

Joint APS/CNM Workshop 2: Advanced Characterizations for Critical Materials Innovation and Sustainability

Wednesday, May 8, Afternoon

Session Chairs: Dr. Hua Zhou and Dr. Ahmet Uysal

- 1:30 – 1:40 Workshop Organizers
Opening Remarks
- 1:40 – 2:10 Peter Sushko (Pacific Northwest National Laboratory)
Tracking Hydrogen-induced Transformations in Hierarchical Nanomaterials
- 2:10 – 2:40 Linsey Seitz (Northwestern University)
Characterizing Dynamic Materials for Sustainable Electrocatalytic Energy Conversion Technologies
- 2:40 – 3:10 Pietro Papa Lopes (Argonne National Laboratory)
Surface Evolution and the Nature of Active Sites in Electrochemical Materials
- 3:10 – 3:30 Break
- 3:30 – 4:00 Mark Schlossman (University of Illinois at Chicago)
X-ray Studies of Liquid Interfaces that Probe the Extraction of Rare Earth Elements
- 4:00 – 4:30 Benjamin Doughty (Oak Ridge National Laboratory)
Reverse Size Selectivity in the Solvent Extraction of Lanthanides: Interfaces and Dynamics
- 4:30 – 5:00 Michael Servis (Argonne National Laboratory)
Phase Transitions and Mesoscale Aggregation in Liquid-liquid Extraction of Rare Earth Elements
- 5:00 Adjourn

Thursday, May 9, Afternoon

Session Chairs: Dr. Yuzi Liu and Dr. Luxi Li

- 1:30 – 2:00 Chong Liu (University of Chicago)
Materials Design for Critical Element Separation
- 2:00 – 2:30 Xiao Su (University of Illinois Urbana-Champaign)
Leveraging In-situ Neutron Reflectometry (NR) for the Investigation of Ion-selective Electrochemical Separations

- 2:30 – 3:00 Albert Lipson (Argonne National Laboratory)
Li-ion Battery Recycling: Overview and Direct Recycling
- 3:00 – 3:20 Break
- 3:20 – 3:50 Eva Allen (Argonne National Laboratory)
*Three-dimensional Characterization of Cathode Upcycling and Relithiation
Procedures to Enable Direct Recycling*
- 3:50 – 4:20 Linqin Mu (Arizona State University)
*Understanding the Degradation of Layered Oxide Cathodes through
Comprehensive Characterizations*
- 4:20 – 4:30 Closing Remarks
- 4:30 Adjourn

Tracking Hydrogen-induced Transformations in Hierarchical Nanomaterials

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Reducing the dependence of energy generation, capture, and conversion technologies on platinum group elements (PGEs) is central to developing resilient and sustainable energy infrastructure. PGE-based catalysts are unique in their ability to promote chemical reactions. For example, the fast kinetics of hydrogen-related processes on Pt surfaces and solubility of hydrogen in Pd at normal conditions enable the efficient hydrogen evolution reaction, hydrogen purification, and hydrogenation reactions key to chemical manufacturing. Analysis of dissimilarities in the interactions of PGE and non-PGE catalysis with hydrogen is promising for informing the design of alternatives to PGEs.

The efficiency of heterogeneous catalysts is determined by their ability to bind reactants and transport them to the reaction sites, facilitate the reactions, and desorb the reaction products. We will discuss how these properties of heterostructured catalysts can be controlled by imposing network effects, whereby short-range interactions across individual interfaces and long-range interactions that couple the behavior of multiple interfaces give rise to complex responses to external stimuli. In particular, we will examine how strain induced by these interfaces affects their interaction with hydrogen and, in turn, how structural changes induced by hydrogen affect the strain distribution. To reveal these effects, we will examine dissimilarities in the behaviors of heterointerfaces in epitaxial films and assemblies of nanoparticles.

We quantify the effect of interfaces, including grain boundaries, and the strain associated with them on the kinetics of hydride formation by correlating the strain distribution in as-synthesized structures with the results of time-resolved *in-situ* x-ray diffraction measurements in H₂ gas flow. By turning the H₂ supply on and off, we can stimulate hydrogen trapping and release, respectively. The magnitude and rate of structural changes observed during this process, together with a detailed microscopic characterization of the initial and post-treatment structure and composition, provide an insight into the coupling between the strain distribution and hydrogen-induced transformations.

Going forward, we aim to establish the effect of hydrogen adsorption and incorporation on the morphology changes. To this end, we propose to use x-ray photon correlation spectroscopy—a new capability implemented at the APS during the 2023–2024 upgrade—that allows one to measure time correlation functions and thus quantify the time scales of dynamic structural processes of interest.

Characterizing Dynamic Materials for Sustainable Electrocatalytic Energy Conversion Technologies

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Research in the Seitz lab looks to exploit electrochemistry and revolutionize catalytic processes at the foundation of our energy and chemical industries that are currently major drivers of climate change. To achieve this vision, we must understand and harness catalyst material design, synthesis, and “resynthesis” under reaction conditions to enhance activity, selectivity, and stability of electrocatalytic materials and processes. Electrocatalysis provides unique opportunities to effectively utilize and store renewable electricity sources while tuning system performance via applied electric potentials and pH to develop technologies for sustainable production of fuels and chemicals. However, progress in these technologies is impeded by many factors, including knowledge gaps of complex catalyst material dynamics and degradation under reaction conditions.

We use controlled material syntheses and advanced spectroscopy techniques to monitor dynamic behavior of catalysts in response to electrocatalytic reaction conditions. Notably, we have developed a range of iridium-based [1] and precious metal-free [2] catalyst materials to establish electronic structure effects associated with systematic changes in composition, crystallinity, and strain. We also employ a range of reactor geometries spanning fundamental rotating ring disk electrode setups to applied membrane electrode assemblies to probe and understand the relationships between bulk reactor parameters, local catalyst reaction environments, and catalyst performance outcomes. We use these materials, reactor systems, and *operando* spectroscopy techniques to elucidate trends in catalyst structural reorganization and activation/degradation mechanisms induced by relevant reaction conditions. With these tools, we investigate a range of oxidative and reductive processes for water/hydrogen/oxygen/peroxide systems as well as more complex organic species. Benchmarking performance and intrinsic material stabilities for catalysts based on platinum and non-platinum group metals provides a critical outlook for the future of emergent technologies based on these processes [3]. With this work, the Seitz lab aims to exploit electrochemical processes and reaction environments to understand and harness catalyst material dynamics to achieve enhanced activity, selectivity, and stability for sustainable production of fuels and chemicals.

[1] a) J. Edgington, N. Schweitzer, S. Alayoglu, L. C. Seitz, *JACS* **2021**, *143*, 9961-9971; b) B. Lu, C. B. Wahl, X. K. Lu, M. E. Sweers, H. Li, V. P. Dravid, L. C. Seitz, *JACS* **2022**, *144*, 13547-13555; c) R. Li, J. Edgington, L. Seitz, *Energy & Fuels* **2023**; d) R. Li, B. Lu, J. Edgington, L. C. Seitz, *J Cat* **2024**, *431*, 115387.

[2] a) R. Li, D. Nordlund, L. C. Seitz, *Chemistry of Materials* **2024**, *36*, 1299-1307; b) X. K. Lu, B. Lu, H. Li, K. Lim, L. C. Seitz, *ACS Catalysis* **2022**, *12*, 6663-6671.

[3] J. Edgington, L. C. Seitz, *ACS Catalysis* **2023**, 3379-3394.

Surface Evolution and the Nature of Active Sites in Electrochemical Materials

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The design of active and stable materials is imperative for the development of clean energy as well as water remediation technologies. A key aspect is understanding how specific arrangements of atoms create unique electronic structures that can help catalyze electrochemical conversion reactions all the while being stable despite having to interact with reaction intermediates [1]. In this short talk, we will discuss how this seemingly contradictory requirement underpins the activity-stability relationships of many electrochemical materials. We will discuss examples related to transition metal oxides employed to catalyze the O₂ evolution reaction [2,3] as well as formation of reactive oxygen species (ROS). Lastly, we will show how understanding surface evolution at atomic and molecular scale gives us new insights on how to construct interfaces that are either dynamically stable or that can be regenerated.

This work has been conducted at Argonne National Laboratory, a U.S. Department of Energy, Office of Science laboratory, operated by UChicago Argonne, LLC under Contract no. DE-AC02-06CH11357 and acknowledge the support from the Office of Science, Basic Energy Sciences, Materials Sciences and Engineering Division as well as support from the Advanced Materials for Energy-Water Nexus, an Energy Frontier Research Center funded by the Office of Science, Basic Energy Sciences.

- [1] Lopes, Pietro P.; A Framework for the Relationships between Stability and Functional Properties of Electrochemical Energy Materials. **ACS Mater. Au** **3**, **1**, 8-17, 2023.
- [2] Lopes, Pietro P.; Chung, Dong Young; Rui, Xue, Zheng, Hong, He, Haiying; Farinazzo Bergamo Dias Martins, Pedro; Strmcnik, Dusan; Stamenkovic, Vojislav R.; Zapol, Peter; Mitchell, J. F.; Klie, Robert F.; Markovic, Nenad M.; Dynamically Stable Active Sites from Surface Evolution of Perovskite Materials during the Oxygen Evolution Reaction. **J. Am. Chem. Soc.**, **143**, **7**, 2741-2750, 2021.
- [3] Chung, Dong Y.; Lopes, Pietro P.; Martins, Pedro F.B.D.; He, Haiying; Kawaguchi, Tomoya; Zapol, Peter; You, Hoydoo; Tripkovic, Dusan; Strmcnik, Dusan; Zhu, Yisi; Seifert, Soenke; Lee, Sungsik; Stamenkovic, Vojislav R.; Markovic Nenad M.; Dynamic Stability of Active Sites in Hydr(oxy)oxides for the Oxygen Evolution Reaction. **Nature Energy**, **5** (3), 222-230, 2020.

X-ray Studies of Liquid Interfaces that Probe the Extraction of Rare Earth Elements

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Solvent extraction processes are designed to extract a target species of ion from a multi-component aqueous mixture into an organic solvent, then return it to an aqueous phase containing only the targeted species. Ongoing developments of solvent extraction processes are aimed at optimizing the efficiency and kinetics of the separation and recovery of base, rare earth, and precious metals, as well as the reprocessing of spent nuclear fuel and nuclear waste. During solvent extraction, extractants and complexants assist the transport of metal ions across the liquid-liquid interface between an aqueous solution and an organic solvent. We present our recent studies of metals extraction that probe this interfacial process, including our efforts to characterize interfacial ion-extractant complexes and the relevance of the location of complexation, either at or near the liquid interface. These studies utilized the facilities at ChemMatCARS (APS Sector 15).

Reverse Size Selectivity in the Solvent Extraction of Lanthanides: Interfaces and Dynamics

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Chemical selectivity in solvent extraction is traditionally approached using rigid molecular scaffolds with precisely defined local coordination and chemical environments to facilitate complexation and transport. In contrast, nature leverages dynamic structures and strong vibrational coupling to enable specific interactions with target species in complex media. Taking inspiration from nature, we demonstrate unconventional *reverse* size selectivity in the liquid extraction of lanthanide ions using conformationally flexible ligands. We show that these species self-assemble into pseudocyclic molecular complexes at liquid/liquid interfaces, which are then transported to the neighboring oil phase. Using ultrafast vibrational spectroscopies and *ab initio* molecular dynamics simulations, we show how vibrational relaxation and structural dynamics correlate with selectivity. Analogous approaches using interfaces and dynamics to achieve novel functionality and selectivity are expected to advance the energy efficient separation of critical materials from complex sources.

Phase Transitions and Mesoscale Aggregation in Liquid-liquid Extraction of Rare Earth Elements

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Understanding the molecular-scale origins of structure and phase transitions in multicomponent, hierarchically structured liquid phases is a fundamental challenge. One important application affected by these phenomena is liquid-liquid extraction, a predominant low-energy separations technique that is a go-to process for metal ion separations, including recovery and recycling of rare earth elements. A fundamental limitation of liquid-liquid extraction is the undesirable liquid-liquid phase transition, called third phase formation, that occurs upon sufficient loading of metal ions into the extractant-containing organic phase. In this talk, we present ongoing work relating solution structure to that phase transition, connecting the two through the concentration fluctuations associated with the liquid-liquid critical point. We use small angle x-ray scattering and high-speed x-ray photon correlation spectroscopy performed at the APS to measure static and dynamic critical exponents in the organic phase. Further from the critical point, we combine small angle x-ray scattering and molecular dynamics simulations to investigate how process conditions, such as extractant concentration and aqueous feed acidity, affect fluctuations in the organic phase. Connecting these fluctuations to the underlying phase transition will deepen our understanding of how extractant design and molecular-scale interactions control phase behavior, enabling the design of more efficient separations processes.

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Materials Design for Critical Element Separation

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The development of renewable energy technologies and next-generation quantum and optoelectronic devices relies on the secured supply of critical elements. Traditional mining and separation methods are disruptive to the environment, consume large quantities of harsh chemicals, and are unable to access dilute resources due to low elemental selectivity. Therefore, the invention of new separation methods and the fundamental understanding of the separation processes are crucial to realizing sustainable separation while broadening minable resources. In this talk, I will first introduce a platform method, electrochemical intercalation, for selective ion separation. I will introduce several strategies to promote the separation of lithium and lanthanides based on the understanding of complex host behavior upon co-intercalation of competing ions. In the second part, I will introduce our efforts in developing methods to construct (sub)nanometer solid ionic channels and probe the water and ion transport behavior in confinement.

Leveraging *In-situ* Neutron Reflectometry (NR) for the Investigation of Ion-selective Electrochemical Separations

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Innovations in separation technologies are critical to guarantee our supply-chain security, the availability of chemical and materials resources, and clean air and water at a global scale. Electrochemical separations provide a modular, reversible, and energy-efficient separations that can be integrated with renewable energy and eliminates secondary waste. Core to this process is understanding the ion-interface interactions during electrochemical control. Here, we discuss recent advances from our group on the design of redox-(co)polymers for imparting selectivity towards a range of ion-selective separations, including critical element recovery of transition metals, rare-earth elements (REEs), and platinum group metals (PGMs).

Here, we investigate how solvation and ion valency influence selectivity towards metal oxyanions and structure-function relationships with polymer chemistry. *Operando* neutron reflectometry, ellipsometry, and electrochemical quartz-crystal microbalance elucidate swelling behavior and reversibility. NR in particular enables the discrimination of solvent fraction across the nanoscale polymer films and provides insights into the effect of hydrophilic/hydrophobic environments on ion ingress. We expect that a deeper understanding of solvation and valency effects on selectivity mechanisms in redox interfaces will expedite the development of targeted selective ion-electrosorption systems.

Li-ion Battery Recycling: Overview and Direct Recycling

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Li-ion batteries need to be recycled to prevent their toxic components from entering the environment and to enable us to recover the expensive metals contained within them. Commercialized battery recycling technologies currently only recover the metallic elements in the battery for reuse in batteries, which requires reprocessing into battery materials. This makes these processes require more energy, have higher environmental impacts, and overall cost more than recovering the materials as finished battery materials. This talk will discuss the current state of the art and technologies that are being developed to recycle more of the battery and keep some of the materials in forms that can be directly reused in batteries.

This work was performed through the ReCell Center, which gratefully acknowledges support from the U. S. Department of Energy (DOE), Office of Energy Efficiency and Renewable Energy, and the Vehicle Technologies Office. This work was predominantly conducted at the Materials Engineering Research Facility, Argonne National Laboratory, a U. S. Department of Energy Office of Science laboratory operated by UChicago Argonne, LLC under contract DE-AC02-06CH11357.

Three-dimensional Characterization of Cathode Upcycling and Relithiation Procedures to Enable Direct Recycling

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In line with carbon neutrality goals by 2050, the Li-ion battery market has surged. To enhance battery sustainability and circularity, direct recycling methods aim to recover intact cathode materials. However, end-of-life cathode materials are typically 15-20 years old and often have lower energy density compared to current cathode materials. In response, processes of cathode upcycling to boost energy density by converting low Ni-compositions, $\text{LiNi}_{0.33}\text{Co}_{0.33}\text{Mn}_{0.33}\text{O}_2$ (NMC111), into higher Ni-compositions (NMC622) are created. One method uses precipitation to form a Ni-rich coating that diffuses into the cathode core, increasing compositional homogeneity upon high-temperature relithiation. Through *ex-situ* tomographic transmission x-ray microscopy (TXM) and XANES, we quantify Ni:Co:Mn elemental ratios and Ni valence state, confirming that elemental content evens at the secondary particle level, but elemental gradients remain at the primary particle level upon relithiation. *Ex-situ* high-resolution and *in-situ* wide-angle x-ray diffraction reveals concurrent structural changes during the relithiation process. These findings guide further improvements in synthesis for increased initial capacity and retention.

Understanding the Degradation of Layered Oxide Cathodes through Comprehensive Characterizations

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The ever-increasing demand for renewable energy and electric vehicles calls for high-energy-density rechargeable batteries. Cathode materials such as layered oxides play a crucial role in determining the energy density and safety of Li batteries. $\text{LiNi}_x\text{Mn}_y\text{Co}_z\text{O}_2$ (NMC), as the dominating cathode, has been successfully commercialized for many years. However, NMC cathodes are still facing many challenges, particularly, during the perusing of the high Ni concentration and high cut-off voltages. Furthermore, the chemical mismatch between NMC and current solid-state electrolytes, leading to chemical or electrochemical reactions, acts as a barrier to the advancement of all-solid-state batteries. Thus, comprehending the degradation mechanisms of NMC under different conditions can provide valuable insights for designing battery materials and interfaces. In the presentation, we will discuss the degradation of the NMC cathode at multiple length scales by comprehensive imaging and spectroscopic techniques. We will also present the challenges of characterizing the surface properties of the layered oxides cathode and summarize our strategies that can enhance the surface stability of NMCs.