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Understanding the role of diffusion doping in the formation of ferromagnetic CuCr₂Se₄ nanocrystals.

Ezra Bacon-Gershamm

Solution processable ternary nanocrystals are promising materials for a wide range of applications including photovoltaics, photocatalysts, and biomedical applications but involve complex formation mechanisms. Gaining a better understanding of the formation of ternary nanocrystals will allow for improved synthetic techniques, tunability, and functionality. The spinel CuCr₂Se₄ is one such ternary material that exhibits an above room temperature Curie temperature (T_c), high magneto-optical response, and potential applications in memory storage and Faraday isolators. Through X-ray diffraction and atomic composition measurements, the formation mechanism of CuCr₂Se₄ nanocrystals has been determined to proceed through a binary intermediate of copper selenide phases before Cr intercalation takes place via diffusion doping to produce polycrystalline CuCr₂Se₄. For the room-temperature ferromagnetic properties to emerge, high reaction temperatures are required to anneal the particles. Magnetic circular dichroism reveals a localized surface plasmon resonance around 1 eV which shows a large magneto-optical response through coupling to the Cr³⁺. This mechanism results in polydisperse nanocrystals with no size and shape control. Preliminary results use preformed Cu₂Se nanocrystals in the synthesis of CuCr₂Se₄ nanocrystals. This method presents new levers to pull in facilitating shape and size control as well as the potential for the synthesis of new nanocrystalline spinel compositions. Furthermore, Cr incorporation is minimally understood in nanomaterials, and these studies may help us better realize its chemical potential in solution and in the lattice.

Operando screening of metal redox in NMC pouch cells with laboratory XAFS

Helen Chen

Authors: Yeu Chen, Anthony J. Gironda, Gerald T. Seidler, Dan Thien Nguyen, and Vijay Murugesan

The advancement of energy storage technologies hinges on understanding the redox behavior of transition metals, both for established chemistries like nickel manganese cobalt (NMC) cathode materials and also for emerging options that use only earth-abundant elements. In this study, we present a method employing laboratory-based X-ray absorption fine structure (XAFS) spectroscopy for operando screening of metal redox states in NMC pouch cells during cycling. Unlike conventional techniques that require synchrotron radiation, our approach utilizes a lab-scale XAFS setup, making it accessible and cost-effective for routine analysis and potentially for industrial quality control. We aim to systematically quantify the redox dynamics of nickel (Ni) and cobalt (Co) during charge-discharge cycles with temporal resolution sufficient to capture real-time electrochemical processes (noting that manganese is not redox active in NMC). To achieve this, we perform linear combination fit (LCF) to build a model for redox transitions, enabling the identification of the battery's chemical status with minimal data collection. This rapid screening approach with operando capability can be extended to other cathode materials for lithium-ion or sodium-ion batteries.

Accelerating the Research to Production Cycle for Clean Energy

Emma Coester

Authors: Emma J. Coester, Forrest W. Eagle, Brandi M. Cossairt

Magic-sized clusters (MSCs) bridge the gap between molecules and nanocrystals, holding unique material properties due to their intermediate size and atomic precision. Interestingly, since MSCs are obtained as reaction intermediates, they open the door to synthetic modification during the growth of nanocrystals. Due to their meta-stability, MSCs can undergo cation exchange at mild conditions, offering a potential route to obtaining doped nanocrystals and new nanocrystal compositions that may be otherwise inaccessible. Herein, we report transition metal doping of In₃₇P₂₀ MSCs via cation exchange at room temperature to obtain doped InP clusters and nanocrystals. Successful doping of various first row transition metal ions into the In₃₇P₂₀ MSCs was confirmed with spectroscopic and structural characterization techniques (UV-Vis, XPS, XRD, ICP-OES). In prior work we have demonstrated coinage metal (Cu, Ag, Au) doping of InP MSCs with partial and complete exchange of In.¹ With the addition of 5 equivalents of coinage metal salt (per cluster), the ligated surface of the MSCs changes significantly while only minor changes are made to the core. In this study, the change in surface chemistry upon partial exchange was used to introduce other transition metals in the first row series that have resisted direct incorporation under mild conditions. Elemental analysis found that of the coinage metals, copper allowed for the incorporation of the second dopant at higher concentrations than silver and gold. Further reactions of the doped clusters were carried out to synthesize and characterize larger doped InP nanocrystals. This room temperature approach for transition metal doping of MSCs through a sequential pair of cation exchange reactions offers a new route toward doped and multicomponent nanocrystals that hold promise for catalytic and optoelectronic applications.

References

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Leveraging Ordered Voids in Microporous Perovskites for Intercalation and Post-Synthetic Modification

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We report the use of porous organic layers in two-dimensional hybrid organic-inorganic perovskites (HOIPs) to facilitate permanent small molecule intercalation and new post-synthetic modifications. While HOIPs are well-studied for a variety of optoelectronic applications, the ability to manipulate their structure after synthesis is another handle for control of physical properties and could even enable use in future applications. If designed properly, a porous interlayer could facilitate these post-synthetic transformations. We show that a crystalline arrangement of designer ammonium groups allows for permanently porous interlayer space to be accessed at room temperature. Intercalation of the electroactive molecules ferrocene and tetracyanoethylene into this void space can be performed with tunable loadings, and these intercalated perovskites are stable for months. The porosity also enables reactivity at the metal-halide layer, allowing for facile halide replacement. Through this, we access previously unobserved reactivity with halogens to perform halide substitution, and even replace halides with pseudohalides. In the latter case, the porous structure allows for stabilization of new phases, specifically a novel copper-thiocyanate perovskite phase, only accessible through post-synthetic modification. We envision that this broad design strategy can be expanded to other industrially relevant HOIPs to create a new class of highly adjustable perovskites.

Post-Polymerization Modification of Polybutadiene: New Approaches to Crosslinked Rubber

Mercie Hodges

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Polymer upcycling—chemically changing the structure and function polymers to add value—is a promising way to mitigate plastic waste. This poster will outline polymer upcycling via post-polymerization modification, utilizing allylic aminations to add sulfonamides and sulfamates to polybutadiene (PBD). Initial work shows amination changes the thermal properties and wettability of PBD; current efforts target two orthogonal materials: crosslinking polybutadiene utilizing these aminations and modifying commodity cross-linked polybutadiene to limit end-of-life phase separation. The first targets an alternative to vulcanized rubber by using hexafluoroisopropyl sulfamates to aminate PBD; this can then undergo aminolysis with a diamine crosslinker to yield new thermosets with potential for recyclability. The latter material consists of modifying the surface of traditionally crosslinked PBD with sulfonamides. We hypothesize that the polarity of the added functional groups will help compatibilize end-of-life vulcanized PBD to prevent phase separation in its applications as a filler.

NMC Cathode Aging Is Accompanied by a Shift in Asymmetry Charge Transfer

Yuefan Ji

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The aging of nickel-rich NMC lithium-ion battery cathodes is a complex multi-faceted process, but surface reconstruction is widely recognized as a key feature that correlates with the loss of rate capability and capacity during cycling. Recent results using in operando XRD have shown that surface reconstruction pins the adjacent NMC bulk lattice, introducing strain that is responsible for the loss of rate and capacity (so-called fatigued NMC). [1] The strained lattice in fatigued NMC remains electrochemically active and sustains a high Li⁺ solid state diffusivity, but it cannot be fully delithiated. Engineering NMC materials with strain-relieving interphases is an emerging area for reducing the effect of cycle-related strain build-up. [2] Lattice strain alters the electronic structure of NMC, yet a full picture for how the strain responsible for NMC fatigue (and eventually particle fracture) influences electrochemical charge transfer remains unclear, in part, because the experimental reliance on electrochemical impedance spectroscopy means changes in charge transfer rates can be directly measured, but mechanistic details associated with the charge transfer symmetry are not accessible.

We have shown that the mechanistic discriminating power of second harmonic nonlinear electrochemical impedance spectroscopy (2nd-NLEIS), when combined with conventional linear EIS, can provide sensitive characterization to the fatigue of NMC cathode with physical meaningful parameters. The combined analysis of EIS and 2nd-NLEIS enables internally self-consistent parameters estimation given the fact that EIS and 2nd-NLEIS can be obtained simultaneously by driving the battery into the weakly nonlinear regime with a moderately larger current modulation amplitude than EIS.

We perform in operando study of aging and the surface reconstruction in commercial NMC|C cells using a combined EIS and 2nd-NLEIS approach. We quantify charge transfer rates and charge transfer symmetry of the surface reconstruction using a set of complementary analytical models. Our approach has successfully identified, for the first time, that not only is the surface reconstruction responsible for impedance growth and a reduction in charge transfer rates, but it is also associated with a strong SOC- and SOH-dependent breaking of charge transfer symmetry that corresponds to the fatigue of NMC cathodes.

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Architecture Optimization Improves Reverse Bias Stability in p-i-n Structured Perovskite Solar Cells

Fangyuan Jiang

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As perovskite photovoltaics make strides towards commercialization, reverse bias instability has been considered a serious challenge. We systematically investigate methods to improve reverse bias behaviors of p-i-n structured perovskite solar cells, including passivating halide vacancies, changing the electron transporting layer, and systematically varying the hole transporting layers and metal electrodes. Our results suggest that having a robust polymer hole transporting layer and an electrochemically stable electrode are important for preventing reverse bias breakdown of p-i-n perovskite solar cells. This result is surprising since much of the current effort and understanding has focused on the perovskite/electron transport layer/metal electrode interface. Nevertheless, with appropriate hole transporting layers, and optimized top electrode, we demonstrate breakdown voltages exceeding -15 V, comparable to that of silicon photovoltaics. Furthermore, our optimized solar cells demonstrate completely recoverable device performance even after being stressed at high reverse bias for many hours (i.e., at -7 V for 9 hours both in the dark and under partial shading). Following these observations, we propose a self-consistent model which highlights the role of electrochemical reaction pairs that has not been appreciated previously.

Electron Localization in a Cu/Co₆Se₈ Cluster Redox Series

Sebastian Krajewski

Authors: Robert Love Jr., Graduate student, University of Washington, Alexandra Velian,
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Molecular clusters are a powerful platform for modeling the emergent electronic and structural properties of complex systems relevant to heterogeneous catalysis. Our group has developed the synthesis of modular $M_xCo_6Se_8L_6$ (M = transition metal, $x = 1,3$, L = phosphine) clusters that feature one or three edge sites. Here, a series of atomically defined clusters featuring low-valent copper edge sites are synthesized. By treating molecular clusters of the general formula $Co_6Se_8(Ph_2PXTol)_6$ ($X = NH, S$) with copper(I) precursors, we can isolate ternary cluster compounds with well-defined copper edge sites. The nanoclusters are characterized through a variety of methods, such as single crystal X-ray diffraction, heteronuclear NMR spectroscopy, cyclic voltammetry, and X-ray absorption spectroscopy. In the series of clusters with the general formula $[Cu_3Co_6Se_8(Ph_2PNTol)_6]_n^-$ ($n = 0, 1, 2, 3$), we observe that electron transfer is entirely localized on the Co/Se core even when using strong oxidants, allowing for the tuning of cluster electronics through chemical synthesis. Additionally, we observe the chirality of the clusters in both solid state and solution, as the tricopper clusters retain a nanopropeller D_3 symmetry throughout the redox series.

Thermodynamic Modeling of Hard Carbon Sodium Storage Sites for Na-ion Batteries

Rose Yesl Lee

Authors: Daniel T. Schwartz, University of Washington

Hard carbon (HC) is considered one of the most promising anode materials for sodium-ion batteries. However, the dominant sodium storage mechanism in HC is unclear, largely due to a lack of understanding of the energetic environments of the HC sodium sites. This has led to conflicting interpretations of the galvanostatic cycling profile, and overall hinders sodium-ion battery development. Here, we use the Multi-Species, Multi-Reaction (MSMR) physics-based model to identify and thermodynamically characterize four distinct sodium environments in the sodium-HC system, in addition to quantifying the sites associated with each mode of sodium storage. The modeling results are combined with spectroscopic data to correlate the distinct sodium environments with sodium storage mechanisms. We find that two sodium storage mechanisms simultaneously occur in the low voltage plateau, the formation of sodium nanoclusters in nanopores and the insertion of sodium-ions in the expanded graphene stacks, followed by adsorption to defect sites at intermediate potentials. Finally, at increasingly positive potentials, we observe an irreversible chemical process within the first few cycles, which is treated as a sodium sink rather than a sodium storage mechanism. We show that these reactions do not go to completion at the cutoff voltage, leaving sites that are theoretically available for sodium storage, but practically inaccessible. There are unutilized sites associated with all sodium storage mechanisms, indicating that innovations in defect engineering, tuning pore size and accessibility, and optimizing the graphene stack size can yield additional capacity.

Synthesis of Metal-Organic Cages as Platforms for Non-covalent Interactions with Redox Active Molecules.

Jay Lee

Characterized by high surface area and tunability, porous materials have been studied extensively for applications such as gas separation. However, they have been underutilized in areas such as electronics due to their non-conductive nature. We would like to propose a strategy to prepare a porous material that is also electronically conductive. This will be achieved by designing metal-organic cages that can interact with redox active molecules via non-covalent interactions. In pursuit of this, several metal-organic cages with varying appendages were synthesized, with the goal of leveraging redox and supramolecular reactivity. Recently we have prepared a series of Cu-based cage with varying level of pi-surfaces on the top and bottom exterior of cages to promote specifically pi-pi interaction with C60. In addition two cages with redox active tetrathiafulvalene moiety was also prepared which showed reactivity with an electron accepting tetracyanoquinodimethane and 2,3,5,6-Tetrafluoro-tetracyanoquinodimethane.

Site-differentiation of M/Co/Se Nanoclusters via Transmetalation

Robert Love

Authors: Sebastian Krajewski, Graduate Student, University of Washington, Alexandra Velian, Assistant Professor, University of Washington

At solid-state surfaces, active sites are differentiated based on their unique position on the lattice and by metal identity. Here, we explore the synthesis and characterization of ternary molecular nanoclusters that are site-differentiated by metal identity. In our previous work, we developed molecular nanocluster catalysts, $M_3(\text{solv})_x\text{Co}_6\text{Se}_8\text{L}_6$ ($M = \text{Cr, Mn, Fe, Co, Cu, Zn, and Sn}$; solv = solvent; L = Ph₂PN(-)Tol; Ph = phenyl; Tol = 4-tolyl) with three edge sites that are chemically equivalent and have shown to be great catalysts for carbodiimide formation. Upon metalation of $\text{Li}_6(\text{py})_6\text{Co}_6\text{Se}_8\text{L}_6$ with CuCl_2 , we observe the formation of the mixed-metal species $\text{Co}(\text{py})\text{Cu}_2\text{Co}_6\text{Se}_8\text{L}_6$ as the major species rather than the expected $\text{Cu}_3\text{Co}_6\text{Se}_8\text{L}_6$ nanocluster. Magnetic and structural data suggest that Cu^{I} is reduced upon metalation, affording two Cu^{I} edge sites and the third metal edge site being Cu^{II} . In a separate case, treatment of $\text{Fe}_3\text{Co}_6\text{Se}_8\text{L}_6$ with one and two equivalents of CuCl_2 affords $\text{Fe}_2\text{CuCo}_6\text{Se}_8\text{L}_6$ and $\text{FeCu}_2\text{Co}_6\text{Se}_8\text{L}_6$, respectively, which suggests that CuCl_2 plays a prominent role as an oxidant and transmetalation reagent. Here, we utilize a combination of spectroscopic and electrochemical techniques to investigate the electronic structure of these mixed-edge metal systems to understand how the introduction of a different metal on the edge changes the properties of the nanocluster. The reactivity of these clusters with redox non-innocent ligands, such as bis-carbenes, is being investigated to form di-clusters to induce electronic or magnetic communication between the clusters.

Investigating the effect of crystallinity on OMIEC doping kinetics

Khao Ngo

Authors: Dr. Sarah R. Pristash, Alexis M. Glaudin, Juliana Tran, and Prof. Cody W. Schlenker

Organic mixed ionic electronic conductors (OMIECs) have emerged as a promising class of materials with unique properties that can be used in a whole host of devices, including supercapacitors and redox flow batteries. Doping kinetics in OMIECs influence the performance and operation of devices. For OMIEC materials that exhibit both crystalline and amorphous domains, understanding these kinetics is important to rationally optimize the film morphology. Here, we investigate the impact of crystallinity on doping kinetics using blends of the model OMIEC material poly(3-hexylthiophene-2,5-diyl) (P3HT), which can be cast into films with different average regioregularities to span the range from purely amorphous to highly crystalline OMIECs. We performed spectroelectrochemistry and electrochemical quartz crystal microbalance (EQCM) gravimetry experiments as a function of time. Using spectroelectrochemistry, we find that after a voltage is applied, there is a delay in the onset of oxidation of the polymer; however, EQCM shows there is an instantaneous uptake of ions. This phenomenon is not present in Pg2T-TT, an OMIEC that contains hydrophilic sidechains. This data suggests that the hydrophobicity of the sidechains influence this delay, and our preliminary data indicate that delay time increases with higher crystalline fraction in P3HT. We study the factors that influence this delay including electrolyte type, electrolyte concentration, voltage, and cycle number. Understanding the origins of this phenomenon and how to control it will play an important role in the application of OMIECs in devices.

Near Infrared-to-Visible Upconversion With A Heavy-Atom-Free Core-Substituted Thiosquaraine Photosensitizer

Cecily Rosebaum

Authors: Dr. Sarah R. Pristash, Alexis M. Glaudin, Juliana Tran, and Prof. Cody W. Schlenker

Capturing sub-bandgap Near-Infrared (NIR) and Infrared light in solar cells via photon upconversion offers a path toward overcoming the Shockley-Queisser limit. Global scalability concerns warrant pursuing photosensitizers without precious metals or unstable arylhalides. Heavy-atom-free sensitizers, such as thiosquaraines, are scalable alternatives. Herein, we substituted a dicyanovinyl group for one sulfur in a thiosquaraine sensitizer, driving NIR-to-Visible upconversion from 730 nm to 590 nm when paired with rubrene. We integrated this upconversion system into a compatible photovoltaic device, producing photocurrent from transmitted light. To determine whether core-substitution affects the sensitizer's photophysical properties, we compare the intersystem crossing time (τ_s), triplet yield (Φ_T), and quenching rate constant (k_q) of the core-substituted sensitizer against an unsubstituted thiosquaraine control. For the former, we found $\tau_s=1.23$ ns, $\Phi_T=0.15$, and $k_q=1.36E9$ M⁻¹ s⁻¹, and the latter, $\tau_s=1.53$ ns, $\Phi_T=0.24$, and $k_q=1.64E9$ M⁻¹ s⁻¹. The NIR-to-Visible upconversion we report supports thiosquaraines as scalable, tunable UC systems.

Ultra-Bright Perovskite Quantum Dot Light-Emitting Diodes Enabled by Self-Assembled Monolayer Interfaces

Gillian Shen

TBD

Edge Metal Affect on Molecular Cluster Allostery

Ella Spurlock

Authors: Alexandra Velian, Assistant Professor, University of Washington

This work aims to investigate the redox cooperativity between edge active sites and an electron-rich supporting core in designer $M_3[Co_6Se_8L_6]$ (1- M_3 ; $M = Cr, Mn, Fe, Co, Cu, Zn$; $L = PPh_2N(-)Tol$; $Tol = 4$ -tolyl, $Ph = phenyl$) inorganic clusters. These clusters aim to combine the benefits of heterogeneous and homogeneous catalysts by being solution-processible and characterizable while also displaying electronic edge-support interactions. Identity of the edge metal determines the electronic overlap between the metal and the cluster core and thereby its properties. By studying carbodiimide catalysis and its intermediates, I observed allosteric effects modulating the binding affinity of the cluster's three active sites. Exploration of the electronic structure of the clusters through physical characterization and calculation provides insight into the role the cluster core plays in catalytic transformations at the edge metal. Through stoichiometric substrate addition, isolable catalytic intermediates shine light on not only catalytic pathways, but also electron richness of each edge metal.

TBD

Aaron Thomas

Authors: TBD

TBD

Electronically Active Metal-Organic Cages for Metal Separation

Austin Wang

Multi-metallic clusters offer the opportunity to gain molecular insights on how multiple metals cooperate to perform complex chemical and redox transformations. The Velian group has introduced the synthesis of a novel nanocluster $\text{Fe}_3\text{Co}_6\text{Se}_8\text{L}_6$ (Fe_3 , $\text{L} = \text{Ph}_2\text{PN}(-)\text{Tol}$) which features distinct metal-support interactions and a redox active Co/Se core. Initial studies revealed that chemical oxidation of Fe_3 led to the localization of the charge onto the Co/Se core. Herein, we report the facile tri-oxidation of Fe_3 by using inner sphere oxidants to afford a series of halogenated clusters, $\text{Fe}_3\text{X}_3\text{Co}_6\text{Se}_8\text{L}_6$ (Fe_3X_3 , $\text{X} = \text{Cl}, \text{Br}, \text{I}$). Interestingly, spectroscopic, and crystallographic studies suggest that the three charges are delocalized across the Fe edge sites and Co_6Se_8 core. Furthermore, Fe_3X_3 contains labile halides which can be exchanged for a variety of anionic ligands, most notably azides (N_3^-). We find that the bound azides are prone to decomposition under photolytic and thermolytic conditions. In addition, the azides react with dipolarophiles to afford triazolates. In aggregate, this study highlights the unique electronic properties and reactivity of a complex trinuclear Fe nanocluster.
