range and compare the results to that of planar polycrystalline copper. We will discuss the product distribution as a function of pore sizes and new insights from this analysis in the context of the intermediate confinement and how they can be applied to the future design of CO₂-RR catalyst.

11:45 AM ET03.07.11

Photoelectrodes Fabricated by Selective Atomic Layer Deposition in Self-Assembled, Composite Colloidal Films Mya Norman, Peter J. Reed and Robert H. Coridan; University of Arkansas, Fayetteville, Arkansas, United States.

Hierarchically structured materials are employed for applications that depend on the coordination of chemical and physical processes that function on disparate length scales. An example is photoelectrochemical energy conversion, where the electrode structure must optimize the balance of light absorption, carrier collection at a semiconductor-liquid junction, electron transfer, and mass transport of reactants in order to maximize the energy conversion efficiency of the system. Strategies for designing electrodes generally depend on techniques borrowed from semiconductor fabrication, which allow precise control for prototyping, but are not readily transferrable to the development of scalable materials. Here we describe the fabrication of hierarchically structured electrodes based on selective atomic layer deposition of ZnO in composite colloidal films. The distinct chemical susceptibilities of SiO₂ and polystyrene nanospheres can be used to generate hierarchically porous materials. By choice of the initial colloidal components, the characteristic length scales for light absorption, carrier collection, and mass transport can be independently engineered into a thin film electrode for photoelectrochemical applications. Optimized nanostructured conductive scaffolds can be prepared with a facile, continuously tunable, solution-phase synthesis. This approach offers a scalable route for synthesizing nanostructured photoelectrodes based on strategies developed from more complex fabrication techniques.

SESSION ET03.08: Interface and Beyond-Li Batteries

Session Chairs: Weiyang Li and Nian Liu

Wednesday Afternoon, November 28, 2018

Hynes, Level 3, Room 302

1:30 PM *ET03.08.01

Safe Li-Ion Battery Electrolytes—From Aqueous, Nonflammable Organic to Solid State Chunsheng Wang; University of Maryland, College Park, Maryland, United States.

Li-ion batteries are the critical enabling technology for the portable devices, electric vehicles (EV), and renewable energy. However, the safety of current batteries still need to be improved to satisfy these requirements. We systematically investigated the electrochemical stability window of the electrolytes, interface/interphase stability and resistance between electrodes and electrolytes, reversibility and robustness of the cells using these electrolytes. The critical issues limiting these safe electrolytes will be discussed.

2:00 PM *ET03.08.02

Interface Design and Materials in Batteries—From Liquid to Solid-State Xueliang A. Sun; University of Western Ontario, London, Ontario, Canada.

The control and understanding of reactions at the electrode/electrolyte interface (EEI) is essential to develop strategies to enhance cycle life and safety of lithium batteries. The poor cell lifetimes of Li/Na batteries are rooted mainly in side reactions occurring at the electrode-electrolyte interface. The use of

surface coatings to control of the electrode-electrolyte interface is an important strategy to design new electrodes. Atomic layer deposition (ALD) and molecular layer deposition (MLD) are ideal techniques to synthesize ultrathin and conformal coatings due to the self-limiting nature [1,2,3]. This talk will include three parts related to interface control:

In the first part, we will report our work on the applications of atomic layer deposition (ALD) in Li ion batteries including coating materials on NMC cathode in Li ion batteries[4,5] and MLD coating on Li-S batteries operating at 55C [6].

In the second part, we will discuss our recent results on ALD and MLD coatings on Li metal protection and interface control between solid-state electrolyte and cathode/anode materials for solid-state batteries [7-10].

Reference:

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- [2] J. Liu and X. Sun, *Nanotechnology* **26** (2015) 024001 (review)
- [3] Y. Zhao, X. Sun. *ACS Energy Lett.* (2018),3,899-914.(invited review)
- [4] B. Xiao, H. Liu, J. Liu, X. Sun, et al., *Adv. Mater.* (2017).1703764.
- [5] P. Yan, X. Sun, C. Wang, and J. Zhang, et al., *Nature Energy*, (2018) in press.
- [6] X. Li, A. Lushington, X. Sun, et al, *Nano Lett.*, **16** (2016) 3545-3549.
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- [8] Y. Zhao, X. Sun, et al., *Nano Lett.*, **17**, (2017) 5653-5659.
- [9] C. Wang, X. Sun et al., *Nano Energy*, **48** (2018) 35-43.
- [10] C. Wang, X. Sun et al., *submitted*, 2018

2:30 PM BREAK

3:30 PM ET03.08.03

Ionic Liquids and Dilute Electrolytes—The Surprising Connection Matthew A. Gebbie¹ and Jacob N. Israelachvili²; ¹Stanford University, Stanford, California, United States; ²University of California, Santa Barbara, Santa Barbara, California, United States.

Solid-electrolyte interfaces are critical elements of many electrochemical devices. Nevertheless, key questions surround the nature of solid-electrolyte interfaces in highly concentrated electrolytes, particularly in nanoconfined environments. I will discuss using a novel technique that combines molecular force measurements with *in situ* electrochemical spectroscopy to characterize nanoscale ionic liquid-electrode interfaces. As single component liquids composed entirely of ions, it was thought that ionic liquids contain extremely high free ion densities. Yet, the conductivities of most ionic liquids are orders of magnitude lower than aqueous electrolytes. I will present our discovery that the electric double layers formed by ionic liquids can extend more than 20 ion diameters away from charged surfaces, indicating that greater than 99.99% of the ions actually behave as neutral pairs, in equilibrium with a small population of thermally-dissociated charges. This picture provides insight into the low conductivities of typical ionic liquids, and I will also highlight a molecular framework for designing high performance ionic liquids. More broadly, our findings suggest new ways of envisioning concentrated electrolytes in nanoconfined interfaces, with implications for understanding diverse electrochemical processes in nanoscale materials.

3:45 PM ET03.08.04

Interfacial Interaction between Chemically-Engineered Copper Host and Metallic Sodium for Facilitating Highly Stable Sodium Metal Anode Chuanlong Wang, Huan Wang, Edward Matios, Xiaofei Hu and Weiyang Li; Dartmouth College, Hanover, New Hampshire, United States.

Sodium (Na) metal is the most promising alternative for lithium metal as an anode material for the next-generation energy storage systems due to its high theoretical capacity, low cost and high natural abundance. However, huge volume change and severe dendrite growth of Na metal anode during repeated electrochemical stripping/plating cycles result in rapid electrode degradation, low Coulombic efficiency, and even the risk of explosion caused by short circuit of the batteries. The volume and morphology change of the “hostless” Na severely aggravates the growth of Na dendrites. Thus, it is essential to seek an ideal host to support Na metal so as to maintain the high integrity of the electrode. Despite the most recent research in using porous carbon or aluminum substrate as Na host, current research in Na metal is still in its infancy, and the exploration on promising matrixes for Na metal anode is highly desirable. More important, a systematic and thorough understanding on the interfacial interaction between metallic Na and the host materials as well as its impact on the stability of Na metal anode is critical, but missing.

Through a facile and cost-effective surface treatment on commercially available Cu foam, a chemically engineered 3D porous copper (Cu) matrix with a cylindrical core-shell skeleton structure as a highly stable host for metallic Na anode was manufactured as a composite anode for Na-based batteries. It is noted that the unique surface characteristics of the as-obtained matrix can not only facilitate uniform impregnation and confinement of Na within the matrix pores promoted by the chemical interaction between Na and the matrix, but also can divert the Na plating from the matrix skeleton towards the Na reservoirs within the pores upon cycling. These special features significantly suppress the volume change and dendritic Na growth over repeated Na stripping/plating process. Benefiting from the delicately surface-engineered matrix as a host for Na, an excellent Na anode cycling stability in carbonate electrolyte without any additives over 100 cycles (300 hours) at a current density up to 2 mA cm⁻² with a high cycling capacity up to 3 mAh cm⁻². A full cell made of Na₃V₂(PO₄)₃ as cathode and the as-prepared surface-treated Na composite as anode is further tested, showing superior cycling performance and high rate capability (at 5C) compared with that using bare Na metal as anode.

To fundamentally understand performance improvement, we systematically investigated the interfacial interactions between treated/untreated Cu matrixes and metallic Na to reveal how the surface property of the matrix skeleton greatly influences the electrochemical stability of Na anode. We believe that our approach provides a facile and low-cost route to the fabrication of stable Na metal anode for high-energy Na-based batteries, and could be a viable strategy for other metallic anode systems.

4:00 PM ET03.08.05

High-Performance All-Solid-State Li-Se Batteries Enabled by Facial Sulfide Electrolyte-Electrode Interface Xiaona Li, Jianwen Liang, Xia Li, Changhong Wang, Jing Luo and Xueliang A. Sun; University of Western Ontario, London, Ontario, Canada.

All-solid-state Li batteries using inorganic solid electrolytes are attracting intensive research interests due to the highest safe system and high energy densities. However, these systems are still confronted with major challenges in terms of rechargeability, cycling stability, Coulombic efficiency and rate performance, which are far from commercialization.[1]

The fatal weaknesses of all-solid-state Li batteries are poor Li⁺ and electron transports between the electrode and the electrolyte. Unlike batteries with liquid electrolytes that can easily wet the electrodes and ensure smooth Li⁺ transport, the Li⁺ transport in solid-state batteries is highly limited at the electrode-electrolyte interface. Although many of sulfide-based solid-state electrolytes exhibit high Li⁺ conductivities (10⁻⁴ to 10⁻² S cm⁻¹ at room

temperature),[2] the Li⁺ transport through the interface can be lagged by several orders of magnitude. For instance, the Li⁺ conductivity of Li-argyrodite phase Li₆PS₃Cl electrolyte is reported as high as 1.3×10⁻³ S cm⁻¹ as a bulk, but the conductivity is dramatically reduced to ~10⁻¹¹ S cm⁻¹ at the interface with the Li₂S cathode.[3]

Therefore, developing new cathode materials with compatible interface between electrode and electrolyte to achieve high Li⁺ transport in the interface and high electronic conductivity in the electrochemical active electrode particles is one of the main point to realize the high performance all-solid-state Li batteries. Herein, all-solid-state Li-Se battery chemistry with the commercial Li₃PS₄ electrolyte was explored. Apart from the high electron conductivity (1×10⁻³ S cm⁻¹) of Se, a high Li⁺ conductivity of 1.4×10⁻⁵ S cm⁻¹ across the Se-Li₃PS₄ interface can be achieved. Such high Li⁺ conductivity within the interface should be due to the formation of interfacial species of PS_{4-x}Se_x³⁻ proved by *in-situ* Raman test. The Se cathode exhibited significantly high electrochemical kinetics process with high utilization and low polarization during cycling. All-solid-state Li-Se cell showed a high reversible capacity of 652 mAh g⁻¹ (96% of theoretical capacity) and good cycling stability with 585 mAh g⁻¹ remained after 100 cycles at room temperature. This work demonstrates all-solid-state Li-Se batteries as promising high-energy storage system and provides new insights of the solid-state electrode/electrolyte interfacial chemistry.[4]

Reference

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3. Yu C, Ganapathy S, de Klerk N J J, et al., *J. Am. Chem. Soc.*, **2016**, 138(35), 11192-11201.
4. Li X, Liang J, Sun X, et al. submitted, **2018**.

4:15 PM ET03.08.06

Effect of Stoichiometry and Architectural Expression on the Activity of Oxygen Reduction and Evolution Electrocatalysts Debra R. Rolison, Jesse S. Ko, Christopher N. Chervin, Mallory N. Vila, Paul A. DeSario, Joseph F. Parker and Jeffrey W. Long; U.S. Naval Research Laboratory, Washington, District of Columbia, United States.

Next-generation air-breathing cathodes in alkaline fuel cells and metal-air batteries will require discovering and formulating catalysts with higher activity for the reduction of molecular oxygen (ORR catalysis) and for the oxidation of water/hydroxide back to O₂ (OER catalysis). Strategies to enhance production of solar fuels will especially need improved catalysts for oxygen evolution. The design platform around which our team creates high-activity electrocatalysts entails the use of porous nanoarchitectures, which are built with covalently bonded catalytic nanoparticles intermingled with nanoscale void. These structural attributes give the catalyst designer extra dimensions of control when tailoring electrocatalysts to the demands inherent to reducing and evolving oxygen. Even the free volume within the architecture can be adjusted from >85% (aerogel) to 40–70% (ambigel). In the nickel-ferrite (Ni₃Fe_{1-x}O_x) ambigel-vs-aerogel series, we find that the emphasis in literature studies on stoichiometry only (the Ni-to-Fe ratio) limits the ability to tune catalytic activity. A single variable does not serve as a definitive predictor of catalytic performance, whether that variable is surface area, crystallite size, Ni:Fe stoichiometry, or single-phase purity. Significant interplay is at work between all four—not surprising in light of the mechanistic complexity inherent to cycling molecular oxygen electrochemically, but an indication that much remains to be done to design the optimal catalytic nanoscale interphase. We test catalytic formulations in technologically relevant air-breathing electrode structures in order to evaluate the activity and stability of their nanoarchitected electrocatalysts. Our ultimate goal is to prototype a rechargeable zinc-air battery that pairs NRL's rechargeable, dendrite-suppressing zinc sponge anode with a "trifunctional" air cathode that reduces oxygen, provides pulse power, and evolves oxygen.

4:30 PM ET03.08.07

Zinc Anode Design for Rechargeable Aqueous High-Energy Zn-Air Batteries Yamin Zhang¹, Yutong Wu¹, Yu Yan^{1,2} and Nian Liu¹; ¹Georgia Institute of Technology, Atlanta, Georgia, United States; ²University of Science and Technology of China, Hefei, China.

As an energy storage system, Li-ion batteries are not safe because they use flammable organic electrolytes. A safer alternative is rechargeable Zn-based batteries with aqueous electrolytes. Among them, Zn-air batteries have high theoretical volumetric energy density (4400 Wh/L), which can even compete with lithium-sulfur batteries. Alkaline electrolyte is preferable for Zn-air batteries. However, the performance of Zn anodes in alkaline electrolyte is limited by passivation, dissolution and hydrogen evolution. Through SEM investigation, critical passivation size was found to be ~ 2 μm. Sub-micron-sized Zn anodes will not have passivation problem. As a result, we focus our research on nanoscale. However, Zn dissolution of nanosized anodes will be accelerated because of large electrode-electrolyte surface area.

Thus, anode modification and protection are needed to alleviate the dissolution. We designed a (1) Zn mesh@GO anode: GO layers on the Zn mesh surface deliver electrons across insulating ZnO and can slow down the Zn dissolution; (2) lasagna-inspired ZnO@GO anode: ZnO nanoparticles encapsulated by GO can solve simultaneously the passivation and dissolution problems; (3) core-shell ZnO@TiN nanorod anode: thin and conformal TiN coating mitigates Zn dissolution, mechanically maintains the nanostructure, and delivers electron to nanorods.

Hydrogen evolution is a competitive side reaction on the zinc anodes, which causes low efficiency of Zn based batteries. Two approaches are investigated to suppress hydrogen evolution, including (1) modify the anode with a hydrogen suppressive material: core-shell ZnO@TiO₂ nanorod anode was made with hydrogen suppressive TiO₂ coating, which solves hydrogen evolution, passivation and dissolution problems at the same time; (2) design a hydrogen evolution suppressive nanostructured alloy anode: Zn-Ag alloy with increased standard reduction potential was used, which is more competitive compared with hydrogen evolution and more stable in aqueous electrolyte.

All of these anodes show superior performance compared with unmodified anodes. These anodes can be paired with air cathodes to make high energy Zn-air batteries. The nanoscale design principles here can potentially be applied to overcome intrinsic limitations of other battery materials.

4:45 PM ET03.08.08

Spontaneous Corrosion of Mg₂Sn in APC Electrolyte Zeyu Wang^{1,2}, Hemant Kumar¹, Vivek Shenoy¹ and Eric Detsi¹; ¹Materials Science & Engineering, University of Pennsylvania, Philadelphia, Pennsylvania, United States; ²Materials Science & Engineering, State Key Laboratory of Advanced Welding and Joining, Harbin Institute of Technology, Harbin, China.

Although the rechargeable battery industry is currently dominated by lithium-ion battery (LIB), there is a growing concern for the limited availability of raw lithium and cobalt resources used in commercial LIBs. The desire to keep pace with a growing market has led to intensive research of alternative rechargeable battery technologies that are safer and utilize earth-abundant elements such as magnesium-ion batteries (MIBs). Progress toward practical MIBs has been halted partly by the absence of suitable electrolytes that are compatible with magnesium (Mg) metal. In particular, most of the simple salts and/or organic solvents containing unsaturated carbon atoms yield a Mg-blocking passive film on metallic Mg. As a result, only a handful of electrolytes including all-phenyl-complex (APC) are compatible with Mg metal as the negative electrode [1]. Despite the huge success of APC for reversible Mg plating, this electrolyte has been reported to corrode current collectors and stainless support in battery cells at operating voltages above 2.2 V vs. Mg,

limiting in that way the operating voltage window below 2.2 V vs. Mg. Chloride ion has been pointed out as the corroding agent in APC electrolyte, and this corrosion phenomenon has been investigated only electrochemically when the cell is under a bias voltage. On the contrary, the spontaneous corrosion (*i.e.* without any applied voltage) in APC of Mg metal and Mg alloys used as anodes in MIBs has been barely reported. In this talk, I will demonstrate that APC electrolyte has adverse effect on MIB anodes even in the absence of applied bias voltage. In particular, we have found experimentally that Mg spontaneously dissolves from Mg₂Sn—a very promising MIB anode with in the presence of APC. We attribute this spontaneous corrosion to galvanic replacement, during which at least one of the following anions: Ph₄Al⁻, Ph₂AlCl₂⁻, PhAlCl₃⁻ and AlCl₄⁻ present in APC electrolytes extract electrons from the Mg in Mg₂Sn, resulting in Mg dissolution and aluminum metal deposition, as confirmed by X-ray photoelectron spectroscopy in our work. In addition, density functional theory (DFT) was used to determine the redox potentials of Ph₄Al⁻, Ph₂AlCl₂⁻, PhAlCl₃⁻ and AlCl₄⁻, in order to confirm that these anions are susceptible to dissolve Mg. This work raises fundamental questions regarding the origin of the relatively poor cycling longevity of alloy-type anodes in MIBs operating in APC electrolytes [2].

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SESSION ET03.09: Poster Session III: Electrocatalysis
Session Chairs: Bin Liu and Karthish Manthiram
Wednesday Afternoon, November 28, 2018
8:00 PM - 10:00 PM
Hynes, Level 1, Hall B

ET03.09.01

Understanding the Competition between Two-Electron Reduction Products for Carbon Dioxide Electrocatalysis Divya Bohra¹, Isis Ledezma-Yanez², Guanna Li¹, Evgeny Pidko¹ and Wilson Smith¹; ¹Chemical Engineering, Delft University of Technology, Delft, Netherlands; ²Process & Energy, Delft University of Technology, Delft, Netherlands.

The electrochemical reduction of carbon dioxide (CO₂ER) employing heterogeneous catalysis at the electrodes is a highly promising technological solution providing a means to manage renewable electricity production by converting it to a chemically valuable form while recycling harmful anthropogenic CO₂ emissions. The two-electron reduction products of CO₂ER namely carbon monoxide (CO) and formic acid (HCOOH) are considered most feasible owing to their relatively high thermodynamic efficiency as well as existing industrial value chains and demand. High achievable current density and relatively lower cost have led to several recent performance studies for silver (Ag) CO₂ER catalysts showing promising results for CO production. It is widely accepted that the formation of CO from CO₂ goes via a surface species *COOH whereas the formation of HCOOH proceeds via a O-bound bi-dentate surface species *OCHO. Consideration of only the binding energies of reaction intermediates dictates that the formation of HCOOH is thermodynamically more feasible on Ag surfaces than CO. This conclusion does not reconcile with the experimental observations which have clearly shown that at intermediate potentials, Ag produces CO as the major product, H₂ as a by-product with only trace quantities of HCOOH. The reasons for this discrepancy and the role of the stable specie *OCHO in the catalytic performance of Ag are not well understood.

In this study, we investigate the competition between the reaction pathways for formation of CO, HCOOH and H₂ on Ag(110) surface for CO₂ER. In particular, we address the mechanistic differences in the formation of *OCHO and *COOH and their respective interactions with the H₂ production pathways. We use Bader charge analysis as a first step to motivate the mechanistic study and demonstrate that it is fundamentally easier to control the selectivity between H₂ and CO than it is for H₂ and HCOOH. We perform climbing image nudged elastic band (CI-NEB) calculations to estimate reaction barriers for the formation of *OCHO and *COOH to show that *OCHO is not only thermodynamically more favorable than *COOH on Ag surfaces but also has a significantly lower kinetic barrier for formation and that solvation by the surrounding water plays a critical role in determining this barrier. Further, we investigate the influence of *OCHO on the adsorption energies of *COOH and *H species to understand how its presence on the surface can potentially influence the overall selectivity of Ag. Finally, we provide experimental evidence using surface enhanced Raman spectroscopy (SERS) of the presence of O-bound bi-dentate species on polycrystalline Ag catalyst during CO₂ER to validate our theoretical findings. Developing an understanding of the competition and interaction between the various reacting species can potentially provide the necessary handles to design highly selective, and therefore efficient CO₂ER catalysts.

ET03.09.02

Enhanced Photoelectrochemical Properties of ZnO/Cu₂O Heterostructures by Built-in Potential From p-n Cu₂O Homo Junction Photovoltaics Joon-Soo Yoon, Joo-Won Lee and Yun-Mo Sung; Korea University, Seoul, Korea (the Republic of).

There have been suggestions integrating a photoelectrochemical (PEC) cell and a photovoltaic (PV) cell, known as PV-PEC cell, to further utilize the sunlight more efficiently. In this system, additional photovoltage can be obtained from the photovoltaic cell, which makes the maximum of theoretical efficiency much higher than that of single or tandem PEC cell.

Herein, we report the fabrication method for n-type Cu₂O thin films using the electrodeposition of p-type Cu₂O layers and the successive conductivity type transition to n-type by a simple solution treatment. The p-n homo junction was constructed by additional electrodeposition of p-type Cu₂O on the n-type Cu₂O layers. This approach could allow the fabrication of high-quality p-n Cu₂O thin films. Au thin film was sputtered onto p-n Cu₂O and ZnO NRs were hydrothermally grown on the Au thin film to complete PV-PEC cells. XRD, SEM, UV-vis spectroscopy analysis were performed to identify each component. The Mott-Schottky analysis, photoresponse measurement and linear sweep voltammetry support the enhancement of ZnO NRs/Au/p-n Cu₂O compared to ZnO NRs/Au/n-Cu₂O with respect to photovoltage and photocurrent. Finally, band structures are suggested to visualize the working mechanism. The built-in potential occurred spontaneously because of p-n homo junction. The built-in potential offered additional potential so that the photocurrent onset was shifted to the cathodic direction and the photocurrent was increased under illumination.

Based upon the band diagram, it was clarified that z-scheme structure and the buried p-n junction work effectively for our PV-PEC system. As a result, the enhancement of photocurrent density by 237% was achieved for ZnO-pn via the photocurrent-time measurements under 0.2 V vs. SCE.

ET03.09.03

Mesoporous Co₃N/Amorphous N-Doped Carbon Nanocubes via Co₃[Co(CN)₆]₂ Nanocubes as an Efficient Electrocatalysts for the Oxygen Evolution Reaction Bongkyun Kang², Sung Hoon Kwag², Dong In Jeong¹, Hyung Wook Choi¹, Dae ho Yoon¹ and Woo Seok Yang²; ¹Sungkyunkwan University, Suwon, Korea (the Republic of); ²Korea Electronics Technology Institute, Seongnam-si, Korea (the Republic of).

In recent years, the water splitting process with electrocatalytic and photocatalytic, as one of the next generation energy conversion technology for producing hydrogen and oxygen molecules has been widely considered in solving energy and environmental problems. However, half reaction of oxygen evolution reaction (OER) plays a critical role in improving overall conversion efficiency of the water splitting process because the OER system encounters the bottle-neck of a kinetically sluggish reaction with multistep proton-coupled electron transfer and considerable overpotential value (> thermodynamic value: 1.23 V).

Precious metal and oxide materials (Pt, RuO₂, and IrO₂) as the superior active catalyst for OER have been used, however, high cost, poor stability, and scarcity of these metals hinder widespread practical and technical use. Hence, extensive research activities have focused on inexpensive earth-abundant metal based materials such as multi-composite transition metal (Ni, Fe, Mn, and Co etc.) compounds (nitride, oxide, and hydroxide), as well as hybrid structures with carbon-based materials (graphite, graphene, and carbon nanotubes (CNT)) as candidate catalysts for alternative developed OER electrocatalyst. Surprisingly, the suitable materials, metal nitrides, are a promising class of electrocatalyst materials for highly efficient oxygen evolution reaction (OER) because they exhibit superior intrinsic conductivity and have higher sustainability than oxide based materials. Herein, we report successful design and fabrication of unique mesoporous Co₃N@amorphous N-doped carbon (AN-C) nanocubes (NCs) based on in-situ nitridation and calcination via Prussian blue analogue (PBA) of Co₃[Co(CN)₆]₂ NC precursors. Unique architectures (mesoporous and AN-C hybrid) could assign well dispersed pore, highly active sites, and good durability of Co₃N NCs for OER. Mesoporous Co₃N@AN-C NCs electrode exhibits outstanding performance of low overpotential of 280 mV at 10 mA cm⁻² as well as excellent stability at 20 mA cm⁻² in alkaline (1.0 KOH) solution for 24 hours.

ET03.09.04

2 Dimensional Structured Iron Nickel Nitride/Reduced Graphene Oxide Hybrid Composite as Oxygen Evolution Reaction Electrocatalysts for Efficient Water Splitting Sung Hoon Kwag, Bongkyun Kang and Woo Seok Yang; Nano Materials & Components Research Center, Korea Electronics Technology Institute, Gyeonggi-do, Korea (the Republic of).

In water splitting, oxygen evolution reaction (OER) is important process because high overpotential is required to achieve the current density for the reaction. Transition-metal nitrides (TMN) used as electrocatalyst materials for OER are being recently studied because of high yield, easy operation, and excellent catalytic activity by high electrical conductivity. In particular, iron-nickel nitride has very high catalytic activity due to owing to high electrocatalytic and high stability. Reduced graphene oxide (rGO) known as 2 Dimensional (2 D) carbon materials is extensively used as supporting material owing to high conductivity, large theoretical specific surface area, and excellent stability.

In this study, we successfully synthesized Fe₂Ni₂N/rGO hybrid composite for OER electrocatalyst material through two-step process with hydrothermal method and annealing. The morphology of precursor and Fe₂Ni₂N/rGO hybrid composite was analyzed by FE-SEM. The crystallinity of sample was confirmed by XRD. GO was confirmed by Raman spectroscopy. And the components of as-prepared precursor were measured by FT-IR spectra. Furthermore, we analyzed electrochemical properties of synthesized sample.

ET03.09.05

La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-δ} Decoration With Co₃O₄ Nanoparticles and the Effect on Its Performance as SOFC Cathode Julian Ascolani Yael^{1,2}, Alejandra Montenegro-Hernandez¹, Laura Baque¹, Alberto Caneiro¹ and Liliana Mogni¹; ¹CNEA - CAB, Bariloche, Argentina; ²Instituto Balseiro, Bariloche, Argentina.

Reducing fuel cells degradation and cathode polarization losses are currently two of the most important challenges in order to achieve more efficient and cost competitive SOFC's. One strategy has been to reduce operation temperatures to the range between 600 °C and 800 °C (IT-SOFC), which reduces degradation rates but increases activation over potentials as a consequence (mainly the cathode reaction overpotential, due to the high activation energy of oxygen reduction reaction -ORR-). Several approaches have been taken to counteract this problem and recently, promising results [1] have been obtained by modifying the electrodes surface using the impregnation technique. This technique consists of synthesizing catalyst nanoparticles on the electrode surface through a liquid solution-based process [2, 3].

The mechanisms through which the impregnated catalysts reduce the polarization resistance and even enhance durability are not completely well understood yet, especially when non conventional catalysts are impregnated, as the performance improvement relies upon the microstructure and coupled interactions between the materials.

In this work, a SOFC cathode surface modification by nanoparticle decoration was carried out. La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-δ} -LSCF- ceramic cathodes impregnated with cobalt oxide (Co₃O₄) nanoparticles were characterized with Scanning and Transmission Electron Microscopy -SEM and TEM-, X-ray diffraction -XRD- and Raman Spectroscopy. The electrochemical response as a function of temperature and oxygen partial pressure -pO₂- (10⁻⁴ < pO₂ < 1 atm) was evaluated by electrochemical impedance spectroscopy -EIS-. The impregnation was found to reduce the cathode polarization resistance -R_{p,c}- around 50% in the temperature range between 400°C and 700°C.

Through EIS measurements varying pO₂, the rate-limiting steps of the O₂ reduction reaction are identified as well as how these are affected by the presence of Co₃O₄ nanoparticles. The EIS spectra show at least two arcs, where the pO₂ dependence of each one allows to model the electrochemical response by a complex mechanism where the oxygen reduction reaction is co-limited by oxygen ion diffusion and oxygen surface exchange.

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ET03.09.06

First-Principles Study of Bi-Functional Electrocatalytic Activity on Bi₂Ru₂O₇: Pyrochlore Oxide Gwan Yeong Jung¹, Joohyuk Park^{1,2}, Sung O Park¹, Jaephil Cho¹ and Sang-Kyu Kwak¹; ¹School of Energy and Chemical Engineering, UNIST, Ulsan, Korea (the Republic of); ²Department of Materials, University of Oxford, Oxford, United Kingdom.

Among the various electrochemical conversion and storage systems, rechargeable Zn-air batteries have been considered as a promising candidate for future electric devices due to their high specific energy density. To improve the sluggish rate of oxygen reduction reaction (ORR) and oxygen evolution reaction (OER), which has been pointed out as a critical limitation of Zn-air batteries, pyrochlore oxides (A₂B₂O₇) can be used as a highly efficient bi-functional electrocatalyst because of high charge transfer activity during ORR and OER. However, catalytic origin of them has not been fully explored due to complexities in structure and reaction mechanism. In this work, we investigated the reaction mechanisms for ORR and OER particularly in bismuth

ruthenate pyrochlore oxide ($\text{Bi}_2\text{Ru}_2\text{O}_7$) via density functional theory (DFT) calculation. Initially, we determined the energetically stable surface terminations for each low-index surface (i.e., (100), (110), and (111)). Next, we calculated the adsorption free energies of intermediates for oxygen-involving electrochemical reaction (i.e., OOH^* , O^* , and OH^*). Finally, we constructed a 2D activity map of theoretical overpotentials (η) based on the adsorption free energies, which was used as a descriptor for bi-functional catalytic activity. Interestingly, the Bi and Ru sites were clearly separated in the activity map, induced by differences of binding strengths of reaction intermediates. The active sites with the minimum η were identified to be Bi site for ORR, and Ru site for OER, respectively. Based on the results, we theoretically demonstrated that the $\text{Bi}_2\text{Ru}_2\text{O}_7$ pyrochlore oxide is the excellent bi-functional electrocatalyst, which intrinsically contains different active sites separately working for ORR and OER, due to the distinct binding characteristics by each metal species.

ET03.09.07

Effect of Size and Density of Ni Nanoparticles on Photoelectrochemical Water Splitting Songwoung Hong¹, Hyo-Chang Lee^{1,2} and Ansoo Kim^{1,2}; ¹Korea Research Institute of Standards & Science, Daejeon, Korea (the Republic of); ²University of Science and Technology, Daejeon, Korea (the Republic of).

Photoelectrochemical (PEC) hydrogen production via splitting of water is a theoretically practical and environmentally friendly strategy for efficient renewable energy production. Silicon has been considered as a good candidate material of photoanode materials for the OER, owing to the appropriate bandgap (1.12 eV) and high carrier mobility. However, the Si has not only low stability for the PEC cell due to the photo-induced corrosion in contact with electrolytes but also poor catalytic property for the photo-drive electrolysis.

Electrodeposited Ni or Ni-Fe alloy was shown to effectively stabilize and catalyze the Si photoanode continuously for 24 h of water splitting. However, even thin film of Ni or Ni-Fe alloy, it blocks the light absorption in the underlying photo-absorber, leading to the reduced photocurrent. Also, the film limits the surface area of a cocatalyst for the OER. Therefore, we formed Ni nanoparticle layer on the photoanode to enhance the light absorption. In this presentation, the effect of OER efficiency depending on the size and density of Ni nanoparticles will be discussed.

ET03.09.09

Cu@Cu₂O for Selective Reduction of CO₂ to C₂ Products Longmei Shang and Gengfeng Zheng; Laboratory of Advanced Materials, Fudan University, Shanghai, China.

Searching for an effective catalyst to reduce CO₂ to value-added hydrocarbons has been a key challenge for CO₂ utilization. Here we design the Cu@Cu₂O catalyst by taking advantage of copper featuring a thin oxide layer on the surface under ambient conditions. Our results demonstrated that Cu(I) oxide species on Cu@Cu₂O surface can remain relatively stable against reduction under CO₂ electroreduction condition, and the synergism between surface Cu⁺ and Cu⁰ in Cu@Cu₂O composites contributes to boosting its efficiency and selectivity towards to C₂ products. This Cu@Cu₂O catalyst achieved low onset potential (-0.8V vs RHE) as well as excellent selectivity (up to be 50% at -1.0V vs RHE) for C₂ (C₂H₄ and C₂H₅OH) production.

ET03.09.10

Unraveling the Role of Reducing Atmosphere in Activating Wide Bandgap Semiconductors for Enhanced Solar-Assisted Water Splitting Samar Fawzy, Mostafa M. Omar and Nageh K. Allam; American University in Cairo, New Cairo, Egypt.

Bandgap tuning of semiconductors via induced defects is vital to control their optical and electrical properties. The need to extend the absorption spectrum to NIR and Visible regions of the light spectrum is crucial to enhance their characteristics as efficient photoelectrodes in photoelectrochemical water splitting. However, the nature of defects, whether deep or shallow and how they influence the photoelectrochemical performance of TiO₂ is yet to be understood. Herein, four factors were utilized to increase the defect density, and eventually decrease the bandgap: alloying with Nb and Zr, nanostructuring in the form of multipodal nanotubes, annealing in a reducing atmosphere (H₂), and deposition of solvothermally prepared narrow bandgap CZTS nanoparticles on the nanotubes. Air-annealed samples were used as a reference to study the effect of reducing atmosphere. SEM images verified the formation of uniformly distributed MPNTs. XRD, XPS, and Raman Spectroscopy for the Hydrogen-annealed samples confirmed the presence of ZrTiO₄ in addition to Ti-Nb-Zr-O as single mixed oxide possessing an anatase crystal structure. XPS core spectra fitting verified the presence of Ti³⁺. The presence of a large number of Ti³⁺ defects/Oxygen vacancies justified the 4-orders of magnitude increase in the donor density exhibited when Mott-Schottky analysis was performed. These results were further confirmed by XPS valence band spectra showing the presence of valence band tail states. These tail states resulted in a decrease in the bandgap, besides forming a tail in the absorption spectra reaching NIR/Vis. region. Bare MPNTs showed a 25 times enhancement in the photocurrent compared to Air-annealed samples. Decorating the MPNTs with CZTS lead to further 6 times enhancement. However, on testing several cycles, CZTS showed a lack of stability in the alkaline electrolyte. This large current was attributed to the formation of a p-n junction with the desirable band alignment; enhancing charge separation and leading to charge carriers' injection on the NTs/particles interface. Hence, annealing in a reducing atmosphere is capable of producing disordered and defective structures. This would stimulate an intriguing route for activating other promising metal oxides for water splitting via tailoring their optical and electronic properties.

ET03.09.11

Mechanism of Cathodic Performance Enhancement by Cathode/Electrolyte Interface Engineering of Solid Oxide Fuel Cells Alireza Karimaghhalou and Min Hwan Lee; Department of Mechanical Engineering, University of California Merced, Merced, California, United States.

Oxygen reduction reaction (ORR) is a sluggish process that causes significant cell voltage losses in low- and intermediate-temperature solid oxide fuel cells (SOFCs).¹⁻⁴ Surface engineering of electrolytes with nanostructures and thin-film interfaces introduced between the cathode and electrolyte can mitigate the voltage losses associated with ORR on the cathode.⁵⁻⁸ In this presentation, we study the role of the metal oxide-based nanoscale interlayer inserted between the cathode and electrolyte in the kinetics and rate-limiting steps of ORR process through a series of electrochemical analyses and imaging techniques. Ultrathin yttria-doped ceria (YDC), yttria-stabilized zirconia (YSZ) and ceria (CeO₂) layers with different stoichiometry and thickness were inserted as the interlayer by atomic layer deposition (ALD) technique⁹ on a gadolinia doped ceria (GDC) layer that was screen printed on YSZ electrolyte supported cells. A series of electrochemical tests have been performed with two different cathode materials – lanthanum nickel ferrite (LNF) and lanthanum strontium cobalt ferrite (LSCF) cathodes – with different electronic and ionic conductivities to examine the interface engineering impact on ORR.¹⁰⁻¹² ORR kinetics tested under different oxygen partial pressures ($p(\text{O}_2)$) ranging from 0.04 to 1.0 atm. The reaction order m , defined in the relation (R_p : cathodic polarization resistance; $p(\text{O}_2)$: O₂ partial pressure) is a widely used indicator of the rate-limiting step in ORR.^{13,14} In addition to the dependency on $p(\text{O}_2)$, the wide variation in the dependency on temperature and overpotential suggests that the interface treatment not only changed the overall ORR kinetics but also shifted the bottleneck process of ORR. However, it was found that most of the samples are largely rate-limited by the charge transfer processes, but mostly in conjunction with chemical processes such as diffusion of electroactive species and/or dissociation processes.

ET03.09.12

Mesoporous CuO_x-Derived Nanostructured Copper Catalysts for CO₂ Reduction Giorgio Giuffredi^{1,2} and Fabio Di Fonzo¹; ¹Istituto Italiano di

Tecnologia, Milano, Italy; ²Department of Energy, Politecnico di Milano, Milano, Italy.

The electrochemical reduction of anthropogenic CO₂ to fuels and complex hydrocarbons represents a promising solution to reduce global CO₂ emissions and, at the same time, to efficiently store intermittent, renewable energies-generated electricity in the form of chemical energy of carbon-based fuels. The progress of the technology is still hindered by the unsatisfactory efficiency and stability of currently employed electrocatalysts. The thermodynamic stability of CO₂ requires a large overpotential to be applied for the reaction to take place at a satisfying rate. Moreover, electrocatalysts often undergo deactivation after a limited operation time because of poisoning due to incorrect reduction of CO₂.

Copper, among the many metals tested as CO₂ reduction electrocatalysts, is interesting because of its ability to reduce CO₂ to complex hydrocarbons with good efficiency. However even copper catalysts, when their structure and morphology are not nano-engineered, require high overpotentials and have limited selectivity and stability.

To overcome these problems, oxide-derived copper catalysts are being studied: they show improved CO₂ reduction efficiency, higher selectivity towards complex hydrocarbons and have longer stability. Morphology also plays a critical role in determining activity and selectivity of oxide-derived copper nanostructures: a controlled morphology in fact allows to maximize the exposed active sites and to increase the surface area, resulting in higher Faradaic efficiency towards CO₂ products and lower overpotentials.

In this contribution, we propose Copper Oxide (CuO_x) mesoporous nanostructures synthesized through Pulsed Laser Deposition (PLD) as oxide-derived Cu catalysts for CO₂ reduction.

We evaluate the influence of both morphology and composition of the nanostructures on the final electrochemical performance, by carefully tuning the process gas kinetics and process gas type during the synthesis. We are thus able to fine-tune the deposit morphology and composition up to the nanoscale: we obtain films with different degrees of nanostructuration, from compact films to porous nanostructures, and compositions ranging from Cu₂O to CuO. The PLD-synthesized nanostructures are composed of an amorphous matrix with embedded crystalline CuO_x seeds, differently from other reported, purely crystalline oxide-derived Cu catalysts. This morphological feature allows for a higher availability of undercoordinated surface active sites which, coupled with the high surface area, can enhance the activity of the catalysts.

The nanostructures are characterized electrochemically, showing good current densities even at low overpotentials. The influence of both composition and morphology of the nanostructures on Faradaic efficiency and selectivity are evaluated.

This contribution shows the potential of a PLD-based technique for the synthesis of efficient oxide-derived Cu nanostructured catalysts with controlled morphology and composition.

ET03.09.13

Investigation on the Nano Size Effect of Ultra-Small Manganese Oxide Nanoparticles Kang Hee Cho, Sunghak Park, Hongmin Seo, Kang Gyu Lee, Yoon Ho Lee and Ki Tae Nam; Department of Materials Science and Engineering, Seoul National University, Seoul, Korea (the Republic of).

Nowadays, nanotechnology is really close to our daily lives and its applications are diverse such as energy, biomedical, sensors and foods. Especially in energy fields, rational design and synthesis of highly efficient nanocatalysts for various reactions are an important issue. And because of some characteristics such as large exposed surface area, morphology tuning at nano scale and electronic confinement effects within NPs, they show specific nano size effects.

Recently, our group newly synthesized partially oxidized sub-10 nm MnO NPs which show superior catalytic performance compared to the bulk manganese oxides.^[1] And in further study which was reported in JACS last year, we implemented various *in-situ* electrochemical analysis and *in-situ* spectroscopic tools such as XAS, UV-VIS and Raman and we found completely different mechanistic behavior of our NPs compared to the conventional Mn-based catalyst.^[2]

Herein, we extend our understanding on nano-size effect to our manganese oxide NPs. For synthesis of ultra small NPs, various size-control parameters and synthesis methods were pre-screened. And very recently, we successfully synthesized average size of 4.1 nm NPs which show superior OER activity compared to sub-10 nm NPs. Using these as-synthesized NPs, applicability for chirality manganese oxide NPs formation will be explored and also we expect enhanced surface focused spectroscopic analysis for the capture of reaction intermediates. Additional studies on the relation between OER performance and the size of NPs will also proceed.

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ET03.09.14

Nitrogen Doped Carbon Nanonions for Oxygen Reduction Reaction (ORR) Electrocatalysis in Fuel Cells for Microgravity Conditions Armando Pena-Duarte¹, S.H. Vijapur³, T.D. Hall², E. Jennings Taylor³ and Carlos R. Cabrera²; ¹Department of Physics, University of Puerto Rico at Río Piedras, San Juan, Puerto Rico, United States; ²Department of Chemistry, University of Puerto Rico at Río Piedras, San Juan, Puerto Rico, United States; ³Faraday Technology Inc, Englewood, Ohio, United States.

Nitrogen doped carbon nanostructures have been previously used as catalyst support in ORR [1,2]. A metal-free mesoporous nitrogen-doped carbon catalyst showed a high electrocatalytic activity, durability and selectivity toward peroxide by electrocatalysis of O₂ in a non-corrosive neutral as well as in acidic reaction medium [3,4]. Human space travel requires several technological developments that support the energy-efficient preservation of closed systems in microgravity spaceship environments. Especially, a technique for the in-situ generation of cleaning/sanitizing solutions such as H₂O₂ is needed to meet personal hygiene necessities during space missions. Accordingly, we developed an alternative post-synthesis nitrogen doping of CNOs by Chemical Vapor Deposition Method (CVD) in atmospheric pressure, using dicyandiamide as nitrogen precursor. The operational parameter conditions of the CVD reactor were a reaction temperature 700 °C, 2 mL/min of total argon gas flow, and a composition of precursors 2:1 DCDA:CNOs. The structural properties of the NCNOs were investigated using X-ray diffraction, Raman spectroscopy, scanning electron microscopy, and X-ray photoelectron spectroscopy. Our research involves increase surface area of carbon pristine source and improve its electronic structure and understanding of the nitrogen intercalation process by possible pyrolytic-nucleophilic mechanism of N-C doping reaction. NCNOs electrochemical characterization revealed higher performance than CNOs due to N doping. Nitrogen doping in the CNOs enhances the electronic conductivity and specific capacitance. An analysis of the rotating disk electrode (RDE) technique data was done to evaluate the ORR kinetics, including *n*-values which are related to the mechanism of oxidation, at the NCNOs, using the Koutechy-Levich (K-L) equation. The pH Effect on Oxygen Reduction Reaction over N-Doped CNOs in O₂ saturated 0.2 M Na₂SO₄ was evaluated by a scan rate of 10 mV/s at different rotation rates: 300, 700 1100, 1500, and 1900 rpm. Our results could be evidence that the H₂O₂ or H₂O selectivity, two-electrons and four-electrons transfer pathway, respectively, depend on the supporting electrolyte, *i.e.*, pH value and nature of electrolyte, and increases to 0.2M Na₂SO₄ according to neutral (2.5 electrons) > acidic (1.4 electrons) > alkaline (3.4 electrons). Therefore, our approach would be promising to control of two-electrons route kinetics of ORR by the supporting electrolyte, through nitrogen carbon nanonion electrocatalyst systems for fuel cells in aerospace technologies.

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ET03.09.15

First-Principles Studies of B-Site Doped PrCoO_{3-d} Perovskite Jianguo Yu; Idaho National Laboratory, Idaho Falls, Idaho, United States.

Solid-oxide fuel cells (SOFC) based on proton-conducting (PC) ceramics are gaining wide interest as promising green technologies for H₂ production and conversion. However, its large-scale deployment has been hindered by severe limitations at electrodes, which must ensure catalytic activity, electronic conduction, and high proton diffusion rates. Perovskite oxides are highly desirable as the promising electrode candidates for SOFC.

In this work, we present results of a density-functional theory (DFT+U) study of B-site doped PrCoO_{3-d} (PCO) perovskite. The investigation was focused on the key processes that determine proton transport, i.e., oxygen vacancy formation, water dissociative incorporation into the defective lattice, and proton transfer along the oxide sublattice. The materials are PCO and B- substituted derivatives with Ni. The effects of the crystal structural from cubic, tetragonal to orthorhombic and surface will also be discussed.

ET03.09.16

Promoting Surface Charge Utilization by Incorporating Novel Ternary ZnCoMn Layered Double Hydroxide Nanowall with Bismuth Vanadate for Efficient Photoelectrochemical Water Oxidation Truong-Giang Vo, Yian Tai and Chia-Ying Chiang; National Taiwan University of Science and Technology, Taipei, Taiwan.

Strategically integrating a highly efficient oxygen evolution reaction electrocatalysts with a semiconductor film to reduce surface recombination and enhanced photocurrent is known as the bottleneck in solar-driven water splitting [1]. Herein, a novel integrated ZnCoMn layered double hydroxides (LDHs) photoanode with the high-quality interface was directly and conveniently deposited on a BiVO_4 to enhance photoelectrochemical water oxidation performance via fast and facile preoxidation coupled electrochemical method. Uniform two-dimensional LDH nanowalls with controlled composition anchoring onto the surface can be accomplished at room temperature within tens of seconds. Benefiting from efficient exposure of active sites, favorable charge transport and enhanced surface reaction kinetics, surface modification with ZnCoMn-LDH exhibits about 170% increment in photocurrent density at 1.23 V vs. RHE and a 280 mV shift in onset potential compared to bare bismuth vanadate. More interestingly, charge injection efficiency at the BiVO_4 /electrolyte interface, which is well-known as one of the critical limiting factors in achieving efficient photoelectrochemical water splitting [2], reaches almost 100%. The results obtained here suggest the possibility of using ternary LDH as low-cost earth-abundant co-catalysts for solar water splitting. This work also provides a facile and cost-effective synthesis route that holds great promise for large-scale industrial manufacture and can be potentially used in energy conversion devices.

[1] M. Chhetri, S. Dey, C.N.R. Rao, Photoelectrochemical Oxygen Evolution Reaction Activity of Amorphous Co–La Double Hydroxide- BiVO_4 Fabricated by Pulse Plating Electrodeposition, *ACS Energy Lett.* 2 (2017) 1062–1069.

[2] X. Lv, L. Tao, M. Cao, X. Xiao, M. Wang, Y. Shen, Enhancing photoelectrochemical water oxidation efficiency via self-catalyzed oxygen evolution: A case study on TiO_2 , *Nano Energy*. 44 (2018) 411–418.

ET03.09.17

Stable GaAs Photoanode with Manganese Modified TiO_2 Protective Coatings for Water Oxidation Xin Shen and Shu Hu; Chemical Engineering, Yale University, New Haven, Connecticut, United States.

Artificial photosynthesis, commonly used to refer to any scheme for capturing and storing the energy from sunlight in the chemical bonds of a fuel (a solar fuel), has long been considered as option to mitigate energy crisis and global climate change. Photoelectrochemical (PEC) water splitting converts water into hydrogen and oxygen, and is a major research topic of artificial photosynthesis. However, there are still lots of challenges in designing an efficient PEC cell to split water. Except for efficiency and cost, stability problem of efficient semiconductor/liquid interfaces like Si and GaAs has greatly hindered the development of many potential excellent photoanode materials as these material undergoes positive photo-corrosion during PEC operation.

So, it is imperative that through this project we: 1 Understand typical photoanode corrosion process with a detailed description for the different corrosion stages with the help of our in-situ laser set-up; 2 Find the main factors influencing anode stability during PEC water oxidation; 3 Determine an optimized condition for stable and efficient GaAs water oxidation, as our preliminary results showed the relative neutral PH condition (PH 5 to 9) is beneficial for PEC water oxidation by greatly lower electrode overpotential. Particularly, in this project we would also compare GaAs/TiMnOx/Ir to traditional GaAs/ TiO_2 /Ni to show the superiority of acid stable TiMnOx/Ir as a novel protective coating/co-catalyst system.

ET03.09.18

Preparation of Vertically Oriented Carbon-Coated Titanium Dioxide Nanorods as Alternative Catalyst Support to Carbon for Fuel Cells Applications Naser Mohammadi¹ and Mohamed Mohamedi²; ¹Énergie Matériaux Télécommunications, INRS, Montreal, Quebec, Canada.

At present, catalyst supports in fuel cells electrodes are often made of carbon-based materials, such as graphite fiber brush, carbon paper, reticulated vitreous carbon, carbon nanofibers, etc. TiO_2 is one of the most attractive metal oxides used in many areas concerning solar cells, photocatalysis, sensors, supercapacitor, etc. TiO_2 has very good chemical stability, biocompatibility, and also is abundant as well as environment-friendly. These advantages are very attractive for practical fuel cell electrodes. Because of their special application in fuel cells, the growth of one-dimensional single-crystalline TiO_2 nanostructures on a flexible substrate is receiving intensive attention [1].

In this study, TiO_2 nanorods are hydrothermally grown on carbon paper (CP) and Titanium foil. Then Platinum layer deposited onto TiO_2 nanorods by pulsed laser deposition (PLD) at room temperature. Scanning electron microscopy (SEM), X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) were employed to characterize the synthesized nanorods, According to the SEM study, the synthesized particles have 200 nm in diameter. The catalyst showed the highly dense TiO_2 nanorods were directly grown on the Titanium foil and carbon Paper substrates, also the Pt-coated onto the surface of TiO_2 nanorods were uniform. Cyclic voltammetry (CV) and chronoamperometry were employed to study the electrocatalytic properties and durability of thus synthesized Ti/ TiO_2 /Pt and CP/ TiO_2 /Pt samples towards ethanol electro-oxidation, the reaction that is of fundamental significance to direct ethanol fuel cells (DEFCs). The Ti/ TiO_2 /Pt and CP/ TiO_2 /Pt electrocatalysts have a larger active surface area as compared to the Ti/Pt and CP/Pt electrocatalysts. Meanwhile, the Ti/ TiO_2 /Pt and CP/ TiO_2 /Pt electrocatalysts display much better catalytic activity and higher stability for the ethanol electrooxidation in acidic than the Pt/C and Pt/Ti electrocatalysts as a result of the synergistic effect of Pt and the TiO_2 support. Thus, the prepared electrode with low platinum loading and high stability is a promising material for fuel cells and TiO_2 nanorods substrate is a potential alternative to carbon paper substrate for fuel cell technology.

SESSION ET03.10: Electrochemical Capacitors and H₂ Storage

Session Chairs: Weiyang Li and Nian Liu

Thursday Morning, November 29, 2018

Hynes, Level 3, Room 302

8:00 AM *ET03.10.01

Directional Flow-Aided Sonochemistry Yields Graphene with Tunable Defects to Provide Fundamental Insight on Sodium Metal Plating Behavior David Mitlin¹ and Wei Liu²; ¹Chemical and Biomolecular Engineering and Mechanical Engineering, Clarkson University, Potsdam, New York, United States; ²Institute of New-Energy and Low-Carbon Technology, Sichuan University, Sichuan, China.

This is the first report of a novel directional flow-aided sonochemistry (FAS) exfoliation method to synthesize graphene with nearly ideal structure. The FAS treatment allows for control of graphene structural order and chemical uniformity not possible through prior top-down wet methods. Graphite is exfoliated into single-nm scale thickness graphene that is nearly defect free (at-edge sonication graphene "AES-G") or is highly defective (in-plane sonication graphene "IPS-G"). The AES-G has a Raman G/D band intensity ratio of 14.3 and an XPS derived oxygen content of 1.3 at.%, while the IPS-G has I_{G/D} of 1.6 and oxygen content of 6.2 at.%. Graphene and related carbons are widely employed as templates and protection layers to improve metal plating behavior in sodium and lithium metal battery (SMBs, LMBs) anodes. We then use AES-G and IPS-G to examine the role of structure and chemistry of graphene supports in promoting efficient Na metal cycling. The graphene serves a dual role in stabilizing the Na metal anode, being a nucleation template and serving as a protective layer to keep the metal from severely reacting with the electrolyte. We are the first to demonstrate that graphene defects are actually quite deleterious for efficient Na plating and stripping. AES-G yields state-of-the-art Na performance, with stable cycling at 2 mA/cm² at 100% Coulombic efficiency (CE), and an areal capacity of 1 mAh/cm². Meanwhile IPS-G performs on-par with the baseline Cu support in terms of severe charging instability. The explanation is that the defective graphene demonstrates much more copious SEI formation due to its defects and oxygen groups being catalytic. A thicker SEI results in a larger overpotential and worse CE loss during subsequent Na plating/stripping, manifesting in severe mossy metal dendrite growth and periodic electrical shorts. We therefore propose the following design rule for next-generation supports for Na metal: An ideal architecture will not only possess a large surface area for copious preferred heterogenous nucleation, but itself will be non-catalytic for SEI formation.

8:30 AM *ET03.10.02

Nanostructured Graphene-Coated Cathodes for High-Performance Lithium-Ion Batteries Mark C. Hersam; Northwestern University, Evanston, Illinois, United States.

Efficient energy storage systems based on lithium-ion batteries represent a critical technology across many sectors including consumer electronics, electrified transportation, and a smart grid accommodating intermittent renewable energy sources. Nanostructured electrode materials present compelling opportunities for high-performance lithium-ion batteries, but inherent problems related to the high surface area to volume ratios at the nanometer-scale have impeded their adoption for commercial applications. Here, we demonstrate a scalable materials and processing platform that realizes high-performance nanostructured lithium manganese oxide (nano-LMO) spinel cathodes with conformal graphene coatings as a conductive additive. Graphene coatings provide a chemically stable interface between the electrode and electrolyte, which minimizes the formation of the solid-electrolyte interphase and mitigates electrode chemical instabilities such as manganese dissolution [1]. The resulting nanostructured composite cathodes concurrently resolve multiple problems that have plagued nanoparticle-based lithium-ion battery electrodes including low packing density, high additive content, and poor cycling stability [2]. Moreover, this strategy enhances the intrinsic advantages of nano-LMO, resulting in extraordinary rate capability and low temperature performance. With 75% capacity retention at a 20C cycling rate at room temperature and nearly full capacity retention at temperatures as low as -20 °C, this work advances lithium-ion battery technology into unprecedented regimes of operation.

[1] L. Jaber-Ansari, *et al.*, "Suppressing manganese dissolution from lithium manganese oxide spinel cathodes with single-layer graphene," *Advanced Energy Materials*, **5**, 1500646 (2015).

[2] K.-S. Chen, *et al.*, "Comprehensive enhancement of nanostructured lithium-ion battery cathode materials via conformal graphene dispersion," *Nano Letters*, **17**, 2539 (2017).

9:00 AM ET03.10.03

Titanium Nitride Films as Electrodes for High Power Electrochemical Capacitors Tianye Zheng, Mohammad H. Tahmasebi and Steven T. Boles; Hong Kong Polytechnic University, Kowloon, Hong Kong.

Electrochemical capacitors (ECs) with high-power capabilities and stable cycling can effectively improve the state of the art in power delivery and energy storage. In this study, we investigate reactively sputtered titanium nitride (TiN) electrodes on three-dimensional (3D) substrates with various electrolytes and high-rate cycling conditions. These electrodes exhibit cycling stability with negligible capacitance fading after thousands of cycles and a great rate capability, allowing the (dis)charge rate to extend from 0.1 to 10 V s⁻¹ and retaining nearly 50% of the capacitance in a three-electrode system. Symmetric devices made with TiN/Ti electrodes are capable of working at scan rates up to 100 V s⁻¹, yielding a remarkable power density. To further maximize the energy density, the aqueous electrolyte can be replaced with an organic one. Despite not having energy density of carbon-based supercapacitors, other aspects of TiN-based systems are very attractive for future applications. Strategies for further maximizing the performance of this system will be discussed, as material synthesis and device processing options suggest that 3D TiN structures can enable a new class of high-power ECs with enhanced stability compared to their carbon- and pseudo- counterparts.

9:15 AM ET03.10.04

Energy Storage Mechanisms in Niobium Oxides with Different Electrolytes Jiahe Zhang and Haitao Zhang; Chinese Academy of Sciences, Beijing, China.

Electrical energy storage and conversion devices, electrochemical capacitors and batteries, are attracting broad interests due to their advantageous

features of high round-trip efficiency, long cycle life. Among of different compounds, niobium oxides are pursued drastically owing to their high specific capacitance. Numerous nanocarbons are being utilized to modify these electron insulating niobium oxides to fully manifest their high specific capacitance. In addition, these compounds are also excellent candidate anodes for solid state devices. Therefore, the energy storage processes become more complicated once solid state and formulated electrolytes are employed. Generally, there are two storage behaviors involved, surface behavior and bulk charge behavior. Here we are going to present our recent results related to the energy storage mechanisms in niobium based oxides with ionic liquids based electrolytes. (1) Qualitative analysis, the contribution of the capacitive and diffusion-limited elements are separated in different environments by using the b value. The ionic liquid system that has the highest b value can deliver the biggest capacitive contribution than organic and gel systems. (2) Quantitative analysis, we calculated the capacitive contributions at various scan rates in three systems. The highest capacitive ratio exists in ionic liquid system at all scan rates. The ionic liquid system's capacitive contribution increased gradually with increasing scan rate. (3) Effect of temperature on the mechanisms was evaluated to optimize the formula. We found that the capacitive ratio increased gradually and ionic liquid system could achieve maximum ratio with increasing temperatures. Our finding suggests that the ionic liquids could offer more capacitive contribution and regulate the storage mechanism.

9:30 AM ET03.10.05

Solvent-Driven Morphology Controls of Nanomaterials for High Performance Supercapacitors Jae-Jin Shim, Debananda Mohapatra, Marjorie Baynosa, Van Quang Nguyen and Ganesh Dhakal; Yeungnam University, Gyeongsan, Korea (the Republic of).

Energy storage is essential for steady supply of renewable energy such as solar energy and wind energy. A supercapacitor is an important energy storage device together with rechargeable battery. Numerous researchers have been developing novel materials for electrochemical energy storage. Graphene and carbon nanotubes have been used to enhance conductivity of active electrode materials such as metal oxides, sulfides, or hydroxides. In addition, 3-D materials have also been synthesized to increase the surface area and pore sizes for a better charge collection and transfer.

In this study, the morphology of nanomaterials has been successfully controlled by using different reaction medium and by use of microwave and ultrasonicators. Several different morphologies will be shown and their synthesis processes will be discussed. Some of them show excellent energy storage performances. The materials synthesized by these new methods may be used for energy storage devices, sensors, and photocatalysts in the near future.

9:45 AM BREAK

10:15 AM ET03.10.06

High Performance Electrochemical Capacitors Based on Conductive Two-Dimensional Metal-Organic Frameworks Maria Lukatskaya and Zhenan Bao; Stanford University, Stanford, California, United States.

As electronic technology advances, the need in safe and long-lasting energy storage devices that occupy minimum volume arises. Short charging times of several seconds to minutes, with energy densities comparable to those of batteries, can be achieved in electrochemical capacitors (supercapacitors), in particular pseudocapacitors, which utilize fast redox reactions to store charge and, thus, feature high energy densities. However, metal oxides that are currently used in energy storage technologies have certain limitations. Due to low intrinsic electrical conductivity they might suffer from poor cyclability and deterioration of electrochemical performance for thick electrodes. As an alternative, conductive materials with build-in redox centers pose particular interest.

Herein, we report on the new family of the conductive 2D porous metal organic frameworks and we investigated their potential for electrochemical capacitors. A perspective of usage of the metal organic frameworks for the energy storage is particularly appealing since it can enable energy-efficient way of the room temperature synthesis of the electrode materials. Our evaluation demonstrated impressive gravimetric capacitance up to 500 F/g coupled with high volumetric capacitances up to 760 F/cm³. Moreover, we demonstrate excellent scalability of the electrochemical performance for this system: upon increase in electrode thickness up to 350 μ m, the areal capacitance did not plateau and reached a value over 20 F/cm². This demonstrates that redox-active conductive MOFs can potentially outperform other traditional materials in energy storage applications. We also discuss charge storage mechanism and factors affecting electrochemical performance of the conductive MOFs.

10:30 AM ET03.10.07

Nanoscale Ostwald Ripening—Characterizations and Effects on Realizing Fast Charging Capability of Electrochemical Capacitors with Abundant Manganese Dioxide Tianyu Liu¹, Yu Song^{2, 1}, Xiaoxia Liu² and Yat Li¹; ¹Department of Chemistry and Biochemistry, University of California, Santa Cruz, Santa Cruz, California, United States; ²Department of Chemistry, Northeastern University, Shenyang, China.

We recently discovered that, nanoscale Ostwald ripening of a thick layer of manganese dioxide (MnO₂) nanosheets could be induced by a facile hydrothermal treatment. This nanoscale process coalesced the surface nanosheets into a highly crystalline and porous coating layer, forming a well-resolved core-shell structure. The presence of this crystalline coating was capable of substantially facilitating both ion diffusion and electron transport throughout the thick MnO₂ film, which was desirable for practical electrochemical capacitors with high mass loading of active materials. The core-shell structure, when deployed as a pseudocapacitive electrode with 9 mg cm⁻² of MnO₂, achieved a geometric areal capacitance of 618 mF cm⁻² at a fast scan rate of 200 mV s⁻¹. The MnO₂ mass loading could further be promoted to as remarkably high as 23.5 mg cm⁻² without greatly compromising its fast charge-storage capability. This performance was among the best values ever reported for MnO₂-based electrodes with comparable mass loading. This presentation will first cover the characterization results of the Ostwald ripening-induced core-shell structure (including morphology, composition and porosity), followed by discussions on their mechanistic links to the observed superior electrochemical energy storage performance.

10:45 AM ET03.10.08

Nano-Sized Structurally Disordered Metal Oxide Composite Aerogels as High-Power Anodes in Hybrid Supercapacitors Haijian Huang¹, Xing Wang^{1, 3}, Elena Tervoort¹, Guobo Zeng², Tian Liu¹, Xi Chen¹, Alla Sologubenko¹ and Markus Niederberger¹; ¹ETH Zurich, Zurich, Switzerland; ²University of California, Berkeley, Berkeley, California, United States; ³Paul Scherrer Institute, Zurich, Switzerland.

With rechargeable battery technology moving to an era of medium/large-scale applications, the development of next-generation energy storage devices offering not only high-energy density but also high-power density becomes more and more imperative. Rechargeable lithium-ion batteries usually have high energy density, whereas their power density and cycle life are far from satisfactory. Alternatively, supercapacitors exhibit rapid power delivery, but are limited by their low charge storage capability. To integrate high-energy output with high-power delivery, lithium-ion hybrid supercapacitors (Li-HSCs) have been explored in recent years. One of the main challenges on the way to fabricating high-performance Li-HSCs is the development of high-power Faradaic anodes to solve the kinetic imbalance between the sluggish Faradaic anode and the capacitive cathode.

In this work, we developed a general method for synthesizing nano-sized metal oxide nanoparticles with highly disordered crystal structure and their processing into stable aqueous dispersions.[1] With these structurally disordered nanoparticles as building blocks, a series of nanoparticles@ reduced graphene oxide (rGO) composite aerogels are fabricated and used as binder-free high-power anodes for lithium-ion hybrid supercapacitors (Li-HSCs). To clarify the effect of the degree of disorder, control samples of crystalline nanoparticles with similar particle size are prepared. The results indicate that the structurally disordered samples show a significantly enhanced electrochemical performance compared to the crystalline counterparts. In particular,

structurally disordered $\text{Ni}_x\text{Fe}_y\text{O}_z/\text{rGO}$ delivers a capacity of 388 mAh g^{-1} at 5 A g^{-1} , which is 6 times that of the crystalline sample. Disordered $\text{Ni}_x\text{Fe}_y\text{O}_z/\text{rGO}$ is taken as an example to study the reasons for the enhanced performance. Compared with the crystalline sample, density functional theory calculations reveal a smaller volume expansion during Li^+ insertion for the structurally disordered $\text{Ni}_x\text{Fe}_y\text{O}_z$ nanoparticles, and they are found to exhibit larger pseudocapacitive effects. Combined with an activated carbon (AC) cathode, full-cell tests of the lithium-ion hybrid supercapacitors are performed, demonstrating that the structurally disordered metal oxide nanoparticles@rGO||AC hybrid systems deliver high energy and power densities within the voltage range of 1.0–4.0 V. These results indicate that structurally disordered nanomaterials might be interesting candidates for exploring high-power anodes for Li-HSCs.

[1] H. Huang, X. Wang, E. Tervoort, G. Zeng, T. Liu, X. Chen, A. Sologubenko, M. Niederberger, *ACS Nano* 2018, 12, 2753.

11:00 AM ET03.10.09

Towards Intercalation Based Electrochemical Capacitors—Ion Intercalation and High-Rate Pseudocapacitance of Two-Dimensional V_2CT_x MXene Armin VahidMohammadi and Majid Beidaghi; Auburn University, Auburn, Alabama, United States.

High-energy and high-power density energy storage systems capable of ultrafast storage and delivery of electrical energy are crucial for the development of mobile electronics and future electric transportation systems. Electrochemical capacitors (ECs) can provide charging times of seconds to minutes, resulting in power densities that exceed those of batteries and still offer long cycle life of over hundred thousand cycles. However, ECs suffer from low energy densities. An effective approach to increase the energy density of ECs is through the use of electrode materials that store charge based on pseudocapacitance mechanism.¹ In particular, intercalation-based pseudocapacitive materials have recently received increasing attention as potential electrode materials for future ECs. In this type of electrodes charge is stored through pseudocapacitance mechanism in the bulk of the material by ultrafast intercalation of ions into its structure.² While there are not many materials that can store charge based on this mechanism, a large family of two-dimensional (2D) transition metal carbides and nitrides, called MXenes, have shown promising performances as electrode materials for intercalation-based pseudocapacitive energy storage. For example, a MXene with the composition of $\text{Ti}_3\text{C}_2\text{T}_x$ is reported to deliver record high specific capacitances and high rate capabilities.³ However, despite the promising electrochemical properties shown for $\text{Ti}_3\text{C}_2\text{T}_x$, pseudocapacitive performance of other members of the MXene family of materials, which so far includes about 20 different composition and structures, has rarely been explored. This is partly due to instability and rapid structural degradation of some of these materials when synthesized through the current synthesis methods. In this talk, we will present our recent work on synthesizing highly stable electrode materials based on 2D V_2CT_x . We demonstrate that this MXene can intercalate a variety of cations, deliver volumetric capacitances of more than 1200 F cm^{-3} , maintain gravimetric capacitances in excess of 200 F g^{-1} at extremely high charging rates of over 100 A g^{-1} , and provide life cycle and capacitance retention that excel those of $\text{Ti}_3\text{C}_2\text{T}_x$. The research findings summarized in this presentation will provide a path for designing a variety of high-performance pseudocapacitive electrodes based on MXenes.

1. Lukatskaya, M. R. *et al.* Cation intercalation and high volumetric capacitance of two-dimensional titanium carbide. *Science* 341, 1502–5 (2013).
2. Augustyn, V. *et al.* High-rate electrochemical energy storage through Li^+ intercalation pseudocapacitance. *Nat. Mater.* 12, 518–22 (2013).
3. Lukatskaya, M. R. *et al.* Ultrahigh-rate pseudocapacitive energy storage in two-dimensional transition metal carbides. *Nat. Energy* 17105, 1–6 (2017).

11:15 AM ET03.10.10

3-Dimensional Substrates Associated with Iridium Oxide Nanoparticles for the Improvement of Specific Capacitance Kris Senecal¹, Shannon McGraw¹ and Kwok Fan Chow²; ¹US Army RDECOM, NSRDEC, Natick, Massachusetts, United States; ²Chemistry, University of Massachusetts Lowell, Lowell, Massachusetts, United States.

We seek to address the power and energy (P&E) needs of the Soldier by investigating commercial fabric materials as an enabling technology for energy storage on fabric platforms with minimal burden for the soldier in the field. Army scientific community state the dismounted soldier P&E needs will require advanced materials research to include power sources, power management and renewable energy solutions to enable remote power generation to lighten the Soldier's load. Structures that can be electrically charged and lightweight are desirable for a wide range of Army systems from batteries to sensors. In this work we investigated the specific capacitance of commercially available nonwoven and knitted cotton textiles that had been modified with a conductive carbon coating and 3-D carbon nanotube/graphene 'felt' with and without the addition of redox reactive nanoparticles. Nonwoven materials were investigated due to inherent properties such as flexibility and high surface area that could contribute additional energy storage capacity. These substrates were coated with varying permutations of carbon based coatings (carbon nanotubes and graphene oxide). The transition metal, iridium oxide, was electrodeposited as nanoparticles of less than 2 nm in size to serve as a supplemental redox active component for increased energy capacitance. Studies were conducted on the application and electrical properties of these iridium oxide nanoparticles when integrated in a 3-D fibrous electrode configuration, monitoring the increase in capacitance in textile based energy storage and performance devices (charge and discharge) for low power applications. Coated textile platforms were characterized using SEM and digital optical microscopy for coating association/adhesion on the fibers. Cyclic voltammetry was used to measure electron transfer properties and specific capacitance/gram of textile. Additionally we measured electrical resistance, air permeability, and charge/discharge rates. Results show up to a 5x increase in specific capacitance over the coated textile alone with the added deposition of iridium oxide nanoparticles and the highest specific capacitance was found in the 3-D carbon nanotube/graphene felt. These high surface area materials are being developed to potentially serve as the electrode platform component in a novel textile capacitor. This research will advance the fundamental understanding of the relationship between high surface area and the use of redox reactive nanoparticles on electrochemical charge storage mechanisms.

11:30 AM ET03.10.11

Electrochemical Intercalation of MoS_2 Composites for Supercapacitor Electrodes Using Non-Hydrated Cations Pawin Iamprasertkun^{1,2}, Wisit Hirunpinoyas^{1,2}, Mark A. Bissett^{2,3} and Robert A. Dryfe^{1,2}; ¹School of Chemistry, University of Manchester, Manchester, United Kingdom; ²National Graphene Institute, University of Manchester, Manchester, United Kingdom; ³School of Materials, University of Manchester, Manchester, United Kingdom.

Nanochannels can be spontaneously fabricated by forming "membranes" of two-dimensional materials. MoS_2 has attracted attention in this respect for fundamental studies and due to its superior properties in energy storage applications [1]. However, the charge storage mechanism, including surface ion adsorption and intercalation, are not yet fully understood. In this work, free-standing MoS_2 composite electrodes are prepared and studied *via* the intercalation of non-hydrated cations (without hydration shell). It is found that tetramethylammonium chloride (TMACl) provides double the capacitance compared to tetraethylammonium chloride (TEACl) and tetrapropylammonium chloride (TPACl). This is because MoS_2 provides an interlayer spacing of 0.615 nm, which is greater than the crystallographic diameter of TMA^+ (0.558 nm). In contrast, the crystallographic diameter of TEA^+ (0.674 nm) and TPA^+ (0.758 nm) are greater than that of MoS_2 . This can lead to storage of the charge only on the surface of the materials, through ion adsorption. Moreover, we have found that using the TPA^+ ion that is larger than the interlayer spacing of MoS_2 leads to the partial re-exfoliation of the as-prepared materials, which can enhance the capacitance retention during cycling. These results improve the understanding of charge storage mechanism of layered 2D materials.

SESSION ET03.11: Fuel Cells
Session Chairs: Bin Liu and Karthish Manthiram
Thursday Afternoon, November 29, 2018
Hynes, Level 3, Room 302

1:30 PM *ET03.11.01

Carbon-Based Metal-Free Electrocatalysis for Efficient Energy Conversion and Storage Liming Dai; Case Western Reserve University, Cleveland, Ohio, United States.

Green and renewable energy technologies, such as fuel cells, batteries, and water-splitting systems, hold great promise to solve current energy and environmental challenges. However, noble metal catalysts (*e.g.*, Pt, Pd, RuO₂, IrO₂) are generally needed to promote the *hydrogen evolution reaction* (HER) for hydrogen fuel generation from photo-electrochemical water-splitting, *oxygen reduction reaction* (ORR) in fuel cells for energy conversion, and *oxygen evolution reaction* (OER) in metal-air batteries for energy storage. The high cost of precious metal-based catalysts and their limited reserve have precluded these renewable energy technologies from large-scale applications.

Along with the recent intensive research efforts in non-noble metal based ORR catalysts, we have previously demonstrated that vertically-aligned nitrogen-doped carbon nanotubes could actively catalyze ORR *via* a four-electron process free from the CO poisoning effects with a 3-time higher electrocatalytic activity and better long-term durability than that of commercial Pt/C catalysts. The improved catalytic performance was attributed to the doping-induced charge transfer from carbon atoms adjacent to the nitrogen atoms to change the chemisorption mode of O₂ and to readily attract electrons from the anode for facilitating the ORR.

Subsequently, it was demonstrated that various graphitic carbon materials, doped with heteroatoms of different electronegativities from that of carbon atom, physically adsorbed with certain polyelectrolytes, and even without any apparent dopant or physically adsorbed polyelectrolyte, could also exhibit good ORR performance. More recent studies have further demonstrated that certain heteroatom-doped carbon nanomaterials could act as metal-free bifunctional catalysts for ORR/OER in metal-air batteries for energy storage, and even ORR/OER/HER trifunctional catalysts for self-powered water-splitting to generate hydrogen fuel and oxygen gas from water.

In this talk, I will summarize some of our work on the metal-free catalysts based on carbon nanomaterials for various energy-related reactions, along with an overview on the recent advances and perspectives in this exciting field.

2:00 PM *ET03.11.02

Electrochemically Driving High Hydrogen Concentrations into Palladium via Aqueous and Solid Electrolytes Yet-Ming Chiang¹, Jesse D. Benck¹, Ariel Jackson¹, David Young¹ and Daniel Rettenwander²; ¹Massachusetts Institute of Technology, Cambridge, Massachusetts, United States; ²TU Graz, Graz, Austria.

Metal hydrides are critical materials in numerous energy technologies including hydrogen storage, gas separation, and electrocatalysis. Here, using Pd-H as a model metal hydride, we perform electrochemical insertion studies of hydrogen via liquid and solid state electrolytes at 1 atm ambient pressure, and achieve H:Pd ratios near unity, the theoretical solubility limit, in nanometer-scale films. We show that the compositions achieved result from a dynamic balance between the rate of hydrogen insertion and evolution from the Pd lattice, the combined kinetics of which are sufficiently rapid that operando experiments are necessary to characterize instantaneous PdH_x composition. We use simultaneous electrochemical insertion and X-ray diffraction measurements, combined with a new calibration of lattice parameter versus hydrogen concentration, to enable accurate quantification of the composition of electrochemically synthesized PdH_x. Furthermore, we show that the achievable hydrogen concentration is severely limited by electrochemomechanical damage to the palladium and/or substrate. The understanding embodied in these results helps to establish new design rules for achieving high hydrogen concentrations in metal hydrides.

2:30 PM ET03.11.03

Computational Study of Nanoscale Active Sites in PGM-Free Electrocatalysts for Proton Exchange Membrane Fuel Cells Kexi Liu, Boyang Li, Zhenyu Liu and Guofeng Wang; University of Pittsburgh, Pittsburgh, Pennsylvania, United States.

Proton exchange membrane fuel cells (PEMFCs) can convert chemical energy stored in hydrogen fuels to electricity and produce environmentally benign product water. However, the commercialization of PEMFCs is hindered by the present requirement of expensive Pt group metals (PGM) as their electrocatalysts. To advance PEMFC technology, it is of great interests to develop earth-abundant, non-precious metal based catalysts in replacement of Pt, especially for oxygen reduction reaction (ORR) occurring at the cathode of PEMFCs. Recently, non-precious transition metal/nitrogen doped carbon (TM-N-C) catalysts have drawn much attention as a promising PGM-free ORR electrocatalyst due to its ORR activity approaching to Pt. However, the chemical structure of the active sites in these TM-N-C catalysts and their catalytic mechanism for ORR have not been fully understood. To gain insight into the nature of the nanoscale active sites in the TM-N-C catalysts, we have performed density functional theory (DFT) calculations to investigate the progression of ORR on various types of TM-N₄ (TM = Fe, Co) moiety substitutionally embedded into a graphene layer. On each possible TM-N₄ active site, we calculated the adsorption energies of all the relevant chemical species, namely, O₂, O, OH, OOH, HOOH and H₂O, and the activation energies for O-O dissociation reactions involved in ORR using the DFT method. On FeN₄ and/or CoN₄ embedded in an intact graphene plane, our DFT calculations predicted that the ORR could happen through 4e⁻ associative pathway on the FeN₄ site, whereas follow a 2e⁻ pathway on the CoN₄ site due to high activation energy for O-O bond splitting and extremely weak adsorption of H₂O₂ on the CoN₄ site. These theoretical results are in agreement with experimental observations. In addition, we studied the ORR on a FeN₄ moiety bridging two adjacent armchair like graphene edges as well as a FeN₄ moiety bridging two adjacent zigzag graphene edges with a porphyrinic architecture. Among the three FeN₄ moieties, the porphyrin-like FeN₄ moiety was predicted to catalyze ORR with the highest onset potential. Moreover, we found that the O-O bond scission had lower activation energy on the FeN₄ moieties bridging graphene edges than on the FeN₄ moiety embedded in an intact graphene layer. Consequently, our computation results suggest that introduction of micropores in the TM-N-C catalysts would enhance their catalytic activity for ORR through improving not only the specific area but also the intrinsic activity of the active sites.

2:45 PM ET03.11.04

Design of Cathode Materials for Solid Oxide Fuel Cells—A Mechanistic Approach M. Ali Haider and Uzma Anjum; IIT Delhi, New Delhi, India.

Molecular Dynamics (MD) simulations were utilized to calculate the oxygen anion diffusivity (D) in the lattice of the $\text{LnBa}_{1-x}\text{Sr}_x\text{Co}_y\text{Fe}_{1-y}\text{O}_{5+\delta}$ (LnBSCF, Ln = Gd, Pr) double perovskite structure. Oxygen anion diffusion coefficient for the $\text{PrBaCo}_2\text{O}_{5+\delta}$ (PBCO) material was calculated to be $3 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$ at 873 K in the a - b (Pr-O and Co-O) direction, which was observed to be higher than in the Ba-O plane ($D = 8 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$ at 873 K). On doping, the A'-site of PBCO with Sr and B-site with Fe, the resultant $\text{PrBa}_{1-x}\text{Sr}_x\text{Co}_y\text{Fe}_{1-y}\text{O}_{5+\delta}$ (PBSCF) structure was calculated to show an order of magnitude higher diffusivity ($D = 1.1 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ at 873 K) as compared to PBCO. Calculated diffusivity coefficients compared well with the measured electrocatalytic activity of the material. The electrochemical measurements were performed on a geometrically well-defined nanostructured thin-film electrode, fabricated as a symmetric cell using a spray pyrolysis deposition method. In combination with density functional theory (DFT) and MD simulations, experiments provided an insight into the operating mechanism. Following the hypothesis of a characteristic thickness (L_c) below which the performance is expected to be predominantly controlled by surface reaction, the L_c for layered perovskite LnBSCF at 973 K was calculated to be well above 1000 μm . Interestingly, a dense thin-film electrode of PBSCF (1 to 3 μm thick) deposited using the spray pyrolysis method showed a thickness dependent electrochemical performance suggesting bulk diffusion limitation. To understand the origin of this diffusion limited electrochemical performance, DFT calculations were utilized to calculate the surface energy (γ) and oxygen vacancy (E_{ov}) formation energies. For example, the E_{ov} in the Gd plane (98.4 kJ/mol) of $\text{GdBaCo}_2\text{O}_{5+\delta}$ (GBCO) was calculated to be lower than that of Ba plane ($E_{\text{ov}} = 266.3 \text{ kJ/mol}$). However, the surface energy of the Ba plane was calculated to be minimum ($\gamma = 7.2 \text{ kJ/mol \AA}$), which makes it the most exposed surface, while it is least diffusive. GBCO nanoparticles of reduced size were expected to expose higher energetic Gd plane, which may enhance diffusivity at the surface. The particle size of GBCO was reduced to 20 nm using a bio-milling approach, wherein the chemically synthesized particles were subjected to fungus *Saccharomyces Cerevisiae*, for 72 hours. The measured impedance of the electrode made up of bio-milled nanoparticles was improved by 20% as compared to the chemically synthesized material. MD simulation on the GBCO nanoparticles indicated two distinct regimes of diffusion; one corresponding to the surface and other to the bulk region of the nanoparticle. The diffusivity of the shell regime ($D = 6.8 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$ at 1073 K) was calculated similar to that of core ($D = 5.7 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$ at 1073 K). Thus, nanoparticles showed improved electrochemical performance as compared to the bulk electrode, likely due to the disruption of the Ba-plane at the surface.

3:00 PM BREAK

3:15 PM *ET03.11.04.5

How Strain Affects Reactivity at the Nanoscale [Andrew A. Peterson](#), Shubham Sharma, Cheng Zeng and Alireza Khorshidi; Brown University, Providence, Rhode Island, United States.

The reactivity of nanoscale surfaces drives the functional nature of materials such as catalysts, electrocatalysts, sensors, and batteries. This reactivity is known to be a function of the strain applied to the material. Here, we present a new way to rationalize such strain effects via an eigenstress model, which at the nanoscale manifests itself in simple force-displacement terms. We show how this can quantitatively rationalize such effects, and can lead to new designs at the nanoscale, such as anisotropic strain, which can break conventional constraints of materials design (such as the adsorbate scaling relations).

3:45 PM ET03.11.05

Theoretical Insights into the Effects of Transition Metal Doping on the Structure and Enhanced Stability of Pt-Ni Nanoparticles [Liang Cao](#) and Tim Mueller; Department of Materials Science and Engineering, Johns Hopkins University, Baltimore, Maryland, United States.

We present the use of *ab-initio* calculations and the kinetic Monte Carlo method to develop atomic-scale structure-stability relationships for Pt-Ni nanoparticles, promising catalysts for the oxygen reduction reaction (ORR). Although the practical use of Pt-Ni catalysts is limited by Ni dissolution under cell operating conditions, it has recently been shown that it is possible to stabilize octahedral Pt-Ni nanoparticles by alloying them with transition metals (e.g. Mo, Cu, and Rh). We discuss two examples of alloyed Pt-Ni nanoparticles: Mo-Pt-Ni and Cu-Pt-Ni. Using a newly developed kinetic Monte Carlo (KMC) model based on cluster expansions, we demonstrate that Mo atoms are preferentially located on the vertex and edge sites of Mo-Pt-Ni in the form of oxides which are stable within the wide potential window of the electrochemical cycle. These surface Mo oxides help protect Ni in sub-surface layers against acid dissolution. KMC simulations reveal that the enhanced stability of Cu-Pt-Ni is likely due to the reduction of the number of Ni and Cu atoms on the surface during synthesis, reducing the opportunity for Ni and Cu atoms in sub-surface layers to move to the surface and dissolve.

4:00 PM ET03.11.06

Ionomer Distribution Control in Fuel Cell Catalyst Layer via Pt Surface Modification [Gisu Doo](#), Seongmin Yuk, Sungyu Choi, Dong-Hyun Lee, Dong Wook Lee and Hee-Tak Kim; KAIST, Daejeon, Korea (the Republic of).

An universal structure of catalyst layer for polymer electrolyte membrane fuel cell is a mixture of proton conducting ionomer and carbon supported Pt nanoparticle catalyst. Such structure is commonly used because of its large catalyst surface area with abundant multiscale pores for gas diffusion. But, since the mixture is fabricated just by a vigorous mixing process, it has a limitation on the uncontrollable distribution of ionomer on catalyst particles. And because of the high polar-polar attraction between Pt and ionomer, the ionomer generally tends to distribute on Pt surface, forming few nanometer film. The ionomer films on Pt surface retard the oxygen transfer for the oxygen reduction reaction and adversely affect the power performance especially at a low Pt content in cathode. In this sense, nano-scale ionomer distribution modification toward the ionomer film reduction is needed for the enhancement of performance per Pt content. Herein, it is realized by selective masking of Pt surface with a typical hydrophobic adsorbate for Pt. The molecular dynamic simulations demonstrate that the hydrophobic masking induces a lowered interaction between the Pt and ionomer, and thus makes the ionomer film on Pt thinner. The lessened ionomer film can be observed and the recovery of the Pt catalytic activity is successfully carried out by electrochemical desorption of masking substances during the unit cell break-in step. The lessened ionomer film results in a dramatically enhanced power performance as a consequence of the enhanced oxygen transport in catalyst layer, which is attributed to the reduced ionomer film resistance.

4:15 PM ET03.11.07

Mapping Lattice Distortions with Sub-Nanometer Resolution in Strained Core-Shell Nanoparticle Fuel Cell Catalysts [Elliot Padgett](#)¹, Megan E. Holtz¹, Paul Cueva¹, Anusorn Kongkanand², Venkata Yarlaagadda² and David Muller^{1,3}; ¹Applied and Engineering Physics, Cornell University, Ithaca, New York, United States; ²Global Fuel Cell Business, General Motors, Pontiac, Michigan, United States; ³Kavli Institute at Cornell for Nanoscale Science, Cornell University, Ithaca, New York, United States.

Strain and lattice distortions play an important role in a variety of electrochemical energy materials, such as enhancing activity in catalytic nanoparticles and driving fracturing in lithium ion battery materials. However, detailed understanding of strain in many real nanoscale systems has remained elusive because of challenges for effective strain characterization. Localizing strain in nanomaterials requires spatial resolution unavailable in conventional diffraction, while sample instabilities and random crystallite orientations frequently hinder strain characterization by conventional high-resolution direct imaging techniques. With a new generation of fast, high-dynamic range electron cameras, scanning nanobeam diffraction provides a powerful approach to mapping lattice structure and distortions across a variety of length scales, from multi-micrometer battery particles to nanometer-sized core-shell nanoparticles.

Here we apply this approach to Pt-Co nanoparticle fuel cell catalysts, where a Pt-Co alloy core exerts a compressive strain on the surrounding Pt shell. This compressive strain is believed to enhance the oxygen reduction activity by modifying the electronic structure and oxygen binding strength at the catalyst surface. However, the relationship between activity and the structure of the nanoparticle and shell, as well as mechanisms by which strain may be relaxed, remain poorly understood. Using scanning nanobeam diffraction with new algorithms, we map lattice distortions with picometer precision and sub-nanometer spatial resolution. In combination with composition mapping by electron energy loss spectroscopy, this allows us to establish the connection between the nanoparticle structure, composition, and strain distribution. We examine the impact of variable Pt shell thickness on the surface strain, including unique strain relaxation effects due to the geometry of core-shell nanoparticles, and investigate the implications for catalyst activity. We also explore the mechanisms of strain loss after electrochemical aging in fuel cell membrane electrode assemblies leading to catalyst activity losses.

4:30 PM ET03.11.08

Anion-Exchange Membrane Fuel Cells with Improved CO₂-Tolerance—Impact of Chemically Induced Bicarbonate Ion Consumption Yu Katayama^{2,3,1}, Kosuke Yamauchi³, Kohei Hayashi³, Takeou Okanishi³, Hiroki Muroyama³, Toshiaki Matsui³, Yuuki Kikkawa⁴, Takayuki Negishi⁴, Shin Watanabe⁴, Takenori Isomura⁴ and Koichi Eguchi³; ¹Massachusetts Institute of Technology, Cambridge, Massachusetts, United States; ²Yamaguchi University, Ube, Japan; ³Kyoto University, Kyoto, Japan; ⁴Tokuyama Corporation, Tsukuba, Japan.

Over the last few decades, owing to the significant development of anion exchange membranes, increasing efforts have been devoted the realization of anion exchange membrane fuel cells (AEMFCs) that operate with the supply of hydrogen generated on-site. In this work, ammonia was selected as a hydrogen source, following which the effect of conceivable impurities, unreacted NH₃ and atmospheric CO₂, on the performance of AEMFCs was established. *In situ* surface enhanced infrared absorption spectroscopy (SEIRAS) revealed that the degradation of the cell performance was primarily due to the inhibition of the hydrogen oxidation reaction (HOR). This is attributed to the active site occupation by CO-related adsorbates derived from (bi)carbonate adsorbates. The degradation in the HOR activity is suppressed in the presence of both NH₃ and HCO₃⁻ due to the bicarbonate ion consumption reaction induced by the existence of NH₃. A fuel cell test was conducted by using the practical AEMFC with the supply of NH₃-contained H₂ gas to the anode and ambient air to the cathode. The coexistence of NH₃ and HCO₃⁻ improved CO₂-tolerance of AEMFCs, the cell performance was nearly 95% of that without any impurity in the fuels. These results clearly show the impact of the chemically induced bicarbonate ion consumption reaction on the realization of highly CO₂-tolerent AEMFCs.

4:45 PM ET03.11.09

Scale up of Advanced Fuel Cell Catalysts Rongyue Wang, Kris Pupek, Trevor Dzwiniel, Nigel Becknell, Pietro Lopes, Haifeng Lv, Eric Coleman, Nenad Markovic and Vojislav Stamenkovic; Argonne National Laboratory, Lemont, Illinois, United States.

A recently discovered Pt₃Ni(111) catalyst exhibits 90-fold improvement of catalytic activity compared to commercial Pt/C catalyst toward oxygen reduction reaction (ORR). Following this exciting development a variety of Pt alloy nanostructures with controlled size, morphology, composition, and surface arrangements have been synthesized using wet chemistry methods. Significant performance improvement has been observed in rotating disk electrode (RDE) measurements for many of the new materials. However, their performance in membrane electrode assembly (MEA) have been rarely tested because of the difficulty of producing larger quantity of uniform, high quality nanoparticles. One of Argonne's Materials Engineering Research Facility (MERF) programs is devoted to investigate the chemistry and processes that govern the reproducibility and scalability of nanomaterials synthesis. The aim of this program is to develop scalable processes for making large quantity of materials without sacrificing performance and to eliminate batch-to-batch variation in order to accelerate the transition of new discovers from lab to industrial applications. In this presentation, I will talk about our recent efforts in scaling up advanced fuel cell catalysts. A multi-layer Pt-skin PtNi nanoparticles have been successfully scaled up from tens of milligrams to several grams per batch with improved ORR activity in RDE measurement which is a 10-fold improvement over commercial Pt/C catalyst. The material was synthesized in a sufficient amount to enable MEA tests to be carried out. The results revealed significant performance improvements compared to commercial Pt/C catalyst. Our recent effort to remove restraints associated with batch processes lead us to develop a continuous flow synthesis platform. Our approach to gain fundamental understanding of the particle formation mechanism in microfluidic reactors will also be discussed.

SESSION ET03.12: Poster Session IV: Battery
Session Chairs: Weiyang Li and Nian Liu
Thursday Afternoon, November 29, 2018
8:00 PM - 10:00 PM
Hynes, Level 1, Hall B

ET03.12.01

Light-Weight 3D Co-N-Doping Hollow Carbon Spheres as Efficient Electrocatalyst for Rechargeable Zinc-Air Battery Shengmei Chen; City University of Hong Kong, Hong Kong, Hong Kong.

Rational design of cost-effective, nonprecious metal-based catalysts with desirable oxygen reduction reaction (ORR) performance by simple and economic synthesis route is a great challenge for future fuel cell and metal air batteries commercialization. Herein, the light-weight 3D Co-N-doped hollow carbon spheres (Co-NHCs) has been fabricated via a facile emulsion approach followed by carbonization. The prepared 0.1-Co-NHCs catalyst with suitable Co doping content exhibits favorable ORR catalytic activity (onset potential of 0.99 V and half-wave potential of 0.81 V vs. RHE), comparable to that of the commercial Pt-C (onset potential of 1.02 V and half-wave potential of 0.83 V vs. RHE) and rivals that of Pt-C with better cycling stability. The excellent performance of the catalyst is attributed to the synergistic effect of Co and N doping with high total ratio of active sites, high surface area and good conductivity of the material. More impressively, the assembled rechargeable zinc-air batteries base on the 0.1-Co-NHCs catalyst outperforms those afforded by commercial Pt-C. The progress represented by this reported work is of great importance in the development of outstanding non-noble metal based electrocatalyst for the fuel cell and metal air battery industry.

ET03.12.02

Hierarchical Sb₂MoO₆ Hollow Microspheres with Distinctive Capability of Self-Constructing Conductive Buffer Matrix for Sodium-Ion Batteries Xuan Lu^{1,2}, Hongkang Wang¹ and Weiyang Li²; ¹Electrical Engineering, Xi'an Jiaotong University, Xi'an, China; ²Thayer School of Engineering, Dartmouth College, Hanover, New Hampshire, United States.

In order to solve the capacity degradation problem caused by the severe volume expansion in alloy-type Sb anode materials, we report a simple and

efficient microwave-assisted hydrothermal method of hierarchical Sb_2MoO_6 hollow microspheres (denoted as h-SMO-hms) assembled by one-dimensional (1D) nanobelts without use of any surfactants, as well as a special conductive $\text{Na}_x\text{MoO}_x\text{:NaMoO}_2$ buffer matrix is firstly proposed. When used as an anode material for sodium-ion batteries (SIBs), it delivers large reversible discharge capacities of $\sim 637.3/498.7$ mA h/g at current densities of 200/1000 mA/g after 100 cycles, respectively, and an exceptional rate capability with ~ 428.1 mA h/g retained at 5A/g. By means of ex-situ XRD, XPS, (HR)TEM, STEM-EDS mappings and results of the first-principles calculations, such superior electrochemical performances can be attributed to their distinctive capability of self-constructing conductive $\text{Na}_x\text{MoO}_x\text{:NaMoO}_2$ buffer matrix during the discharge/charge process, which not only efficiently buffer the volume expansion of the Na-Sb alloying-dealloying upon cycling, but also provide good electronic conductivity to facilitate electron transfer. More importantly, the novel Sb_2MoO_6 anode materials can achieve excellent electrochemical behaviors without the need to hybridize with any carbonaceous materials (ex. carbon nanotubes, graphene and carbon nanofibers) in contrast to those of Sb-C composites. This kind of materials may offer new strategies for researchers to design high-performance energy storage devices.

ET03.12.03

Single-Site Active Iron-Based Bi-Functional Oxygen Catalyst for a Compressible and Rechargeable Zinc-Air Battery [Longtao Ma](#); Department of Materials Science and Engineering, City University of Hong Kong, Hong Kong, Hong Kong.

With the ever-increasing energy demands for portable electronic equipment, numerous researches have been done to develop related functional (e.g., stretchable, compressible, bendable/flexible, self-healing) electrochemical energy storage and conversion devices. Zinc-air battery, which is typically comprised of air electrode containing a catalyst painted on gas diffusion layer, alkaline electrolyte and metallic zinc electrode to provide a high theoretical energy density (1370 Wh/Kg), is a promising energy storage appliance for next-generation portable electronics. For rechargeable zinc-air battery, a high-efficient, low-cost and stable non-noble metal-based catalyst with oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) simultaneously, as air electrode material is significantly crucial. Meanwhile, the compressible flexibility of a battery is the prerequisite of wearable or/and portable electronics.

Herein, we present a strategy *via* single-site dispersing Fe- N_x species on a two dimensional (2D) highly-graphitic porous nitrogen-doped carbon layer to implement superior catalytic activity toward ORR/OER (with a half-wave potential of 0.86 V for ORR and an over-potential of 390 mV at 10 mA/cm² for OER) in alkaline medium. Furthermore, an elastic polyacrylamide (PAM) hydrogel based electrolyte with the capability to remain great elasticity even under highly corrosive alkaline environment, is utilized to develop a solid-state compressible and rechargeable zinc-air battery. The creatively developed battery performs a low charge-discharge voltage gap (0.78 V at 5 mA/cm²) and large power density (118 mW/cm²). It could be compressed up to 54% strain and bended up to 90° without charge/discharge performance and output power degradation. Our results reveal that single-site dispersion of catalytic active sites on porous support for bi-functional oxygen catalyst as cathode integrating specially designed elastic electrolyte are feasible strategies for fabricating efficient compressible and rechargeable zinc-air batteries, which could enlighten the design and development of other functional electronic devices.

ET03.12.04

Silicon Nanoparticles in Lithium-Ion Batteries—Influence of Size and Morphology [Samson Y. Lai](#)¹, Thomas J. Preston², Hallgeir Klette², Trygve T. Mongstad², Jan Petter Mæhlen² and Alexey Y. Kopusov²; ¹Neutron Materials Characterization Department, Institutt For Energiteknikk, Kjeller, Norway; ²Battery Technology Department, Institutt For Energiteknikk, Kjeller, Norway.

Silicon as a negative electrode material attracts significant research and development attention for next-generation lithium-ion batteries (LIBs). To counteract the high volume expansion associated with lithiation, silicon nanoparticles are materials designed to extend cycle life. However, silicon nanoparticles can be synthesized using different routes that result in variations in particle size, size distribution, and morphology, which then influence the overall electrochemical performance. The optimal size of the particles is still disputed in the literature. Correlating morphology and size with battery properties is needed to apply the diverse knowledge of these different approaches toward understandable behavior of silicon nanoparticles in LIBs.

In the present work, we examine silicon nanoparticles synthesized by pyrolysis of silane gas and correlate morphological characteristics with battery performance. We demonstrate that temperature and silane concentration during synthesis influence the size and morphology of the silicon nanoparticles. For example, relatively low temperatures typically produce a mixture of small and large round particles with smooth surfaces while relatively high temperatures produce particles with rougher surfaces with a narrower size distribution. These differences are correlated to crack formation and propagation in the electrode during formation cycles, as evidenced by post-mortem analysis. Furthermore, although charge-discharge capacities and Coulombic efficiencies of half cells made with these particles are initially high, the degradation rate of particles with rougher surfaces is noticeably worse, suggesting a separate mechanism in action. Thus, although nanoparticles smaller than a widely cited 200 nm size may resist cracking individually, the size and morphology of the nanoparticles appears to influence macro-scale crack formation in the electrode and consequently, electrochemical performance. As silicon nanostructures become more defined and controlled through synthesis, understanding the relationship between structure and properties of silicon nanoparticles is important in order to take full advantage of this promising approach in LIBs.

ET03.12.05

LiNi_{0.5}Mn_{0.3}Co_{0.2}O₂/Au Nanocomposite Thin-Film Cathode with Enhanced Electrochemical Properties [Zhimin Qi](#)¹, Jie Jian¹, Jijie Huang¹, Jialiang Tang², Han Wang¹, Vilas G. Pol² and Haiyan Wang¹; ¹Materials Engineering, Purdue University, West Lafayette, Indiana, United States; ²Chemical Engineering, Purdue University, West Lafayette, Indiana, United States.

Li(Ni_xMn_yCo_{1-x-y})O₂ (NMC) is considered as one of the most promising cathode materials for Li-ion batteries. Highly textured LiNi_{0.5}Mn_{0.3}Co_{0.2}O₂ (NMC532) thin films with well dispersed Au nanoparticles (~ 5 nm in average diameter) were deposited by pulsed laser deposition. Microstructure studies reveal the epitaxial nature of the Au nanoparticles and NMC matrix, and their lattice matching relationships. The Au nanoparticles are uniformly distributed and form faceted interfaces with NMC matrix. NMC with 2 at.% Au shows the highest volumetric capacity, best initial columbic efficiency, highest cycling performance, best rate capability and highest capacity retention among all the samples, due to alteration of chemical environment of transition metal while keeping high crystallinity. Moreover, the electrochemical impedance spectroscopy shows that the incorporation of the Au nanoparticles also reduces charge transfer resistance compared to the pure NMC. The results suggest that appropriate Au nanoparticle incorporation enhances the volumetric capacity and promotes the charge transfer process, and thus could lead to enhanced battery performance.[1]

Keywords: Au nanoparticles; NMC; Nanocomposite; Lithium ion battery; Cathode

[1] Z. Qi, J. Jian, J. Huang, J. Tang, H. Wang, V.G. Pol, H. Wang, LiNi_{0.5}Mn_{0.3}Co_{0.2}O₂/Au nanocomposite thin film cathode with enhanced electrochemical properties, Nano Energy. 46 (2018) 290–296. doi:10.1016/j.nanoen.2018.02.011.

ET03.12.06

The Initial Stages of Polaron Formation in Energy Materials [Shuaishuai Yuan](#), Zi Wang and Kirk H. Bevan; McGill University, Montreal, Quebec,

Canada.

Polaron transport severely limits the conduction properties of most transition metal oxides utilized electrochemical energy storage and conversion applications. Thus, to improve the charge performance of such energy devices, it is essential to delve more deeply and understand the fundamental stages of polaron formation. To this end, we have conducted extensive first-principles studies of polaron evolution in the peroxide family of materials: lithium peroxide (Li_2O_2), sodium peroxide (Na_2O_2), and potassium peroxide (K_2O_2). Our analysis points to competing lattice and electronic realization phenomena driving the rapid localization of polarons very early on in the relaxation process. They also indicate that the formation of polarons may be mitigated by suitably engineering the electronic structure response to lattice distortions, through a delayed electronic relaxation mechanism. Overall, these results point towards a systematic bottom-up approach for engineering the conductivity and overall electrochemical rate performance of metal oxide energy materials.

ET03.12.07

Novel Application of Magnetite Nanospheres as Supercapacitors—Synthesis, Magnetic, and Electrocapactive Study Dipesh Neupane, [Deepa Guragain](#), Sanjay R Mishra and Ram Gupta; Pittsburg State University, Pittsburg, Kansas, United States.

Among various morphologies of nanomaterials, hollow spheres are of great interest because of their high ratio of surface to volume, large pore volume and low density, which could be exploited for applications in controlled encapsulation-release of drugs and medical diagnostic, energy storage and conversion, photocatalysis, chemical sensors, and photonic crystals. In the context of magnetism, magnetic hollow spheres can show unique physical properties compared to those of flat thin films and their solid counterparts of the same sizes, due to their confined hollow geometry and curved surfaces. It is known, that coercivity is dependent on domain-wall motion and the barrier to domain-wall propagation along a curved surface is larger than that of a flat surface. Due to growing application of nanoscale magnetic hollow spheres in biomedical end energy fields it remains important to understand the influence of growth parameters to prepare Fe_3O_4 with highly homogeneous features in terms of size and shape.

In this work, effect of hydrolyzing agents such as urea, ammonium bicarbonate (ABC), dodecylamine (DDA) on morphology, size and electrochemical activity of Fe_3O_4 nanospheres was investigated. For comparison, Fe_3O_4 nanospheres were also synthesized without hydrolyzing agent. The structural and morphological assessment of the synthesized Fe_3O_4 nanopowder was performed using x-ray diffraction, scanning electron microscopy and surface area analysis. The room temperature magnetic properties were studied via vibrating sample magnetometer. The scanning electron microscopy images showed nanospheres of Fe_3O_4 with a range of sizes (150-330 nm) which depend on hydrolyzing agents used. All the synthesized samples were crystalline in structure with distinct signature of magnetite phase. The surface area analysis indicated that these particles were mesoporous in nature. VSM measurement show that Fe_3O_4 prepared via hydrolyzing agent display high magnetization ~ 85 emu/g with average coercivity in the range of 150 Oe. Different hydrolyzing agents were observed to have minimum influence on the magnetic property of Fe_3O_4 hollow spheres. Electrochemical characteristics were investigated using cyclic voltammetry and galvanostatic measurements. Cyclic voltammetry measurements were performed in three different electrolytes viz. KOH, NaOH, and LiOH and observed that specific capacitance of the synthesized Fe_3O_4 depend on electrolyte used. Relatively high specific capacitance of 173.8 F/g was observed for Fe_3O_4 prepared using DDA in 3M KOH electrolyte. Fe_3O_4 -DDA also showed excellent cyclic stability as well, retaining 107% of specific capacitance value at up to 5,000 cycles measured. The study clearly elucidates the effect of hydrolyzing agent on physical and morphological properties of Fe_3O_4 . In addition, through electrochemical testing the study illustrates the choice of aqueous electrolyte in optimizing the electrocapactive performance of Fe_3O_4 nanospheres.

ET03.12.08

Population Dynamics of Driven Reactive Mixtures Applied to Li-Ion Battery Electrodes [Hongbo Zhao](#) and Martin Bazant; Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

Li-ion batteries manifest intriguing asymmetric autocatalytic or autoinhibitory reaction kinetics during charge or discharge through experimental techniques such as X-ray imaging or diffraction performed on lithium iron phosphate and $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ (NMC). We use a population-dynamics approach to model such asymmetry, as the phenomenon arises from an assemble of particles that consist of the electrode. We study the collective dynamics of such systems with thermodynamically consistent nonequilibrium kinetics. When chemical driven, autocatalytic or autoinhibitory reactions lead to broadening or narrowing of the population distribution in terms of the state of subsystems compared to the intrinsic variance due to thermodynamic fluctuations and system noises. As an application, we obtain the inherent reaction kinetics from XRD and electrochemical experiments performed on NMC and demonstrate the agreement between experiments and simulation.

ET03.12.09

Current Density Dependency of Crack Formation in Si Wafer Electrode [Taeho Yoon](#), Chuanxiao Xiao, Jun Liu, Seoung-Bum Son and Chunmei Ban; National Renewal Energy Laboratory, Lakewood, Colorado, United States.

Silicon (Si) is regarded as a most promising anode material because of its high energy density, the earth-abundant, and low toxic nature. However, the electrochemical reversibility of Si degrades upon cycling; mainly due to huge volume changes and crack formation during lithiation and delithiation. Recent work has investigated the cracking formation mechanism and the impact of capping layer on the mechanical deformation behavior. Here, we will focus on the effects of current density on crack formations and propagation. The information from this research is essential to develop high-capacity and high-power Si electrodes for next-generation fast charging lithium-ion batteries. Si (100) wafer has been used as a model electrode to establish a systematic understanding of cracking behavior as a function of lithiation/delithiation rate. Moreover, the internal strain energy developed at the high current density and the strategies to mitigate cracking formation and propagation will be discussed in this work.

ET03.12.10

Effect of Graphene Oxide on Electrochemical Behavior of MnO_2 Supercapacitor [Rahul Singhal](#)¹, Justin Fagnoni¹, David Thorne¹ and Mani Manivannan²; ¹Central Connecticut State University, New Britain, Connecticut, United States; ²Global Pragmatic Materials, Morgantown, West Virginia, United States.

Supercapacitors have received a lot of attention due to their high-power performance, long cycle life, and low maintenance, for applications in hybrid electric vehicles, portable electronic devices, and power back-up devices [1-3]. Various researchers studied MnO_2 cathode materials for application in electrochemical capacitors, because of its low cost and natural abundance [2, 3]. However, MnO_2 has limited electrochemical performance because of its poor conductivity and low surface area. To improve the electrochemical performances of MnO_2 , we have synthesized MnO_2 /graphene oxide (GO) nanocomposite with varying concentration of GO (0.4 mg/ml and 0.8 mg/ml). GO/MnO_2 nanocomposite was synthesized by adding KMnO_4 in a solution of water and ethanol (3:1), containing desired amount of GO. The brown precipitates were obtained after a continuous stirring for 1 hr. The precipitate was washed and dried to obtain the GO/MnO_2 nanocomposites. The electrodes were prepared by spreading a slurry of GO/MnO_2 powder, carbon black, PTFE binder (80:15:5 weight ratio) onto Ni mesh. The electrochemical characterizations were carried out in an aqueous solution of 1M Na_2SO_4 . The charge discharge studies were carried out between 100 mA/g to 5A/g current

range. The discharge capacities were found to be 227 F/g and 90 F/g at a current of 100 mA/g and 5A/g, respectively for 0.4 mg/ml GO. These results will be presented and discussed at the meeting.

References:

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ET03.12.11

Sub-5 nm Graphene Oxide Nanofilm with Exceptionally High H⁺/V Selectivity for Vanadium Redox Flow Battery Seul Chan Park, Moon G. Hyeon, ByungSu Kim and Yong Soo Kang; Energy Engineering, Hanyang University, Seoul, Korea (the Republic of).

Highly H⁺/V selective membranes are desirable in high-performance vanadium redox flow batteries (VRFBs) to overcome the cross-over phenomena of vanadium species. Herein, we first demonstrated that the molecular-sieving nanochannels (~0.84 nm) formed inside a graphene oxide (GO) laminate (~5 μm) efficiently blocked the transport of vanadium ions, while allowing the transport of H⁺. Furthermore, an ultrathin (sub-5 nm) and highly-selective GO nanofilm was successfully coated on a porous substrate to improve the H⁺ flux using a facile spin-coating method. The GO-coated thin-film composite (TFC) membrane showed much higher H⁺ flux, along with an exceptionally high H⁺/V selectivity (up to 850), due to the molecular-sieving nanochannels inside the GO nanofilm, leading to a much more enhanced VRFB performance in terms of the energy efficiency (EE: 84.7%), compared to the benchmark Nafion membrane (EE: 69.2%), at 20 mA cm⁻². This work verifies the potential of the GO membrane for VRFBs for the first time, which paves the favorable way for utilization of GOs and their derivatives as a new class of membrane material for performance advancement of VRFBs.

ET03.12.12

Lattice Strain and Phase Transition Induced by Li Migration in Cyclic NCM111 (LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂) Young-Woon Byeon^{1,2}, Jun-Dong Kim¹ and Jaepyoung Ahn¹; ¹Advanced Analysis Center, Korea Institute of Science and Technology, Seoul, Korea (the Republic of); ²Material Science and Engineering, Korea University, Seoul, Korea (the Republic of).

The phase transformation of LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ (NCM) cathode materials during charging and discharging Li-ion batteries was evaluated by lattice strain measured by nano-beam diffraction (NED) equipped in transmission electron microscopy (TEM). Here we propose a relationship between lattice strain determining by Li contents and phase transition. When Li site in NCM lattice was emptied below 1% by the delithiation during charging, the surface of NCM particles has high strain over 3% and the correlative phase transition also occurred from rhombohedral to spinel structure. The continued Li release in NCM leaded to the expansion of the spinel region from surface. Most of the strain and phase transition occurred near the side planes of NCM, not prism planes. On the Li insertion during discharging, on the other hand, the lattice strain of NCM recovered up to the level, below 0.8%, of pristine NCM due to the reverse phase transition from spinel to rhombohedral structure. However, NCM that had cycled under the harsh condition of 60 cycles at 60°C showed irreversible phase transition to rhombohedral phase, which acted as a reason of a direct degradation. We propose a design rule that can prevent the capacity decrease of batteries by clarifying the relationship between the lattice strain and phase transition, which act as a direct cause of the deterioration phenomenon of NCM.

ET03.12.13

Fabrication and Characterization of the Microporous Foam Thick Electrodes Based on LiFePO₄/Carbon Nanotube Composites Tawaddos S. Alkindi¹, Rahmat Susantyoko¹, Saif Al Mheiri¹, Daniel Choi¹, Sultan N. Al Dahmani² and Hamed Fadaq²; ¹Khalifa University of Science, Technology and Research, Abu Dhabi, United Arab Emirates; ²United Arab Emirates Space Agency, Abu Dhabi, United Arab Emirates.

Although Li-ion batteries are very promising, their areal capacity is quite low (2.09 mAh cm⁻² for conventional LiFePO₄ on aluminum foil). The aim of this work is to create CNT/LiFePO₄ composite thick cathode via Freeze-casting method to enhance the areal capacity of LiFePO₄ cathode. The CNTs form electrically conductive networks that also result in enhancing the charge transport of Li-ions. Conventional Li-ion batteries consist of multiple stacks of electrodes with aluminum and copper separator between them. This cell configuration increases the size of the battery, which increases battery weight, waste of the material, thus, yields to high cost. Using thick electrodes that will provide a favorable electrode to current collector ratio per stack volume, will increase the interface area between electrode and electrolyte, and fewer cutting and stapling steps. However, mechanical stability is also a main challenge in thick electrodes that are synthesized by this method. Various amount of polyvinylidene difluoride (PVDF) additives is added to the CNT/LiFePO₄ mixture to study their effect on the mechanical stability along with the battery performance. After determining the optimum thickness and composition, batteries with the thick electrodes will be assembled and characterized (CV, charge-discharge, EIS) using battery tester and potentiostat/galvanostat. Investigation of the multi-layered CNT/LiFePO₄ sheets by scanning electron microscopy, Raman scattering spectroscopy and X-ray diffraction is also in progress. Preliminary result shows 125 mAh g⁻¹ for 3.14 mm thickness cathode of CNT/LiFePO₄/PVDF (3% PVDF) which is very close to that from the conventional 2.03mm thick conventional CNT/LiFePO₄ electrode (0% PVDF). Mechanical compression results show that we can sacrifice the small decrease in specific capacity for the enhancement in the mechanical stability where CNT/LiFePO₄/PVDF (3% PVDF) exhibited stress value of 0.083752 MPa, while CNT/LiFePO₄ electrode (0% PVDF) exhibited a value of 0.05685036 MPa. Further increased thicknesses of electrodes with improved mechanical and thermal properties are to be pursued in future work. Such thick CNT/LiFePO₄ electrodes is very promising candidate for applications which is very sensitive to weight but not sensitive to size, such as space applications and electrical truck/bus.

ET03.12.14

Facet Engineering in Nanoporous Gold for Improved Oxygen Reduction Activity in Aluminum-Air Batteries Min Wang, Joel Chacko, Eric Detsi and James H. Pikul; University of Pennsylvania, Philadelphia, Pennsylvania, United States.

The electrochemical reduction of oxygen is a critical process for many energy storage and conversion technologies including metal-air batteries and fuel cells. For these technologies, the energy output is proportional to the oxygen reduction reaction (ORR) potential. Although the theoretical potential of the ORR reaction in alkaline media is 0.3 volts vs. Hg/HgO, most electrodes are far below 0.3 volts vs. Hg/HgO due to the slow ORR kinetics. In this abstract, we use surfactant-modified dealloying to synthesize (100) rich nanoporous gold (100-np-Au) electrodes which increased the ORR potential from -0.01 to 0.18 V vs. Hg/HgO when compared to nanoporous gold Au (np-Au) synthesized without surfactant. The 100-np-Au had a higher reduction potential than conventional np-Au because Au (100) is the most active ORR facet of gold in alkaline solution. Density functional theory simulations show that Au (100) activity exceeds platinum in alkaline solution.¹ We observe a similar trend experimentally as the 100-np-Au electrodes (2.1 mg/cm²) had a 2.8% improved ORR potential vs. Hg/HgO compared to high performance commercial platinum coated electrodes with double the mass loading density (4 mg/cm²). When integrated into aluminum-air batteries, the 2.1 mg/cm² 100-np-Au increased the cell energy density to 4256 mWh/g-Al compared to 3575 mWh/g-Al for 2.1 mg/cm² np-Au and 4060 mWh/g-Al for 4mg/cm² Pt/C cathodes by improving both the extracted capacity, through improved activity, and output voltage. The 100-np-Au Al-air battery achieved a 2800 mAh/g capacity at 50 mA/cm² and a peak power density of 176 mW/cm². We synthesized 100-np-

Au by adding sodium citrate to a nitric acid dealloying bath. The stronger binding energy between the citrate ligand and Au (100) surface reduced the (100) growth rate and exposed more (100) facets². This technique could be extended to the design and synthesis of various nanostructured catalysts with specific facets for energy storage and conversion.

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ET03.12.15

Vertically Integrated Method For The Development of Nano-Structured Electrodes for Flow Battery Application [Eugenio Rovera](#)^{1, 2}, Francesco Fumagalli¹, Matteo Zago², Andrea Casalegno² and Fabio Di Fonzo²; ¹CNST@Polimi, Milano, Italy; ²Energy, Politecnico di Milano, Milan, Italy.

Carbon is the more suitable material for nano-structured electrodes for flow battery application, due to their high conductivity, chemical resistance, activity towards ions redox couples (in particular Vanadium) [1].

The need for a fast selection of promising catalyst for vanadium flow battery have to face the problem that testing electrode in a full cell device is a long procedure that may take some days, while testing nano-materials in a 3 electrode cell is faster but not representative of real working conditions.

The proposed fabrication process aim to overcome this issue, proposing a methodology to asses electrode performances in a 3 electrode cell with a look at real working conditions.

In this work a vertical integrated approach for the development of carbon nano-structured electrodes is proposed: starting from a gas precursor this innovative process is able to lead to the functionalization of commercial GDLs with carbon nano-particle (NP), with a fine tuning regarding morphology, chemistry and defectiveness, all crucial parameters in the electrochemical performance.

Gas precursor is a mixture of argon and acetylene, used in a custom NP plasma source. The synthesized particles are characterized from chemical (FT-IR), morphological (TEM, SEM), structural (Raman) and electrochemical point of views to select the more promising materials among all the source can provide.

The first step of the process is the deposition of NP on a silicon substrate, to characterize carbon without the influence of the GDL underneath.

As deposited materials present a disordered structure, that makes them non-conductive and non-active electrochemically: a second step in the fabrication process consists in the annealing at high temperature (800°C) to achieve a good degree of graphitization, allowing the control of the defectiveness.

Raman multiwavelength analysis state that annealing brings the samples to complete sp² hybridization, but not to the formation of a perfect graphite:

Raman D peak, representative of carbon edges, is still a strong signal in the spectra.

The annealed samples are then tested in a three-electrode cell, and modeling is carried on in parallel: cyclic voltammetry is performed and the interpretation (supported with modeling) lead to the selection of an optimized nano-structure to treat a GDL.

The use of this approach allowed to eliminate some materials that were not worth trying in a real device.

The more interesting and promising is then tested in a real VRFB device, where physical properties are correlated to the full cell performances, in order to develop an iterative method where testing leads to the design of an optimized NP functionalization.

[1] - Experimental Diagnostics and Material Characterization Techniques Used on Redox Flow Batteries, M. Mench, Journal of The Electrochemical Society, 165 (5) A970-A1010 (2018)

ET03.12.16

SnS/N-Doped C Composite with Enhanced Li-Ion Storage and Lifetime by Controlled Hierarchical Submicron-/Nanostructuring [Xi Chen](#) and Markus Niederberger; Laboratory for Multifunctional Materials, Department of Materials, ETH Zurich, Zurich, Switzerland.

Hollow particles are regarded as a class of promising anode materials for lithium-ion batteries since they benefit from their shorter Li-ion and electron diffusion paths, an increased amount of electrochemically active sites created by more electrode/electrolyte interfaces, and the ability to better accommodate the strain induced by volume changes during cycling. In this work, we developed a facile and low-cost process for fabricating hierarchical hollow and dense microspheres assembled from SnS nanosheets and protected with a uniform layer of nitrogen-doped carbon. In the synthesis, oleic acid is utilized to form micro-droplets in ethylene glycol as soft templates. We found that by manipulating the precursor concentration and the number of template droplets, the nuclei process is confined to take place either inside the droplet or merely on the surface, leading either to dense or hollow particles. High-resolution transmission electron microscopy showed that the particles are built up by nanosheets with 4-6 atomic layers, wrapped in a uniform carbon shell of 4-5 nm. By using focus ion beam technique, we cut the particles and observe the cross-section by scanning electron microscopy, confirming that the desired morphologies are obtained. The fact that the two hierarchical particles with the same composition and building block dimension only differ in the internal morphology, we got a good opportunity to show the electrochemical merits from the hollow structure. The lithium-ion storage capacities of the hollow and dense spheres were tested and compared as anodes in lithium-ion battery half cells. The hollow microspheres showed low internal charge transfer resistance, good buffering of volume changes during lithiation and delithiation and good rate and cycling performance. After 1000 cycles, the hollow SnS composite still delivered a capacity of 420 mAh g⁻¹ at 1.0 A/g, which is 2.5 times higher than that of the dense spheres. The capacity retention from the second cycle on was 84% and 75%, respectively. Due to the enhanced overall electrical conductivity from the carbon shell and the hierarchical hollow structure, 40% to 70% capacities are contributed from pseudocapacitive behaviors at different cyclic voltammetry scan rates, explaining the good electrochemical reversibility and high capacity at large current rate. To conclude, the superior lithium-ion storage performance of the hollow particles arise from their pronounced porosity, hierarchical architecture from the self-assembled nanosheets and well-controlled uniform carbon shells.

ET03.12.17

Enhanced Cycling Stability of Macroporous Bulk Antimony-Based Sodium-Ion Battery Anodes Enabled through Active/Inactive Composites [Olivia Ruiz](#)¹, Mark Cochrane¹, Yan Yan², Ke Ma¹, Jintao Fu¹, Sarah Tolbert², Vivek Shenoy¹ and Eric Detsi¹; ¹Department of Materials Science & Engineering, Univ of Pennsylvania, Philadelphia, Pennsylvania, United States; ²Department of Chemistry & Biochemistry, University of California, Los Angeles, Los Angeles, California, United States.

Engineering approaches based on 'nanostructuring' and 'active/inactive composites' have been used to improve the performance of alkali-ion battery electrodes. In this talk it will be shown that a combination of both approaches yields an anode material with high cycle life. Specifically, we show that the use of a macroporous Sb/MgF₂ active/inactive composite material creates a high-performance Na-ion battery anode. This composite consists of a porous Sb phase as the electrochemically active component, with pore size in the sub-micrometer range, and a dense MgF₂ phase as the electrochemically inactive component. This good performance is attributed to the "porous active/inactive" configuration. In such a configuration the dense inactive phase absorbs a part of the phase transformation-induced stresses, while porosity in the active phase helps to accommodate part of the phase transformation-induced volume expansions generated in this active phase. Porosity is also expected to help facilitate the electrolyte transfer into the bulk of this composite. This new strategy could be used to improve the performance of high-capacity materials for next generation alkali-ion battery anodes [1, 2].

References:

[1] Eric Detsi, Olivia Ruiz, and Mark Cochrane: "Porous Active/Inactive Composites for High-Performing Alkali and Alkaline-Earth Ion Battery Anodes" PENN Invention Disclosure #18-8677

[2] Olivia Ruiz, Mark Cochrane, Yan Yan, Ke Ma, Jintao Fu, Sarah H. Tolbert, Vivek B. Shenoy and Eric Detsi: "Enhanced Cycling Stability of Macroporous Bulk Antimony-Based Sodium-Ion Battery Anodes Enabled through Active/Inactive Composites" (Under review)

ET03.12.18

Influence of the Carbon Material Structure on the MoS₂ Charge Storage Mechanism Basant A. Ali¹, Ossama I. Metwali², Asmaa M. Omar², Ahmed S. Khalil² and Nageh K. Allam¹; ¹American University in Cairo, New Cairo, Egypt; ²Physics, Fayoum University, Fayoum, Egypt.

Developing materials for energy storage that can maintain both high energy density and high power density is becoming a mandatory demand in our modern society. Supercapacitors can store energy in the electrical double layer (EDL), especially when carbon-based materials are used that store energy in the form of accumulated ions at their surfaces. The other mechanism of charge storage is the pseudocapacitors "faradic materials" in which the material undergoes redox reaction. In order to benefit from both the faradic materials and the carbon materials, hybrid materials are usually used. However, the charge storage and delivery mechanisms are not very well understood for those hybrid materials. MoS₂ has proved to be a good material that undergoes both redox and EDL capacitance mechanisms. Unfortunately, the 2H semiconductor phase of the MoS₂ has a low capacitance but much more stable than the 1T conductor phase.

In this study, flower-shaped MoS₂ was mixed with two different structures of carbon materials in different ratios in order to investigate the effect of the shape of the carbon material and its amount on the charge storage mechanism and the energy density, power density and capacitance. Our results showed that mixing MoS₂ with graphene nanoflakes (GNF) or 8 nm- diameter carbon nanotubes (CNT) increased the capacitance linearly with increasing their amount. However, CNT showed higher capacitance than the GNF mixtures. A mixture of equal weights of MoS₂, CNT and GNF (MCG) showed the highest capacitance among all mixtures and increased the capacitance of the MoS₂ by 111%. The small diameter of the CNT allowed to interfere with the flower shaped MoS₂ and surround it from outside and inside. On the other hand, the GNF sandwiched the MoS₂ flowers between its layers. These different shapes of the carbon materials affected the mechanism of charge storage and the origin of capacitance. From Tafel plots, all the materials studied originate current due to electric faradic mechanism. The contribution of current to the faradic mechanism was larger for the MoS₂ alone and with increasing the ratio of carbon materials, the contribution of current towards the EDL mechanism increased. The contribution of current towards the EDL changed from 11.2 % to 28 % in the MoS₂ and the MGC mixture, respectively. For the capacitance value origin, it was found that more than 98% of the capacitance of the studied materials was diffusion controlled and the carbon materials enhanced the diffusion capacitance of the MoS₂ up to 99.78%.

SESSION ET03.13: Li/Na Battery Cathodes and Thermal Energy
Session Chairs: Weiyang Li and Nian Liu
Friday Morning, November 30, 2018
Hynes, Level 3, Room 302

8:15 AM ET03.13.01

Metallic Carbon and Its Applications in Lithium-Ion Batteries Qian Wang; Peking University, Beijing, China.

Due to the special electronic configuration, small atomic size and flexible bonding features, carbon exhibits many phases with very different physical and chemical properties. In this talk, I will focus my discussion on our recently identified metallic carbon phases, including 3D metallic T6-C¹, Hex-C18² and a 2D metallic ψ -graphene³, and their applications as potential anode materials in lithium-ion batteries (LIBs). These new carbon allotropes are not only dynamically, thermally and mechanically stable, but also metallic. Due to their unique atomic configurations and metallicity, they provide the basis for the storage and transportation of Li ions with good conductivity. For instance, Hex-C18 exhibits exceptional properties such as a large heat capacity, high Debye stiffness, and anisotropic elasticity, while ψ -graphene shows robust metallicity against external strain during the adsorption of Li-ions. We demonstrated that both Hex-C18 and ψ -graphene have promising applications as effective anode materials in LIBs.

References

Stable three-dimensional metallic carbon with interlocking hexagons

S. Zhang, Q. Wang*, X. Chen, and P. Jena

Proc. Natl. Acad. Sci. **110**, 18809 (2013)

Liu, T.S. Zhao, S. Zhang, Q. Wang*

A new metallic carbon allotrope with high stability and potential for lithium ion battery anode material

Nano Energy **38**, 263(2017).

ψ -Graphene: A new metallic allotrope of planar carbon with potential applications as anode materials for lithium-ion batteries

J. Phys. Chem. Lett. **8**, 3234 (2017)

8:30 AM ET03.13.02

Novel Design of Hollow g-C₃N₄ Nanofibers Decorated with MoS₂ and S, N-Doped Graphene for Stable Electrochemical Hydrogen Evolution Reaction Suhee Kang, Joonyoung Jang and Caroline S. Lee; Hanyang University, Ansan, Korea (the Republic of).

Recently, depletion of fossil fuels and contamination of environmental issues leading to the energy crisis is making renewable energy productions extremely important. Among the sustainable energy, hydrogen is considered as one of the most important alternative fuel and the ways to obtain this gas have been widely studied during the past few years. Many catalysts have been developed for hydrogen production but still, its activity is limited owing to wide band gap energy and long-term stability problems. Therefore, electrocatalysts should be proposed to design innovative structures with superior performance.

Graphitic carbon nitride (g-C₃N₄), a non-metallic semiconductor having a bandgap of 2.6 eV, has been attracting much attention due to its easiness to manufacture as well as its environmentally benign and high thermal stability. However, g-C₃N₄ suffers from high recombination rate of charge carriers and low surface area. To overcome these drawbacks, one-dimensional (1-D) structured nanofiber can be considered to be an effective accelerator of the electrons as well as separators of the electron-hole pairs. Moreover, decorated MoS₂ onto g-C₃N₄ nanofibers can be properly matched to band levels and accelerate the electron pathways. Sulfur/nitrogen-doped graphene (SNG) is again applied onto g-C₃N₄/MoS₂ nanostructures to improve charge transportation by increasing its entire surface area.

In the present work, hollow g-C₃N₄ nanofibers (HGCNF) were prepared by electrospinning followed by thermal condensation methods. The prepared hollow g-C₃N₄ nanofibers decorated with MoS₂/SNG are synthesized in-situ by a hydrothermal process at relatively low temperature. The morphologies by

SEM and TEM analysis were used to characterize this fabricated sample. XPS analysis was measured to distinguish its chemical compositions according to their properties. Finally, HGCNF/SNG/MoS₂ showed the lowest Tafel slope of 83 mV/dec as well as the lowest impedance value among those of all prepared samples. This structure also showed the lowest overpotential of 282 mV at 10 mA/cm² from hydrogen evolution reaction among all prepared samples with stable current density at applied potential under 48 hours. Therefore, the optimized heterostructures were proven to be efficient electrocatalytic materials which can be applied to various fields including CO₂ reduction, artificial photosynthesis, solar cell, bio-application and Li-ion battery cell.

8:45 AM *ET03.13.03

Nanostructured Conjugated Polymers as Promising Electrodes for Li-Ion Batteries [Qiechun Zhang](#); Nanyang Tech University, Singapore, Singapore.

Electrode materials play a critical role in approaching high energy density and long cycle life lithium-ion batteries (LIBs). The increasing concern about the traditional inorganic electrode materials on resources and environmental issues has strongly inspired scientists to switch on searching green energy electrodes. Organic compounds are potentially sustainable and renewable materials as many of them can be obtained from natural products and biomass. Additionally, the properties of organic compounds can be tuned through the modification of the structures as well as the introduction of functional groups. In this talk, I will present our recent progress on the preparation of novel conjugated polymers and their application in Li-ion batteries.

9:15 AM ET03.13.04

Measuring Surface Phonon Vibrations on the (010) Surface of LiFePO₄ Platelet Particles [Peter Benedek](#)¹, Nuri Yazdani¹, Hungru Chen², Nils Wenzler¹, Fanni Juranyi³, Martin Månsson⁴, Saiful Islam² and Vanessa Wood¹; ¹ETH Zürich, Zürich, Switzerland; ²University of Bath, Bath, United Kingdom; ³Paul Scherrer Institut, Villigen, Switzerland; ⁴Royal Institute of Technology, Stockholm, Sweden.

LiFePO₄ (LFP) is a commercial cathode material often used for high power applications. Typically, nanoparticles of LFP are used due to the shorter path-length for lithium ions in the [010] transport direction. However, since nanoparticles have a large surface area to volume ratio compared to larger micron-sized particles, the question of how the surface influences ion diffusion and transfer becomes relevant. Here, we report on how surface vibrational modes at the surface of LFP differ from those in the bulk of the LFP particle and how different surface treatments change the vibrational structure at the surface of LFP. To systematically measure the influence of surface, we prepare platelet-shaped LFP particles of different sizes, where the number of atoms at the (010) surface changes from less than 1% of the total number of atoms in the particle to more than 10%. On these different samples, we measure the phonon density of states via inelastic neutron scattering (INS) and find that Li-O bond changes at the (010) surface. Combining our technique with other analytical techniques such as FTIR and XRD as well as density functional theory (DFT) simulations, we find that carbon coating, for example, can be used to influence the Li-O bonding at the LFP surface.

9:30 AM ET03.13.05

Mesoscopic Phase Transition Kinetics in Secondary Particles of Battery Electrode Materials Kai Xiang², Kaiqi Yang¹, Craig Carter², [Ming Tang](#)¹ and Yet-Ming Chiang²; ¹Rice University, Houston, Texas, United States; ²Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

Many battery compounds undergo first-order phase transformations upon composition swing during charge and discharge. While such phase transformations are often studied using single crystalline particles as model systems, real battery electrodes are typically composed of mesoscopic assemblies of nanocrystallites, of which the phase transformation behavior is still not well understood. Here we report systematic measurements of the phase transition kinetics under potentiostatic conditions in secondary particles of several representative intercalation compounds including LiFePO₄, LiMn_{1-x}Fe_xPO₄ and Li₄Ti₅O₇. We find that the measurement results, which are obtained over a wide range of overpotential, composition, primary particle size and temperature, can be self-consistently interpreted in the framework of the Johnson-Mehl-Avrami-Kolmogorov (JMAK) model for nucleation and growth kinetics. This finding suggests that the interfaces between primary particles do not impede the propagation of phase transformation in a secondary particle. Interestingly, the JMAK analysis suggests that the phase growth appears to be predominantly one-dimensional in nature in the systems studied regardless of the lithium diffusion anisotropy, which can be explained by a hybrid growth model in which rapid surface propagation is followed by slower growth into particles.

9:45 AM ET03.13.06

Size-Dependence of Li-Mediated Phase Transformation in Roxbyite Nano-Disks Yuan Yao and [Richard D. Robinson](#); Materials Science and Engineering, Cornell University, Ithaca, New York, United States.

Nanostructuring is one of the best strategies to improve the existing electrode materials due to the decrease in diffusion length and the higher surface area for accessibility of reactions. However, there are many outstanding questions fundamental mechanism behind the size-dependent electrochemical behavior. The Cu_{2-x}S system have been studied extensively as a cathode material for lithium ion batteries due to its high theoretical capacity and ionic conductivity, and low material costs. However, the exact mechanism for the first discharge plateau is still under debate (lithium intercalation versus lithium-induced phase transformation). Within the nanoscience community Cu_{2-x}S nanosynthetic chemistry has progressed to the degree that a high level of size control and size dispersion has been achieved. This makes Cu_{2-x}S a good system for studying the relationship between nanoparticle size and electrochemical properties. Using high concentration synthesis methods, we synthesize a series of roxbyite (Cu_{1.81}S) hexagonal nanodisks ranging from 10 nm to 27 nm. A size-dependent discharge plateau behavior is found on the first discharge plateau: as the size of the particle decreases, the discharge plateau decreases, resulting in lower capacities. As a result, the discharge curve for smallest nanoparticles resemble a supercapacitor, meaning the capacity has a linear relationship with the potential. To understand the reaction mechanism on the first plateau, we use XRD and UV-Vis spectroscopy to study the phase evolution and plasmonic peak change before and after discharge. The reaction mechanism is confirmed to be a lithium induced-phase transformation from Cu_{1.81}S to Cu₂S. Through XRD and HRTEM we find that lithium ions react laterally, through the side (16 0 0) of the nanodisk, and, the extent of the phase transformation reaction is limited for smaller size particle. EELS line scan and XPS are used to study the Cu L_{2,3} edge energy and the oxidization state between different size particles. We find the surface of the nanoparticle is dominated by Cu²⁺, and the core is mainly composed of Cu¹⁺. As a result, the surface of the particle has a lower reaction potential, and, smaller size particles contain more Cu²⁺. This leads to the size-dependent electrochemical behavior. Based on these information, we build a model to simulate the discharge curve. The model successfully captures the size-dependent capacity and plateau length.

10:00 AM BREAK

10:30 AM ET03.13.07

Controlled Nanoscale Morphology of Sodium Rhodizonate Ionic Crystal Realizing Reversible Four-Sodium Ion Storage [Minah Lee](#)¹, Yi Cui² and Zhenan Bao¹; ¹Chemical Engineering, Stanford University, Stanford, California, United States; ²Materials Science & Engineering, Stanford University,

Stanford, California, United States.

Sodium ion batteries (SIB) for grid-scale applications need active materials that combine a high energy density with sustainability. Organic compounds which can be obtained from natural biomass with minimum energy consumption are an attractive low-cost and sustainable choice for battery electrode materials, provided a high energy density and long cycling stability can be obtained. Given the earth abundance and high theoretical specific capacity of 501 mAh g⁻¹, disodium rhodizonate (Na₂C₆O₆) is one of the most promising cathodes for SIB. However, substantially lower reversible capacities have been obtained compared to the theoretical value while the origin of such discrepancy remains unanswered.

Here, we reveal the origin of the limited electrochemical performance of Na₂C₆O₆ and provide an effective path to achieve reversible four-sodium storage. By controlling of nanoscale morphology, we reveal that phase transformation of Na₂C₆O₆ kinetically limited during the desodiation process, being the origin of deteriorating redox activity of Na₂C₆O₆. The reversible phase transformation of Na₂C₆O₆ accompanied with spontaneous nanostructuring of active particles is achieved by decreasing active particle sizes and selecting proper electrolytes, which provides a mechanism to realize efficient four-sodium ion storage with a specific capacity of 484 mAh g⁻¹. Our work highlights the importance of understanding redox mechanisms at nanoscale, which opens up new opportunities to build a high performance and sustainable energy storage system.

Reference

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10:45 AM ET03.13.08

Study of Anisotropic Charge Storage Behaviour of LiNi_{0.5}Mn_{0.3}Co_{0.2}O₂ Using Pulse Laser Deposited Epitaxial Thin Films Rohit Satish, Yang Zhou, Rodney Chua Yong Sheng and Madhavi Srinivasan; Nanyang Technological University, Singapore, Singapore.

To realise future demands of energy storage, enhancements in terms of performance need to be made across the table in all the components of a battery including the Cathode, anode, separator and the electrolyte. A cursory examination of literature would indicate that anode chemistries are already able to store much more energy when compared to their cathode counterparts. This is largely due to the formation of an anode/electrolyte interface which passivates the anode and allows for facile Li migration through it. Unlike its anodic counterpart the cathode/ electrolyte interface is one of the least investigated and one of the least understood aspects of Li-ion battery design. It is thus of high impact to develop an understanding of the charge storage process at the surface of the cathode. In this study we observe the surface of epitaxially grown layered LiNi_{0.5}Mn_{0.3}Co_{0.2}O₂ with an aim to understand the dependence of the cathode/electrolyte interface, material stability and charge storage mechanism, on the direction of Lithium diffusion. Epitaxial LiNi_{0.5}Mn_{0.3}Co_{0.2}O₂ with restricted lattice parameters are grown on single crystal SrTiO₃ substrates oriented along 110, 111 and 100 directions with SRO as conductive buffer layer. The samples oriented along 100, 110 and 111 were probed using Cyclic Voltammetry, Impedance Spectroscopy coupled with X-ray Diffraction and *ex-situ* X-ray reflectivity measurements and *ex-situ* STEM measurements. Initial testing indicated we have been able to grow perfectly epitaxial films with negligible amount of lattice mismatch. Electrochemical studies surprisingly indicate different storage and failure mechanism for each of the samples. Reversible intercalation was observed only along the 110 direction with indication of a stable Ni^{2+/3+} to Ni⁴⁺ transition coupled with an Co^{3+/4+} transition. A combination of X-ray reflectometry measurements carried at specific potentials coupled with *ex-situ* STEM micrographs indicate that for samples grown along the 111 and 100 directions there is a greater tendency towards cation disorder, and loss of the overall layered structure during cycling but in the case of the samples grown along the 110 direction stable structure accompanied with the formation of a thin organic layer on the surface is observed. The SEI layer formed is expected to passivate the electrode at higher potentials and prevent any capacity decay. The results of the study can potentially open the doors for the widespread application of high energy density Ni rich layered structures as cathodes of the future.

11:00 AM ET03.13.09

Towards Three-Dimensionally Interdigitated Energy Storage Nanoarchitectures—A Bottom-Up Battery Synthesis Joerg Werner^{2, 1}, Gabriel G. Rodriguez-Calero², Héctor D. Abruña² and Ulrich Wiesner²; ¹Harvard University, Cambridge, Massachusetts, United States; ²Cornell University, Ithaca, New York, United States.

The traditional design of two-dimensionally layered anode-electrolyte/separator-cathode assemblies has persisted over centuries as the dominating battery architecture for its advantage of separated manufacturing of each component and ease of subsequent assembly. In common batteries these layers 100s of microns thick, soaked with liquid electrolyte for ion transport. The need for energy storage systems that exhibit high energy storage capacity coupled with fast accessibility of the energy manifested by high power output, demands architectures that increase the kinetics of batteries. A major hurdle for fast battery kinetics are ionic transport and solid-state reactions in the electrodes, which has driven the decrease of characteristic lengths scales of the active components. Since ion diffusion in liquid electrolytes and solid-state reactions in nano-dimensions are fast, porous nanostructured electrode materials have enabled much higher power densities of batteries over the past decades. However, the high porosity of nanostructured electrode materials comes at the price of reduced energy density due to a lower volumetric loading of the energy storing material. To overcome these limitations, intriguing 3-D architectures for batteries have been proposed over 15 years ago. In such 3-D designs, the porosity of one nano- or micro-structured electrode is coated and filled with the electrolyte and second electrode materials, respectively. The design principle of 3-D batteries conceptually enables fast diffusion and reaction kinetics due to small electrode dimensions and distances without sacrificing space for porosity. To obtain such intricate architectures with nanoscale dimensions, the battery components have to be synthesized within each other from the bottom up. The difficulties of compatibility and spatial precision in such nanoconfined synthesis of functional materials have significantly held back the development of nano-interdigitated 3-D batteries. Here we present a step-wise bottom-up strategy to such nanoarchitectures with all functional phases synthesized and integrated within a triblock terpolymer derived core-shell double gyroid morphology. Our 3-D interdigitated design comprises a gyroidal carbon anode network that is electrochemically coated with an ultrathin polymer electrolyte in a self-limiting and self-correcting process. The 3-D continuously nanoporous anode-electrolyte monolith is in turn filled with an inorganic-polymer hybrid cathode that is synthesized in the confinement of the nanoporous network. All three-dimensionally networked phases are less than 20 nm in their layer dimensions and integrated throughout a macroscopic monolith. Despite the small separation distances, the solid-state nano-3-D energy storage system exhibits battery-like characteristics and can be cycled numerous times.

11:15 AM ET03.13.10

Hybrid Aqueous Electrochemical System of Lithium Manganese Oxide and Prussian Blue Analogue for Low-Grade Thermal Energy Harvesting Yezhou Liu, Caitian Gao, Soojin Sim, Moobum Kim and Seok Woo Lee; Nanyang Technological University, Singapore, Singapore.

Low-cost and high-efficiency systems are in urgent demand to harvest abundant but mostly wasted low-grade heat sources (<100°C). Existing technologies like thermoelectric for heat-to-electricity conversion shows limited efficiency due to relatively low figure of merit at low temperature differential. Thermally regenerative electrochemical cycle (TREC) is a promising candidate to harvest heat by using dependence of electrode potential on temperature. By varying the temperature in a TREC cycle, the electrochemical cell is charged at a lower voltage and discharged at higher voltage, therefore, converting heat to electricity. Most previous TREC studies focused on materials with negative temperature coefficient (α), such as Prussian Blue Analogs (PBAs). Combining negative- α material with positive- α material without ion-exchange membrane could improve the efficient and reduce the cost. Exploring suitable positive- α material is necessary and urgent for further development of TREC low-grade heat harvesting system. Here we report lithium manganese

oxide, a widely-used lithium-ion battery cathode material, showing positive- α of 0.617mV K^{-1} and stable performance in aqueous electrolyte. An electrochemical cell consists of lithium manganese oxide (LMO) cathode and copper hexacyanoferrate (CuHCF) anode. The electrochemical system is operated in Li^+ and K^+ hybrid aqueous electrolyte without ion exchange membrane. The temperature coefficient of the full cell is 1.161 mV K^{-1} and the relative conversion efficiency of heat-to-electricity convert can reach 3.8% in TREC cycling between 10 and $50\text{ }^\circ\text{C}$ without heat recuperation. This new application of LMO may open the opportunities for positive α material and lead to an affordable and simple-structure low-grade heat harvesting electrochemical system.

11:30 AM ET03.13.11

From Thermopower Waves to Asymmetric Chemical Doping—New Concepts in Energy Storage and Generation Using Molecular Interactions with Single-Walled Carbon Nanotubes Albert T. Liu, Yuichiro Kunai and Michael Strano; Chemical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

There is a pressing need to find alternatives to conventional energy generation techniques, specifically those that rely on elements in finite global supply. Thermopower wave (TPW) devices, which convert chemical to electrical energy by means of self-propagating reaction waves guided along nanostructured thermal conduits, have the potential to address this demand. We show that conversion efficiency can be increased significantly by selecting molecules such as sodium azide or sucrose with potassium nitrate to offset the inherent penalty in chemical potential imposed by strongly p-doping chemicals, a validation of the predictions of Excess Thermopower theory. Such chemical-potential-gradient-induced-electricity can be further exploited in a more direct manner, decoupled completely from the combustion reactions, affording another novel energy generation scheme using only molecular interactions, and subsequent charge transfers, with single-walled carbon nanotubes. Specifically, we demonstrate that chemically-modified carbon nanotube fibers enable unique power sources driven entirely by a chemical potential gradient. Short circuit electrical current ($11.9\text{ }\mu\text{A mg}^{-1}$) and open circuit potential (525 mV) are reversibly produced by localized acetonitrile doping under ambient conditions. An inverse length-scaling of the maximum power as $L^{-1.03}$ that creates specific powers as large as 30.0 kW kg^{-1} highlights the potential for microscale energy generation.

11:45 AM ET03.13.12

Thermal Transport Crossover from Crystalline to Partial-Crystalline Partial-Liquid State in Li-S Batteries Ming Hu¹ and Yanguang Zhou²; ¹University of South Carolina, Columbia, South Carolina, United States; ²University of California Los Angeles, Los Angeles, California, United States.

Phase change materials (crystalline at low temperature and partial-crystalline partial-liquid state at high temperature) are widely used as thermoelectrics (Cu₂Se [Phys. Rev. Lett. 118, 145901 (2017), Proc. Natl. Acad. Sci. 111, 15031 (2014) and Nature Mater. 11, 422 (2012)] and Ag₂Te [Nanotech. 26, 25702 (2014)]) and battery electrodes (Li₂S [Sci. Rep. 7, 5873 (2017)] and LiSi [Nano Energy 18, 89 (2015)]) due to their low thermal conductivity and high ionic conductivity, respectively. Both thermoelectrics and Li batteries are energy related subjects and the relevant researches are hot topics in physics, chemistry and materials fields today. The scientific challenge resides in that, the well-developed computational methods such as anharmonic lattice dynamics coupled with Boltzmann transport equation (ALD/BTE) cannot be straightforwardly used to study such partial-crystalline partial-liquid systems. By performing systematic first-principles and reaxFF molecular dynamics simulations, for the first time we give a robust and detailed explanation of the thermal transport behavior in phase change material (i. e., Li₂S). At the temperature range in which the system can be regarded as a solid, the large hopping of Li is found to be the reason for phonon thermal conductivity's deviation from the traditional $1/T$ relationship. At the high temperature range ($T > 1000\text{ K}$), the contribution of kconvection and kcross increase significantly due to the fluidization of Li ions. The effective mean free path of the crystalline part shows that, at high temperature (e. g., 1300 K), the diffusons, which transport heat via overlap of ions' trajectories, can contribute as much as 44% of the total thermal conductivity, which leads to the unusual increase of kvirial at temperature above 1200 K . These results offer useful guidance for the development of phase change material based thermoelectrics (such as Cu₂Se and Ag₂Te based thermoelectrics), where low thermal conductivity is required to maximize the efficiency, and also suggest a strategy to solve the overheating problem in LIBs. This work will not only be of interest to the thermoelectrics and Li battery community, and the revealed thermal transport mechanism will also have large impact in the nanoscale thermal transport community.