

43rd Annual Symposium on Applied Surface Analysis

And 35th Annual Symposium of the Pacific Northwest Chapter of AVS, The Science and Technology Society



Invited Talks

Invited Talk 1: Identifying Reductant Descriptors and Surface Structures that Enhance Active Site Formation in Mo-Based Heterogeneous Olefin Metathesis Catalysts

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Heterogeneous olefin metathesis has gained significant recent interest due to a series of novel methods for upcycling plastics, helping solve the propylene gap, and production of renewable alkenes from biomass via ethenolysis. Even with this much industrial interest, surprising debate remains in basic attributes of this fascinating reaction chemistry, including the active site formation mechanism for traditional heterogeneous systems. Recent work has highlighted how promoters, often acting like reducing agents, but not always presented as such, like methanol, methane, ethane, ethene, propene, and even organosilicons can be used to drastically increase the population of active sites, while common reductants like H₂ and CO do not increase populations to equivalent levels. This highlights an important question, what descriptors govern supported Mo oxide sites transitioning into olefin metathesis active sites when supported on silica? This work experimentally compared a series of olefins, alkanes, and alcohols of varying structure used as organic reducing agents, seeking to identify the characteristics required to form heterogeneous olefin metathesis active sites. Using gas-phase reactions, temperature programmed surface reactions coupled with Kissinger analyses, traditional thermochemical calculations, and in-situ and operando DRIFTS, our group identified the free energy of reduction needed for single sites of MoO₃ supported on silica and kinetic differences as a function of reducing agent chemical structure. Hydrocarbon-based soft reductants show two temperature regimes in site creation, a low temperature regime, which is governed by soft reductant structure, and a high temperature regime that is structure agnostic, resulting in H₂ and aromatic formation. We identify thermodynamic and kinetic differences between individual or synergistic soft reductants to control olefin metathesis active site populations. Our results, combined with literature results, support the hypothesis that understanding the descriptors that govern metal oxide single site

reduction can facilitate orders of magnitude increases in the population of traditional heterogeneous olefin metathesis active sites.

Invited Talk 2: Molecular Beam Epitaxy of Transition Metal Nitrides

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Transition metal nitrides are employed in a wide variety of electrochemical, structural, photochemical, and plasmonic applications. Among these compounds Mn, Cr, and Ni nitrides have gained interest for their potential in magnetism and spintronics and ZrN is superconducting at low temperatures. These systems are complex with several different metastable phases predicted and experimentally realized. This study uses molecular beam epitaxy to synthesize epitaxial thin films of different Mn-N and Cr-N phases and investigates the electrical and magnetic properties. Both rocksalt MnN and CrN display metallic behavior, with the latter showing a structural-magnetic transition at ~280K. However, combining these elements at similar growth conditions, results in the emergence of a new phase. These alloys retain 4-fold symmetry, but the lattice constants deviate from Vegard's law. The ternary compounds show remarkably different temperature dependent resistivity relative to the binary constituents; some compositions are narrow-gap semiconductors. Epitaxial thin films of Ni and Zr nitrides will also be discussed as an avenue for the epitaxial integration of metals, magnets, semiconductors, and superconductors for emerging technology.

Invited Talk 3: Using Path-Integral Methods to Study Nuclear Quantum Effects in Condensed Phase Hydrogen-Bonded Systems

Britta Johnson

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Nuclear quantum effects (NQE), such as tunneling and nuclear zero-point energy, play a significant role in accurately simulating chemical systems that involve proton transfer and hydrogen bonding. Path-integral based methods, like Path Integral Molecular Dynamics (PIMD) and Ring Polymer Molecular Dynamics (RPMD), are used to introduce NQEs into molecular dynamics simulations. While these methods scale similarly to classical MD methods, the number of particles in PIMD simulations is prohibitive for the study of large systems. A variety of methods have been developed to improve the scaling of PIMD for condensed phase systems. One such method is the mixed-time slicing (MTS) approach where specific particles in the system are treated as ring polymers while other particles remain classical. We have developed a software package, *MixPI*, which uses an MTS-RPMD approach and, working in conjunction with CP2K, generates a flexible MTS scheme for conducting atomistic simulations. Here we present results which compare this implementation with previous classical water simulations to demonstrate the flexibility and improved scaling of *MixPI*. We also apply this method, along with other scaling techniques, to study proton transfer reactions in small, hydrated clusters. This work was supported in part by the DOE Office of Science, Office of Basic Energy Sciences, Division of Chemical Sciences, Geosciences, and Biosciences.

Invited Talk 4: Thermal Laser Epitaxy for Ultraclean Heterostructures

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We have developed a new thin-film deposition technique that is especially suited to the growth of an extremely wide range of heterostructures with atomic precision. Thermal laser epitaxy (TLE) employs continuous wave lasers to simultaneously heat both substrates and freestanding elemental sources [1]. The lasers' virtually arbitrary power density allows for the evaporation of practically all elements of the periodic table in the same setup while maintaining process gas environments up to pressures as high as 10^{-1} mbar [2]. For substrates heated directly via CO₂ laser, temperatures up to and beyond 2000 °C can be reliably reached on virtually all commercially available oxide substrates, unlocking previously inaccessible growth regimes in many materials systems. In combination, these advantages suggest the potential of TLE to greatly expand thermodynamic parameter space for ultraclean epitaxial thin film synthesis. Here, I will introduce and discuss the advantages of TLE for epitaxy and present a wide range of recent results demonstrating the epitaxy of ultraclean thin film heterostructures using the technique [3,4].

[1] W. Braun, J. Mannhart, AIP Adv. 9 (2019) 085310

[2] T.J. Smart, et al., J. Laser Appl. 33 (2021) 022008

[3] D.-Y. Kim, J. Mannhart, W. Braun, Appl. Phys. Lett. Mater. 9 (2021) 081105

[4] D.-Y. Kim, J. Mannhart, W. Braun, J. Vac. Sci. Tech. A 39 (2021) 053406

Invited Talk 5: APS Upgrade and Overview of the Capabilities for the Structural Science Group Beamlines

Tiffany Kinnibrugh¹, Wenqian Xu¹, Kevin Beyer¹, Olaf Borkiewicz¹, Guy Jennings¹, Charles Kurtz¹, Saul Lapidus¹, Tianyi Li¹, Yang Wang¹, Kamila Wiaderek¹, Andrey Yakovenko¹
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The Advanced Photon Source (APS) is upgrading the storage ring to generate brighter X-ray beams enabling new research opportunities. The Structural Science Group (SRS) at APS operates a suite of five X-ray diffraction (XRD) and total scattering beamlines, 11-BM, 11-ID-B, C, D and 17-BM, serving a broad scientific community and for decades have supported experiments ranging from in situ synthesis of materials to operando studies of complex real devices. Two of the undulator beamlines,

11-ID- B and C, have long supported high energy x-ray powder XRD and pair distribution function (PDF) experiments. Recently, they have expanded their capabilities to study thin films and interlayers with the addition of compound refractive lenses for beam focusing and hexapod platforms for precise sample alignment. Beamline 11-ID-D is currently being reconstructed as part of the APS upgrade featuring a combination of XRD and total scattering with small angle X-ray scattering (SAXS) techniques to provide structural information over multiple length scales. Newly developed optics will offer a wide range of photon energy from 26 to 120 keV with adaptable bandwidth and submicrometer focusing. To improve workflow, our group is working closely with the computing and data science groups at APS, to implement tools for automated data processing and on-the-fly data analysis.

Invited Talk 6: Understanding interfacial barriers for Mg-ion batteries: surface diffraction from model cathode thin films during cycling

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Multivalent rechargeable batteries have often been considered a natural successor to current lithium-ion technology. In principle, replacing Li⁺ with a divalent ion, like Mg²⁺, could enable the use of a dendrite-free metal anode and potentially double the specific capacity of the cathode. In practice, Mg-ion batteries using high voltage cathodes – particularly spinel-based materials – have been found to have poor capacity retention and significant voltage hysteresis. Ex situ TEM studies have shown that over-magnesiumation near the surface is one possible culprit. To better understand the origins of these problems, we studied electrochemically driven structural changes in MgM₂O₄ (M = Mn, Cr, V) thin films with varying surface orientation (001, 110, and 111) using *operando* surface diffraction. We find varying stability of the spinel with transition metal species and that stable cathodes, such as MgMnCrO₄, do form a Mg-rich rock-salt phase that is epitaxial with the underlying spinel. Surprisingly, we find that this new phase is surprisingly active for magnesiumation, albeit at lower potential. We discuss the origins of this effect using density functional theory, which predicts that compressive strain can lead to preferential in-plane transport, ultimately leading to surface Mg enrichment. We also discuss how this effect is related to the inherent overpotentials required to charge magnesium cathodes.

Invited Talk 7: Phonon Dynamics and Heat Transfer in Energy Materials: Advanced Theory, Materials Discovery, and Machine Learning

Yi Xia

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Lattice dynamics and thermal transport phenomena are ubiquitous and play a critical role in the performance of various microelectronic devices and energy-conversion materials, such as semiconductors, thermoelectrics, and thermal barrier coating materials. Developing an in-depth understanding of the underlying atomistic mechanisms, advanced strategies for accelerated materials discovery, and machine learning models with improved accuracy and transferability is therefore of urgent need yet remains limited.

My research addresses these challenges by developing advanced first-principles theories for phonon dynamics and heat transfer using density functional theory, constructing quantum materials phonon database via high-throughput computing, and building unified graph neural networks for interatomic interactions. In this talk, I will first show how lattice dynamics calculations considering higher-order phonon-phonon interactions pave the way for an unprecedented understanding of the microscopic heat transfer mechanisms in crystalline semiconductors. Then I will discuss how to effectively discover materials with targeted ultralow thermal conductivity for thermoelectric applications through integrating high-throughput computing with learned chemical physics. Finally, I will demonstrate a theory-guided, data-driven understanding of the lower limit of lattice thermal conductivity in all inorganic solids. Leveraging machine learning models rooted in graph neural network architectures, we can now accurately forecast heat transfer phenomena in amorphous materials. I will also briefly comment on other potential applications of our approaches and future research directions.

References:

Xia et al. Physical Review X 10 (4) 041029, 2020

Xia et al. Physical Review Letter 124(6), 065901, 2020

Xia et al. Proceedings of the National Academy of Sciences 120(26), e2302541120, 2023

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Invited Talk 8: Additively manufactured components and materials for extreme environments: Advanced Characterization

Dr. Brian J. Jaques

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Advancing knowledge at the frontiers of energy sciences will require innovations in materials tailored for energy applications. Accordingly, advanced manufacturing (AM) is revolutionizing the manufacturing industry due to the unparalleled design flexibility of the build process that allows fast innovation and production of complex optimized parts. Despite the transformative potential of AM, the full utility of this material fabrication technology remains unrealized due to an incomplete understanding of the relationship between processing conditions, the evolution of microstructure, mechanical properties, and the stability of printed parts in extreme environments. In this presentation, characterization of several AM techniques will be discussed, including materials jetting and extrusion, laser powder bed fusion, and laser/arc wire AM. A multifaceted approach to high throughput and robust materials characterization and testing to relate AM processing parameters to relevant performance in extreme environments will be discussed.

Invited Talk 9: Probing Nanoparticle Surface Sites with DNP-NMR

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Characterizing the composition and distribution of nanoparticle surface sites is a key challenge in the process of understanding their interfacial reactions and interactions, with nanosized MgO in particular being a material generating widespread interest. By leveraging the new magic-angle-spinning, dynamical nuclear polarization (MAS-DNP) capability at PNNL, this work extends comparatively insensitive solid-state NMR techniques to the interrogation of challenging ^{25}Mg surface sites, identifying both minor constituents in the model nanodisc $\text{Mg}(\text{OH})_2$ system and the hydroxide surface layer in the target nanoparticle MgO. By performing ^{25}Mg - ^{25}Mg exchange spectroscopy (EXSY) on the nanosized MgO surface sites, an experiment which would be completely infeasible in solid-state NMR without DNP enhancement, the presence of 'islands' of hydroxylated MgO sites distributed between regions of hydroxide shell is demonstrated. Synergies with a selection of complementary surface analysis techniques will also be discussed.

Invited Talk 10: Pulsed Laser Deposition and Characterization of Intrinsic and Alloyed Ga_2O_3 Thin Films for Optoelectronics

Ramana Chintalapalle

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Designing and creating innovative functional materials, which will have the potential to greatly advance the future generation of technologies, is a challenging problem that the scientific and engineering community is presently confronting in this 21st century. Optimization of materials for functionality and durability in extreme environments is even more challenging. Recently, ultra-wide band gap (UWBG) semiconductors emerged as potential candidate materials for advanced electronics. Recent breakthrough in commercial availability of large-scale crystals/substrates brings the hope to push the boundaries of future electronics and energy technologies. This talk will highlight our ongoing research related to functional materials' design and development by considering specific and illustrative examples based on the intrinsic and doped gallium oxide (Ga_2O_3), an emerging UWBG semiconductor. Understanding the physics & chemistry and optimization of phase-stabilized Ga_2O_3 made by pulsed-laser deposition and/or sputtering allowed us to derive tailor-made, vertically aligned nanostructures (VAN) with structure and property control. When doped with tungsten (W), we realize self-assembled vertically aligned $\beta\text{-Ga}_{2-x}\text{W}_x\text{O}_3$ nanocomposite (GWO-VAN) architecture-assisted ultrafast deep-ultraviolet (DUV) photodetectors on a silicon (Si) platform. GWO-VAN architectures exhibit exceptionally high (ultrafast) selectivity as a DUV-detector. Few other examples of Ga_2O_3 alloying with other transition metals will also be shown to realize functional materials for energy applications, such as batteries and photocatalysis.

Emerging Leader Award Finalist Talks

EMLA 1: Hydrogenic defects in conductive metal-organic frameworks

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Typical metal-organic frameworks are constructed by combining organic acids with transition metals to form 3D arrays of metals/metal clusters suspended by Lewis basic organo-linkers. During this assembly, entropy drives the inclusion of defects, and these defects may have dramatic impact on the bulk material properties. Hydrogenic adatoms are particularly interesting, as they should be present due to incomplete deprotonation of the organic acids. Yet, these defects are experimentally difficult to detect. In this talk we discuss avenues to control the number of adatomic hydrogen atoms by affecting the nuclearity of the MOF nodes, highlighting a unique molecular-like property afforded to MOFs: site isolated redox events. In systems with delocalized electronic structures, the adatomic hydrogen atoms can be used to dope the framework, affecting the Fermi level. Together, we highlight that adatomic hydrogen is likely a prevalent defect in MOFs and may be useful for control bulk material properties.

EMLA 2: Mapping Ion and Polaron Densities in Organic Mixed Conductors at the Nanoscale

Connor Bischak

University of Utah, Salt lake City, UT

Organic mixed ionic-electronic conductors (OMIECs) are emerging as versatile materials for various applications, including biosensors, bioelectronics, neuromorphic computing, and energy storage. These materials typically consist of conjugated polymers capable of transporting both electronic and ionic charge carriers. OMIECs function through a mechanism known as electrochemical doping, where electronic charge carriers are introduced into the OMIEC from an underlying electrode, while ions from the surrounding solution enter the polymer to maintain charge neutrality. The behavior of OMIECs is significantly influenced by the interactions between ion movement, electron transport, and structural changes at the liquid-polymer interfaces. However, these interfaces are challenging to study using conventional microscopy due to the small length scales associated with the polymer's microstructure. To investigate these critical interfaces, we employ nanoscale infrared imaging with photoinduced force microscopy (PiFM). This technique enables us to visualize ion concentrations with high spatial resolution and correlate the physical attributes of the OMIEC with its transport properties. Our research aims to uncover new structure-property relationships in OMIECs, potentially leading to advancements in OMIEC-based technologies, such as enhanced bioelectronics and more efficient energy storage systems.

EMLA 3: Advanced X-ray Photoelectron Spectroscopy for Studying the Surface Chemistry of Li-ion Battery Electrodes

Dan Thien Nguyen

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The solid electrolyte interphase (SEI) at the anode and cathode electrolyte interphase (CEI) formed by interfacial reactions between electrolyte components at the electrode/electrolyte interface are crucial components in Li-ion batteries. These electrode interphases play a pivotal role in facilitating reversible Li⁺ intercalation/deintercalation, preventing continuous electrolyte decomposition, and controlling the kinetics of overall cell reactions. However, establishing a comprehensive chemical understanding of the SEI/CEI remains challenging due to their sensitive chemical nature and the small dimensions of the interphase region (e.g., 18 nm in 1 M LiPF₆ in EC/DEC electrolyte).

Conventional X-ray photoelectron spectroscopy (XPS) postmortem analysis has been widely used to examine the chemical composition of the SEI layer, providing insights into surface reactions. However, this classic method raises significant concerns about SEI decomposition upon electrode removal from the cell and during spectroscopic analysis, the loss of volatile electrolyte components under the ultra-high vacuum required for XPS analysis. Developing a new XPS protocol capable of capturing the SEI in its original form is therefore essential.

Through systematic investigation, we introduce a novel protocol for examining the surfaces of air-sensitive electrodes using used Li-ion battery electrodes as model samples. Combining both *in situ* and *ex situ* cryogenic XPS allows us to directly probe the formation of the interphase as a function of electrode polarization and capture all essential components, including metastable organic components and volatile species. Through this work, our aim is to establish a new protocol for surface analysis not only for battery samples but also for other sensitive samples such as solar cells and fuel cells, thereby laying the groundwork for a deeper understanding of interfacial reactions.

EMLA 4: Controlling Anisotropy in Magnetic Thin-Films for Integrated Device Operation

Amal El-Ghazaly

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Magnetic anisotropy energy dictates the orientation and behavior of a material's magnetization and, therefore, the overall performance of a final integrated magnetic device. Sputter deposition techniques allow for the precise control magnetic anisotropy through the growth (and subsequent patterning) of magnetic multilayers and heterostructures designed to achieve in-plane, out-of-plane, or mixed anisotropy. This talk will present three recent demonstrations of how magnetic anisotropy was controlled through sputter deposition techniques to achieve unique magnetic films for integrated microwave devices and micro-magnetic actuator structures. Amorphous thin films of GdCo that have a ferrimagnetic order (antiparallel spin orientation) with bulk-like perpendicular magnetic anisotropy (PMA) and stoichiometries near its magnetic-compensation have the potential to achieve very high resonance frequencies and operating bandwidths in the microwave frequency regime. We show that sputter-deposited heterostructures of Ta(3 nm)/Pt(3 nm)/GdxCo1-x(t)/Pt(5 nm) on Si/SiO₂(3 nm) substrates exhibit bulk-like PMA for GdxCo1-x thicknesses of 5-12 nm and

stoichiometries where $x = 18-40\%$. A strong uniaxial anisotropy for out-of-plane magnetization with an anisotropy field (H_k) of 0.24 T was observed when the Gd:Co ratio was 35:65, which is near the composition that results in a magnetic compensation at room temperature. Interestingly, it was found that strong PMA in GdCo is possible only with oxygen in the thin film. Thus, a reactive sputter deposition process was pursued with oxygen flow rates adjusted between 0-0.8 sccm during deposition and a maximum effective anisotropy energy density of 105 erg/cc was obtained for a flow rate of 0.5 sccm. We will show how X-ray photoelectron spectroscopy (XPS) and vibrating sample magnetometry (VSM) measurements reveal the source and extent of the very strong PMA observed the final films with stoichiometry of Gd₂₁Co₂₈O₅₁. Even greater PMA is achieved in a heterostructure with 10 repetitions of the Gd-Co-O alloy. These films exhibit an anisotropy field on the order of 11 kOe, which correspond to a ferromagnetic resonance frequency of ~30 GHz. Synthetic antiferromagnets (SAFs), made from ferromagnet/non-magnetic metal/ferromagnet exchange-coupled heterostructures, represent a crucial component of magnetic tunnel junctions, giant magnetoresistance spin valves, and potentially microwave integrated devices. The widespread practice is to grow SAFs with a nonmagnetic metal spacer layer thickness optimized to achieve the first oscillatory peak for antiferromagnetic interlayer exchange coupling. However, recent work by Waring et al. suggests that when Ru is used as the metal spacer material, the second oscillatory antiferromagnetic exchange coupling peak may, in fact, achieve better antiferromagnetic anisotropy resulting from the fact that the slightly thicker Ru layer provides better uniformity of the grown material film [1]. This increased interlayer exchange coupling manifests itself as a narrower resonance peak with fewer damping losses in the SAF



General Talks

General Talk 1: Tracking Elementary Steps in Conversion of Carboxylic Acids on Single Crystalline and Nanofaceted TiO₂(101)

Xingyu Wang

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Ketonization of carboxylic acid used to be a method to produce acetone in industry. Recent interest has focused on this C-C coupling reaction due to its potential for upgrading biomass. The production of acetone from acetic acid was only observed in high pressure reactors on anatase nanoparticles. However, on anatase TiO₂(101) single crystals in ultra-high vacuum (UHV), acetone production from acetic acid has not been observed. This is an example of the material gap in surface science studies. The mechanism of ketonization is also under debate; the two most commonly proposed pathways are β-keto acid pathway and ketene pathway.

In this study, we introduced well-defined nanoparticles (NPs) with mostly (101) surfaces into a UHV chamber to elucidate the ketonization mechanism and bridge the material and pressure gaps in this system. A combined experimental approach of temperature programmed desorption (TPD), scanning tunneling microscopy (STM), X-ray photoelectron spectroscopy (XPS), and reflection absorption infrared spectroscopy (RAIRS) was used, along with theoretical studies. Our finding is that on single crystals, the ketene produced desorbs from the surface without encountering another acetate. In contrast, ketene desorbing from a given NP within a layer of NPs can subsequently react with an acetate on another NP, leading to acetone production. To demonstrate this, we prepared three samples with varying thickness of anatase NP layers, with mostly (101) facets, in an UHV system. We then compared the reaction of acetic acid on these NP layers with its reaction on an anatase(101) single crystal. We found that the production of acetone starts from 10ML of acetic acid exposure, and the yield correlates with the depth of acetic acid absorption into the nanoparticle beds. Along with theoretical studies, we identified a mechanism through a key intermediate, α-enolate acetic acid, which forms through the reaction of gas phase ketene with surface-bound acetate species. Further studies, which involve dosing ketene through a homemade heated quartz tube ketene source onto an acetic acid pre-dosed single crystal surface, are currently underway to confirm this reaction mechanism.

General Talk 2: Coverage-dependent Adsorption, Reactivity, and Morphological Changes of Formic Acid on the Fe₃O₄(001) Surface

José J. Ortiz-Garcia, Marcus Sharp, Bruce Kay, Zbynek Novotny, Zdenek Dohnálek

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Formate is a crucial intermediate in important reactions like the Fischer-Tropsch synthesis and water-gas shift reaction. Iron oxide, an inexpensive and abundant catalyst, is used in both reactions. We investigate the adsorption of formic acid (FA) on the Fe₃O₄(001), followed by stepwise annealing

using a combination of scanning tunneling microscopy, x-ray photoelectron spectroscopy, low-energy electron diffraction, and temperature programmed desorption (TPD). On a clean, $(\sqrt{2}\times\sqrt{2})$ R45° reconstructed surface formed due to subsurface cation vacancies, FA adsorbs dissociatively as a bidentate formate and a surface hydroxyl. Low FA exposure experiments show isolated formates and hydroxyls without clustering. A slight increase in FA exposure leads to a mixture of formate surface periodicities ((1×1), (2×1), and (2×2)) with respect to the reconstructed Fe₃O₄(001) surface. A fully saturated surface at room temperature also shows a (1×1) periodicity due to well-ordered bidentate formate – hydroxyl pairs as well as a (2×1) periodicity due to different arrangements in the monolayer packing. Stepwise annealing enables monitoring of formate and hydroxyl reactivity and surface structural and morphological changes. TPD shows peaks at 525 and 565 K, indicating formate decarbonylation to CO and H₂O, with minor decarboxylation to CO₂. Annealing below 450 K leads to formate rearrangement to their lowest energy configuration on the surface. Annealing to 550 K induces formate conversion, partially recovering the surface reconstruction and a possible formation of single oxygen vacancy defects. Further annealing to 650 K converts all formate species while forming extended pits along the Fe rows. DCOOD adsorption on ¹⁸O labeled Fe₃O₄(001) reveals an oxygen exchange between the surface and the formate both through decarbonylation and decarboxylation mechanisms resulting in isotopologues of CO and CO₂. Complete recovery of the surface is achieved via an oxygen anneal at 930 K. This work highlights the importance of understanding formate interactions with oxide surfaces, which is essential for overcoming kinetic barriers in reaction schemes leading to renewable fuels.

General Talk 3: HS-LEIS and XPS Characterization of Hafnium Zirconium Oxide ALD Thin Films

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Atomic layer deposition (ALD) is based on the sequential use of gaseous precursors and is a variant of the chemical vapor deposition (CVD) technique. One of the strengths of ALD thin films is that it allows for conformal coatings of even high aspect ratio nanostructures, which is difficult to obtain with other deposition techniques such as physical vapor deposition, evaporation and sputtering, and other versions of CVD techniques. Additionally, ALD can be used to produce thin films (less than 10 nm thickness) which is advantageous for certain applications but makes film characterization more challenging.

Many methods have been employed to characterize thin films, including but not limited to Fourier-Transform Infrared spectroscopy, ellipsometry, and energy dispersive X-ray spectroscopy. While the results from these methods can provide useful information for thin films, they are not generally considered to be surface-sensitive techniques because their sampling depth is closer to 1 μm. Among widely used surface analysis instrumentation, Time-of-Flight Secondary Ion Mass Spectrometry (TOP-SIMS) has the shallowest sampling depth of 1-2 nm. Compared with TOP-SIMS, Low Energy Ion Scattering spectroscopy (LEIS) is even more surface sensitive. The modern version of LEIS (HS-LEIS, high-sensitivity LEIS) is a relatively new face in surface analysis technology, but it should play an important role in the characterization of thin films as the only available tool sensitive to the outermost layer. X-ray Photoelectron Spectroscopy (XPS) can be used in conjunction with LEIS to provide complementary chemical bonding data for thin films. Furthermore, the HS-LEIS becomes one of the

best tools to provide the essential quantification data in the first few nanometers of the depth profile in high resolution along the axis perpendicular to the surface by combining with an argon impact ion source as a sputter gun.

In this work, hafnium zirconium oxide (HZO) ALD thin films were characterized using HS-LEIS and XPS. HZO has ferroelectricity and has the potential to be integrated with semiconductor nanofabrication processes. Typical target film thicknesses of this material are up to 10 nm, which matches well with the LEIS-based characterization techniques.

General Talk 4: Growth and irradiation effect of MBE grown Fe-Cr based metallic and oxide thin films

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Fe-Cr alloys are preferred in nuclear applications due to their strength and corrosion resistance. These materials undergo irradiation in reactor environments, leading to complex microstructural changes that affect their properties. Understanding the impact of irradiation on these materials is crucial. To investigate this, it is essential to isolate material heterogeneity and accurately record radiation-induced alterations. We synthesized 100nm Fe-8Cr and FeCr₂O₄ epitaxial films on (001) MgO substrates using molecular beam epitaxy to achieve low-defect, boundary-free structures. The growth temperature was varied and monitored using reflection high-energy electron diffraction (RHEED) to study film quality. The Fe-8Cr film was irradiated with He and Fe ions at doses of 0.5 and 5 displacements per atom (dpa). The penetration and presence of these ions within the film were calculated using the stopping and range of ions in matter (SRIM) simulation and further confirmed by transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS). Results showed a 13% increase in film thickness due to He ion irradiation, while Fe ion irradiation caused negligible changes. The oxide formation on the Fe-8Cr surface was altered by the Fe ion irradiation effect. Meanwhile, FeCr₂O₄ film growth is at the initial stage of growth optimization, where the film quality is determined by X-ray diffraction, XPS, and TEM. An irradiation study will be performed on this film to understand its effect on the oxide layer of Fe-Cr alloy.

General Talk 5: Proton Diffusion and Hydrogen/Deuterium Exchange in Amorphous Solid Water Investigated with Reflection Absorption Infrared Spectroscopy

Megan Dunlap

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Upon heating amorphous solid water films to temperatures between 116 K and 136 K, we find that protons initially formed at a Pt/water interface migrate into the films. Their distribution is monitored *via* the time-dependent exchange of D₂O probe molecules using reflection absorption infrared spectroscopy (RAIRS). We observe the concentration of D₂O decays mono-exponentially at all

temperatures, which reveals that the protons establish an equilibrium distribution prior to significant D₂O exchange. Additionally, we find the proton distribution is governed by the electric field established as the protons migrate away from their counterions within the Pt, and it agrees with the expected distribution of ions within an insulator beside a metal junction. Using this description, we extract a proton diffusion coefficient ranging from 10⁻¹⁷ to 10⁻¹⁴ cm²/s with an activation energy of 0.41 eV. We suspect this is a barrier imposed by translations and rotations of water molecules, which appear to facilitate the proton diffusion within our system.

General Talk 6: Deuterium Adsorption on N-doped Graphene on Ru(0001)

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Hydrogen is among the most promising clean and renewable energy sources. However, its storage is challenging due to its low gravimetric and volumetric densities. Nitrogen-doped graphene (Gr) has emerged as a potential material for improving hydrogen storage capacity. In this study, we examine N-doped Gr on a Ru(0001) using chemical vapor deposition (CVD) of pyridine, N-doping through N₂⁺ beam irradiation, and adsorption of hydrogen atoms with scanning tunneling microscopy (STM) and x-ray photoelectron spectroscopy (XPS). A high-quality Gr film with low nitrogen densities was obtained by pyridine CVD on Ru(0001) at 1100 K. Higher concentrations of N-dopants were introduced to the Gr/Ru(0001) through low-energy N₂⁺ irradiation at 100 eV. Nitrogen can be embedded in the Gr lattice preferentially in two configurations: graphitic N (N substituted in the C lattice) and pyridinic N (substitutional N next to a C vacancy). XPS shows that up to 6.8% of pyridinic N and 3.3% of graphitic N can be embedded into the high-quality Gr film using N₂⁺ irradiation at room temperature, indicating a preferential formation of pyridinic N over graphitic N. Only graphitic N was observed upon annealing the ion-irradiated Gr/Ru(0001) to 1063 K, revealing higher thermal stability of graphitic N over pyridinic N. Atomic deuterium was generated by backfilling the preparation chamber with D₂ (P = 1 × 10⁻⁷ Torr), which was then thermally cracked over a hot W filament positioned about 4–6 cm from the front face of N-doped Gr. XPS data show that the pyridinic N (398 eV) peak transforms to a higher binding energy peak at 399 eV upon D exposure at 330 K, while the graphitic N peak (400 eV) remains unchanged. The onset of D desorption was observed at 473 K, with a complete D desorption from pyridinic N occurring at 573 K. Currently, our efforts focus on D exposure at low temperatures (below 200 K) to explore its interaction with graphitic nitrogen.

General Talk 7: Correlative Surface Analysis: Combining XPS, Electron Microscopy, and Other Spectroscopies

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Comprehensive investigation of the chemistry and structure of surfaces and interfaces is vital to all fields of materials analysis. While an array of analysis exist to examine this region, the most complete understanding is gained from correlating the results of multiple techniques. X-ray photoelectron

spectroscopy (XPS) has become established as a one of the key techniques for measuring surface and interface chemistry. XPS can deliver quantified surface chemistry measurements, and by using depth profiling, an understanding of layer and interfacial chemistry. Advances in instrumentation have enabled XPS to keep pace with current investigative requirements, and further developments will allow it to reach even further. An area of particular interest is addressing the fundamental limits on spatial resolution of XPS, which can prevent it from determining how the surface structure is related to the measured chemical properties. For example, how the changing morphology of the surface during a depth profile could influence the measured composition would be challenging to determine using XPS.

Integrating complimentary information from other experimental techniques, while unable to match the surface selectivity of XPS, can overcome these spatial limitations. Electron microscopy can provide high resolution imaging, with elemental composition provided by energy dispersive X-ray microanalysis, but without the same surface selectivity seen with XPS or Auger electron spectroscopy (AES). This technique is an ideal complement to XPS analysis, provided spatial correlation on areas of interest can be achieved. Expanding beyond the electronic structure measurement of XPS is another pathway that can lead to deeper understanding. Molecular spectroscopy, such as FTIR or Raman, can provide such complementary information to XPS, albeit with different sampling depths, which can be extremely useful to validate measurements or confirm particular molecular structures.

In this presentation we will describe such correlative analysis, implemented both by instrumentation and software. The instrumental approach involves measuring samples in a single instrument designed to integrate XPS with reflected electron energy loss spectroscopy (REELS), low energy ion scattering (ISS or LEIS), and Raman spectroscopy. The software approach involves correlating data from SEM analysis with data from separate surface analysis instruments in an automated fashion. With both methodologies will show how the combination of XPS, Raman and SEM can be used to characterize 2D nano-materials, geological materials, polymer structures and materials for clean energy, as well as investigate corrosion in critical aeronautical components.

General Talk 8: Tracking changes in graphite bonding structures caused by high energy Cs ion implantation using traditional XPS and HAXPES.

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XPS continues to be an invaluable tool for the investigation of surface composition differences and chemical bonding in materials systems. The information provided in the spectral detail informs the researcher of the chemical changes in the surface region. The use of higher energy x-rays allows the information depth to be increased, by analyzing electrons from the same atomic transition but having higher kinetic energy, which escape from deeper into the sample.

While the graphite structure of carbon has garnered great attention in 2D materials applications, its bulk properties continue to be of interest in myriad applications, including its use as a moderator in nuclear reactors. An understanding the structural changes upon irradiation damage are essential for such graphitic materials. Modern XPS systems are well suited for automated acquisitions of data across areal distribution over a sample's surface. In this study, graphite samples implanted with Cs ions at specific energy were studied, utilizing array analyses to determine the Cs implant location.

The array analysis allows identification of differing implant concentration regions to determine the structural chemical changes to the carbon bonding. The relaxation and chemical bonding changes to the graphite structure from Cs ion implantation are expected to model the displacement cascade from neutron irradiation in a reactor and these results are discussed.

General Talk 9: Synergetic Dual-Additive Electrolyte Enables Highly Stable Performance in Sodium Metal Batteries

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Sodium (Na)-metal batteries (SMBs) have been considered one of the most promising candidates for the large-scale energy storage market owing to their high theoretical capacity (1,166 mAh g⁻¹) and the abundance of Na raw material. However, the limited stability of electrolytes still hindered the application of SMBs. Herein, sulfolane (Sul) and vinylene carbonate (VC) have been identified as effective dual additives that can largely stabilize propylene carbonate (PC)-based electrolytes, prevent dendrite growth, and extend the cycle life of SMBs. The cycling stability of the Na/NaNi_{0.68}Mn_{0.22}Co_{0.1}O₂ (NaNMC) cell with this dual-additive electrolyte is remarkably enhanced, with a capacity retention of 94% and a Coulombic efficiency (CE) of 99.9% over 600 cycles at a 5 C (750 mA g⁻¹) rate. The superior cycling performance of the cells could be attributed to the homogenous, dense, and thin hybrid solid electrolyte interphase consisting of **F- and S-containing species** on the surface of both the Na metal anode and the NaNMC cathode by adding dual additives. Such unique interphases can effectively facilitate Na-ion transport kinetics and avoid electrolyte depletion during repeated cycling at a very high rate of 5 C. We believe this electrolyte design will lead to further improvements in the performance of SMBs.

General Talk 10: Sr-Doped barites and their enhanced epitaxial growth of PbSO₄ in lead-acid batteries

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In lead acid batteries, barite (BaSO₄) is often added to the negative (lead metal) electrode, where it serves as an isostructural template for the nucleation of anglesite (PbSO₄) crystals. This helps to prevent the passivation of the lead metal surface, which occurs through the accumulation of large PbSO₄ crystals on the active lead surface. Barite's effectiveness, however, is dependent on its ability to support the epitaxial nucleation and growth of anglesite. In this capacity, barite is limited by a

relatively large lattice mismatch between barite and anglesite, which exceeds 4% in some directions. By adding strontium during the synthesis of barite crystals, a solid solution between barite (BaSO_4) and celestite (SrSO_4) can be achieved that displays a reduced lattice constant, as confirmed by single crystal XRD. This brings the doped barite's lattice constants closer to those of anglesite, while retaining much of barite's stability in sulfuric acid that is essential for repeated battery cycling. Optical microscopy experiments show that the doped material accumulates much more PbSO_4 than undoped barite when exposed to a solution of sulfuric acid and $\text{Pb}(\text{NO}_3)_2$. In-situ liquid AFM experiments reveal the nanoscale nucleation and growth mechanisms of PbSO_4 as it occurs. Upon exposure to supersaturated ($\text{H}_2\text{SO}_4 + \text{Pb}(\text{NO}_3)_2$) solution, layer-by-layer (Frank van-der-Merwe) growth of PbSO_4 is observed on the doped barite surface, in contrast to monolayer + islands (Stranski-Krastanov) growth mode seen on undoped barite in the same conditions. This shows that barite doping can fundamentally alter the crystal nucleation mechanisms to make the nucleation and growth of PbSO_4 much more facile, and points to a novel strategy for creating improved battery additives via lattice-constant engineering, for engineering improved barite additives.

General Talk 11: Elucidating the Effects of Oxygen Vacancies and Electric Fields on Adspecies Adsorbed on La-Based Perovskites

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Perovskite materials can be used in electrochemical CO_2 reduction processes due to their higher stability than metal catalysts such as Nickel but are limited by their catalytic activity towards CO_2 reduction. For perovskites to be an alternative catalyst for this process, the surface chemistry of perovskites needs to be augmented by the introduction of active sites on the surface such as oxygen vacancies or by applying electric fields. We propose using La-based perovskites (LaNiO_3 , LaCoO_3 and LaFeO_3) which are known to be highly active in CO_2 reduction to reduce CO_2 on the surface and we investigate these surfaces using both experimental and theoretical methods. While this proposal specifically focuses on the theoretical nature of the project, we use experimental methods to ground our theoretical calculations. Our first study deconvolutes experimental XPS spectra with theoretical calculations that predict the core level binding energy shifts of various adspecies on the surface (H , O , OH , H_2O and CO_2). Adsorption of species on the surface was favorable with considerable charge transfer occurring between the surface and the adspecies. This study is imperative for understanding the surface chemistry of our system before we augment it with oxygen vacancies and electric fields. We found that the higher energy peak for both LaCoO_3 and LaNiO_3 corresponds to water adsorption while the lower energy peak is due to lattice oxygen. The other species correspond to intermediate satellite peaks. Literature results and temperature dependent XPS spectra confirmed our results were accurate. We will also investigate the effects of coverage and oxygen vacancies on the XPS spectra for several of our surfaces (LaNiO_3 and LaCoO_3). Finally, we investigate the effects of oxygen vacancies and electric fields on the surface activity and adspecies adsorption. Our preliminary studies show that oxygen vacancies can increase the adsorption of CO_2 on the surface and electric fields

change the plane wave averaged potential of the surface. We expect that the influence of electric fields will strengthen the adsorption of CO₂ due to the increase electrons stabilizing the surface. Further work will be completed to explore the effects of electric fields on adsorption strength of CO₂ as well as the formation of oxygen vacancies

General Talk 12: Plasma activation of adherends, interfacial bonding formation mechanism, and stability of adhesively bonded joints

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Structural adhesives have been increasingly utilized in many key industrial areas including both the aerospace and automotive industries. It is very important to understand chemical characteristics to form strong interfacial chemical bonds between activated surfaces and adhesives in the adhesive joining of two dissimilar adherends. For the interfacial chemical bonding of dissimilar joints, substrate surfaces should be activated or modified to match their surface energies. One of easy physical methods is plasma treatment. Plasma treatment leads to surface cleaning, activation of buried functionalities, and new active layer formation (i.e. oxide layer on metals). We used a high power (500W) plasma to optimize surface functionalities to have maximum adhesive joining strength of aluminum alloy-polymer composites by controlling plasma tip height (h), tip speed (v), and stepover distance (d). Plasma treatments enhance adhesive wettability on post-treated surfaces for adhesive joints, but the treated surfaces deactivate quickly in air. Vacuum sealing of AA6061 and CFRP-PA66 reduced the surface energy deactivation over 7 days by at least 230 times and 970 times compared to in air. We also used model adhesives to better understand bonding mechanism on metals and polymer composites, and found that epoxy adhesive forms weak linear polymer bonding on the polymer composites, but it forms strong crosslinking bonding on metals. Finally, the bonding stability of adhesively-bonded joints was tested in 98RH at 35°C. Moisture mainly penetrated into adhesive and interfacial bonding, and degraded joining bonds at the edge and corners of the joints. Experimental approaches, results, and characterization will be discussed in detail.

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General Talk 13: Using XPS to best advantage – Avoiding Common Errors and Extracting More Information

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The value of information obtained using XPS has fueled significant growth in its use in multiple disciplines and by a new generation of analysts as well as ‘casual’ users less familiar with the method. Accompanying this increased use and changes in the nature of the user community are i) increased presence of erroneous data analysis in literature and ii) fewer analysts taking full advantage of the types of information that can be extracted from well-constructed XPS experiments. This talk will suggest information that experienced XPS analysts can pass along to less experienced XPS users to address both issues. First, the status of several efforts being undertaken to address faulty analysis, and incomplete reporting will be described. Second, several useful but underused approaches to XPS data collection and analysis will be described. Examination of literature shows a significant amount of faulty XPS data analysis, often related to peak fitting, and significantly incomplete reporting of data and analysis parameters needed to assess result reliability or enable replication. Recent publications highlight common errors in the effort to encourage analysts to avoid them as well as enable readers and reviewers to recognize them.¹⁻⁴ Analyses also indicate that most publications using XPS ask one or more of three interrelated questions: i) What elements are present? ii) How much of each element is on the surface? iii) What are the chemical states of the elements present? Although very appropriate and important uses of XPS, there is a wider range of material and sample information can be obtained that enable XPS to address several analysis needs. The list of accessible information includes, sample polarizability and dielectric constants, chemically resolved electrical measurements, local electric field and potentials, band offsets and bending, the nature of electrical double layers and local charge dynamics, and changes in microbe cell walls in response to external stimuli. Common XPS analyses assume that the analyzed surface layer is uniform and ignore the impact of sample structure on XPS signals. Information contained within XPS spectra can provide information about elemental distribution in the surface region, and information about coating thickness and uniformity, and size of nanoparticles. Selected references

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General Talk 14: Protein dynamics on minerals resolved by in situ atomic force microscopy and machine learning

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Proteins, as the natural building blocks, possess remarkable innate abilities to assemble into complexes with multiscale orders and diverse functions. The harnessing of protein self-assembly to develop biomimetic materials with applications in energy, bioelectronics, health, and the environment is a testament to their potential. However, creating two-dimensional (2D) protein architectures at mineral surfaces with programmed structures and functions remains a formidable challenge. The complex interplays between protein-protein and protein-mineral interactions and how they shape the energy landscape of protein assembly in response to environmental stimuli, such as electrolytes, at these interfaces is still largely uncharted territory. In-situ characterization of protein assembly processes with high temporal and spatial resolution, combined with statistical analysis, is imperative to navigate this complexity.

Recently, we have developed approaches to direct protein assemblies on mineral surfaces through programmed protein-protein and protein-substrate interactions.^{1,2} In this talk, I will discuss the assembly processes of de-novo-designed DHR10-MicaN protein nanorods into different 2D matrices in response to KCl concentrations and mica surfaces. We used in situ high-speed atomic force microscopy (AFM) to record the in-plane dynamics of the protein nanorods on mica as a function of KCl concentration. Then, we statistically analyzed the data using a machine learning approach adapted for large-volume consecutive AFM data and compared the results to simulations.³⁻⁵ Finally, we quantitatively described the in-plane dynamics of the protein nanorods, determined by MicaN-mica binding affinity, entropic effects, interfacial hydration layers, and substrate symmetries.⁶ These findings provide insight into the remarkable diversity of self-assembled architectures adopted by protein-protein and protein-inorganic interfaces that affect protein assembly at different length scales and extend well beyond the basic designs. The findings also demonstrate the importance of incorporating colloidal forces and hydration structures inherent to 2D protein-metal hybrid materials.

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General Talk 15: Observing Silk Nanofibril Formation in Real Time Unveils a Continuous Nucleation-Growth Pathway

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Nanofibrils play a pivotal role in spider silk, and silkworm silk and are responsible for many of the impressive properties of these kinds of protein materials. To date, no synthetic method has come close to reproducing the properties of natural silk, due to the complexity and insufficient understanding of the mechanism of the silk nanofibril formation. Particularly, the formation of silk nanofibril has never been directly observed. Here, we utilized *in-situ* liquid atomic force microscopy (AFM) and photo-induced force microscopy (PiFM) to directly observe the formation process of nanofibril and define the basic paradigm of individual nanofibrils. We demonstrate that the growth follows the continued nucleation-growth pathway, the amorphous structure acts as the active site to guide the nanofibril forward growth, and accomplish continuous nucleation and phase transition, rather than simple monomer attachment to the nanofibril front. The growth of nanofibrils entails the transformation of unfolded molecules into folded structures. However, the β -sheet structure can be adopted as nuclear to undergo reassembly, even producing a functional protein nanofibril with enzyme-resistance properties. The multistage conformation transition process defines the unique growth mechanism of silk nanofibrils, and the dynamic processes of conformational transition offer a diverse energy landscape, enabling the acquisition of novel and varied silk assemblies by controlling the assembly process.

General Talk 16: Selective dissolution and re-precipitation by pH cycling enables facile recovery of pure manganese from surface nodules

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A rapid shift to renewable energy technologies is essential to meet global sustainable development and climate change targets. Manganese (Mn), a DOE-designated critical element, is indispensable for steel production, batteries, ferroalloys, aluminum alloys, fertilizers, and consumer electronics. Manganese nodules, or polymetallic nodules, offer unconventional domestic feedstocks for manganese and other critical elements. This study presents a comprehensive approach to efficiently extract manganese from Mn nodules sourced from the Oacama site in South Dakota. Our methodology employs bulk characterization techniques, equilibrium modeling, and pH cycling with commodity

chemicals. Bulk characterization and equilibrium model suggest the presence of various metal carbonates, heterogeneous Mn-rich grains, and mixed Mn oxides in the nodules. Acid leaching experiments identify pH 1.5-2 as optimal for the selective dissolution of manganese and calcium. A two-step selective re-precipitation process extracts iron-rich and Mn-rich precipitates from the leachate, achieving approximately 59% manganese extraction efficiency at >83% purity, without the need for specialty chemicals, membranes, ligands, or resins.



Graduate Student Posters

G1. In-Situ Multimodal Analysis of Copper Hydroxy Chloride for Enhanced Thermochemical Energy Storage

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The development of efficient energy storage systems is critical for achieving carbon neutrality and maximizing the use of renewable energy sources. Thermochemical energy storage systems (TCES), a specialized category within thermal energy storage systems (TES), have garnered significant attention as a potential system for storing energy across wide temperature ranges (low/medium/high) based on the TCES material used. Salt hydrates are frequently researched for low and medium-temperature TCES applications due to their high energy density, cost-effectiveness, and environmental benefits. However, the limited availability of suitable salt hydrates for specific applications and the challenges related to phase instability, pulverization, and loss in efficiency due to deliquescence of the material during repeated cycling have prompted the researchers to study the mechanisms of material degradation.

In-situ characterization of TCES materials is essential to identify and understand material degradation modes during energy storage and release cycles, which is crucial for designing advanced, high-performing materials. To address these challenges, we investigated the potential of copper hydroxy chloride (CHC), a double anion salt of copper, for TCES applications. The water insolubility of CHC reduces performance degradation associated with deliquescence over prolonged cycling periods compared to other salt hydrate systems. Our study conducted a comprehensive in-situ evaluation of CHC's dehydration and hydration cycling behavior. We employed in-situ X-ray diffraction (XRD) and in-situ X-ray photoelectron spectroscopy (XPS) to uncover the stepwise breakdown of CHC at different temperatures during dehydration, leading to the release of water and chlorine byproducts. By utilizing techniques such as thermogravimetry-differential scanning calorimetry (TG-DSC) and a calorimeter coupled a humidity generator, we assessed the temperature ranges suitable for CHC's hydration and dehydration, the associated heat changes (enthalpies) and the temperatures at which reaction reversibility is maintained.

The in-situ and multimodal characterization approach utilized in our research is applicable to the study of other TCES materials. These methods are vital for identifying hydration, dehydration, and degradation mechanisms in salt hydrate-based materials, thereby enhancing our understanding of their mechanism of operations which will enable the broader objective of obtaining sustainable and efficient TCES systems.

G2. Crystallographic and Electronic Structure of Lanthanide-Doped CeO₂ Nanoparticles

Peter Jensen and Liane M. Moreau*

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CeO₂ (Ceria) has a variety of uses ranging from biological applications to use in fuel cells. One of the primary uses for the material is in catalytic converters due to its oxygen storage capacity, which arises from the ease at which cerium in CeO₂ can access the Ce(III)/Ce(IV) redox pair. This feature is often exploited for reactions like the oxidation of CO. Nanomaterials already offer benefits over bulk material, including a higher surface-to-volume ratio and more tunable properties like size, shape, and composition. Doping into the fluorite structure of ceria can allow for additional benefits, specifically controlling the concentration of oxygen vacancy defects within the lattice. Ln-doped ceria nanoparticles are made using a two-phase hydrothermal synthesis and capped with oleic acid. Samples are then characterized using x-ray fluorescence (XRF), x-ray diffraction (XRD), small angle x-ray scattering (SAXS), and x-ray absorbance spectroscopy (XANES/EXAFS). The XRF results show a saturation point, before which Ln incorporation tapers off and after which incorporation steadily increases. XRD patterns show the emergence of a new peak which becomes prominent beyond this saturation point, suggesting a phase transition to a cubic sesquioxide. The XANES spectra show a distinct shift in f-orbital occupancy after the saturation point is reached, providing further evidence of a phase transition. These techniques show that the doped ceria maintains its structure with increasing Ln content up to a phase change to that of cubic sesquioxide, Ce₂O₃, indicating a change in the cerium oxidation state from Ce(IV) to Ce(III). This ultimately shows that the oxygen storage capacity of ceria can be controlled using lanthanide dopants.

G3. Interrogating the Fe/U interface towards predictive models for environmental remediation

Benjamin Rooney-Sailand

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Contamination from U.S. Nuclear activity continues to be a concern to human health, safety, and the environment. Key radioactive elements of interest to nuclear science, uranium (U) and plutonium (Pu), tend to move through environmental systems as or adhered to colloids. Studies of samples extracted from nuclear contamination sites have previously documented the formation and structure of actinide oxide colloids, highlighting a transport method for how stored contaminants are able to leak into the environment from waste storage sites. The conditions that determine the formation, stability, surface chemistry, and properties of these actinide nanoparticle (NP) colloids must be fully understood when designing nuclear waste repositories. This proposal seeks to elucidate how varying conditions would affect the transport of U oxide on Fe mineral deposits in the environment, and by doing so to create predictive models for the form of U in contamination sites, to facilitate environmental remediation. I will take advantage of the high surface-area to volume ratio of ultrasmall Fe, Fe₃O₄ and Fe₂O₃ NPs to systematically investigate the Fe/U interface. Fe-containing NPs will be varied in their size, their phase, and their morphology. By using various anisotropic particles, which inherently have different surface facets exposed, I will be able to determine the surface-facet dependence on U uptake and binding motif. Characterization of the U/Fe interface will be performed using multiple x-ray spectroscopy analysis methods. Preliminary characterization

indicates that U oxide is deposited onto the Fe surface until the available Fe surface sites are entirely saturated reaching a maximum thickness (single layer). Further results from this investigation will offer systematic insight for how Fe-containing NP characteristics affect U adsorption and draw further connections to the behavior of U in more complex environmental systems which contain Fe-based minerals. Through analysis of these spectra, we will be able to determine which surface sites the actinide complex is binding to.

G4. Elucidating the growth pathways of actinide oxide nanoparticle formation

William Vance

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Metal oxide nanoparticles are nanoscale particles of metal oxides that exhibit unique electronic structural attributes that make them desirable for applications in various fields such as medicine, catalysis, sensing, and energy. Anisotropic nanoparticles exhibit facet-dependent surface chemistry which results in distinctive optical, electronic, and catalytic properties. Specifically, the high surface energy facets afforded by anisotropic nanoparticles provide energetic hot-spots for molecular sensing, which can be fine-tuned to promote specific molecular binding sites. This anisotropic behavior holds true for actinides as well, which are highly under-explored compared to transition-metal-oxide counterparts. Despite utility in the nuclear fuel cycle and in heterogeneous catalysis, few studies of anisotropic actinide oxide nanoparticles have been reported. Notably, of those which have been reported, uranium and neptunium have a tendency to form spherical nanoparticles (the lowest energy morphology) whereas thorium and plutonium form anisotropic rod-like morphologies. This is unusual given that each of these structures displays cubic fluorite atomic arrangements. Therefore, anisotropic growth can assist in best determining why subtle structural and chemical differences between the actinide elements can so greatly affect their growth pathways. To interrogate anisotropic growth within these particles, time-course growth studies have been pursued and characterized via electron microscopy (TEM) and small angle X-ray scattering (SAXS). Results of this investigation will be used to elucidate differences between the binding structure and structural arrangements of the little-explored early actinide elements.

G5. Elucidating the Morphology of a Ru Nanoparticle on a TiO₂ and a CeO₂ Surface

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As the projected amount of plastic in the ocean is set to exceed the number of fish there maintains a need for processing single-use plastics. Hydrogenolysis upcycles polyolefin (PO) into small alkanes that can be processed to value-added products. Ru can catalyze hydrogenolysis and has resulted in less methane and more desirable longer alkanes. The wetting capability of Ru on CeO₂ has been previously demonstrated to successfully result in the hydrogenolysis of PO without forming a large amount of CH₄¹. Further delving into this phenomenon, the Ru nanoparticles were tested on anatase

TiO₂ to see if the wetting capability was specific to the CeO₂ surface. Through stepwise molecular dynamics calculations, the Ru nanoparticles reordered into an ellipsoidal structure that continued through to the experimental temperature. The final structure then underwent radial distribution analysis of the Ru-Ru interactions and was found to have a comparable structure to experiment. The experimental and theoretical methods agree that Ru nanoparticles do not wet the TiO₂ surface, indicating that the wetting capability is currently specific to the CeO₂ surface.

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G6. Substituent and Central Metal Effects on Self-assembled Phthalocyanine Monolayers on HOPG as Studied by Scanning Tunneling Microscopy and DFT calculations

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Phthalocyanines are planar, macrocyclic, organic molecules with unique spectroscopic and nanomechanical properties. Of particular interest is their capacity to readily self-assemble into monolayers. Scanning Tunneling Microscopy (STM) is a powerful tool for characterizing the structural properties of these thin films. Density functional theory, DFT, is an effective quantum mechanical tool for understanding the structure and electronic properties of adsorbed systems.

STM was utilized to image and characterize substituted phthalocyanine monolayers self-assembled on HOPG. High-resolution drift-corrected images, voltage dependent images, lattice parameters, and epitaxial measurements were all obtained. DFT calculations were performed to elucidate substituent orientation, to determine adsorption energies relative to the gas phase, and to extract the density of states as a function of bias voltage. Results obtained here will be contrasted with results from previous studies of the porphyrin family of complexes. This collaboration between computational and experimental groups provides greater insight than studies by each group alone.

G7. Non-precious Metal Phosphides and Nitrides as HER and OER Catalysts

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Hydrogen splitting for power storage is an attractive method to mitigate the effects of climate change. Unfortunately for hydrogen production to be sustainable hydrogen must be produced via water splitting which is an energetically expensive reaction requiring the use of costly Ir and Ru based catalysts. Nickel phosphides and nitrides have emerged as potential replacements for more expensive catalysts. To evaluate these potential catalysts for use in water splitting, accurate models must be developed. Literature observes the formation of an oxyhydroxide layer on the nickel phosphide and nitride surface in reaction conditions. This suggests the pristine surface may not be the best reference

for understanding the OER and HER reactions on the catalyst surface. To provide a more complete picture of the OER reaction this oxyhydroxide layer must be considered. Using density functional theory calculations, we have constructed a phase diagram to predict the surface's saturation at reaction conditions. The phase diagrams reveal the substitution of phosphorous and nitrogen atoms and the adsorption of OH molecules are favorable with the number of phosphorous or nitrogen atoms substituted being dependent on the chemical potential of oxygen. Interestingly replacing phosphorous and nitrogen atoms with OH molecules was significantly more favorable than replacing phosphorous atoms with oxygen atoms for all chemical potentials considered. For the adsorption of OH molecules the Gibbs free energy became more favorable as the number of adsorbed molecules increased for all chemical potentials considered, suggesting the surface will be highly saturated in reaction conditions. In most cases OH adsorption was more favorable than P or N replacement. After determining the most likely configuration of the nickel phosphide and nitride surface in reaction conditions we modeled the OER reaction on the pristine surfaces and the saturated surfaces likely to be observed in reaction conditions. The formation of the oxyhydroxide layer was found to inhibit the reaction by raising the energy needed to create stable OOH intermediates.

G8. Effect of Si impurities on the hydrogen direct reduction of hematite pellets

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Steelmaking is considered one of the top producers of anthropogenic carbon dioxide emissions. As the steel demand continues to increase, it is pivotal to investigate sustainable alternative routes that reduce or eliminate the emission of contaminant gases. The hydrogen direct reduction of iron oxides is a feasible solution since it eliminates the burning of fossil fuels and the reaction byproduct is water. However, unlike the traditional reduction of iron oxides using the blast furnace (BF), the direct reduction process does not include a slag separation step. Therefore, the effects of common gangue components in the hydrogen reduction of iron oxide must be evaluated. In this work, hematite (Fe₂O₃) pellets with varying SiO₂ content were annealed under Ar - 2.7 % H₂ environment. The microstructures of the specimens were studied under scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS). The chemical and structural changes of the pellets were analyzed using X-ray photoelectron spectroscopy (XPS) and X-ray diffraction (XRD). The multi-scale investigation demonstrates the presence of complex oxide components after heat-treatment. Elucidation of the underlying mechanisms in the redox reaction will help to improve the efficiency of hydrogen-based reduction of iron oxides and decarbonize the iron and steel industry.

G9. Tuning magnetic and ferroelectric properties of 2D materials via shear deformation

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Mechanical manipulation provides a direct method to systematically tune lattice constants and crystal symmetries via strain. These structural changes impact properties, such as electronic and magnetic behavior, motivating the use of established methods like uniaxial tension where properties are measured as the crystal is stretched along a single axis. In layered 2D materials, however, interlayer shifts can directly affect magnetic ordering and electronic phases suggesting that shearing rather than pure tension may be a more natural experimental tuning knob. Here we develop a new approach for applying shear deformations to 2D materials and carry out proof-of-principle measurements on the 2D layered magnet CrI₃ and the 2D ferroelectric AB-stacked hBN.

Our first system of study, few layer CrI₃, has a monoclinic structure and is anti-ferromagnetic (AFM), but mechanical perturbations (e.g. pressure, puncture) have been seen to irreversibly shift it to ferromagnetic (FM) and a rhombohedral structure. We aim to systematically probe these deformations using an optically transparent scanning probe to apply shear forces to CrI₃, enabling measurements of sample magnetization via the magneto-optical Kerr effect as shear force is applied. In our second system, the 2D insulator hBN is found to be ferroelectric when parallel stacked at 180 degrees. In this configuration, there are two metastable AB or BA stackings with opposite polarizations related to each other through interlayer shifts. We probe polarization of AB-stacked hBN by incorporating it into a graphene-based transistor device and carrying out resistivity measurements while applying shear deformations with a modified version of our scanning probe. Our preliminary results demonstrate the ability to repeatably tune the graphene resistivity by shear deformations. Beyond these two materials, we believe shearing techniques will be useful in probing a wide variety of magnetic and ferroelectric 2D materials.

G 10. Highly Textured Sn-Doped Ga₂O₃ Epilayers for Economically Viable Solar-Blind Ultraviolet Photodetectors with High Responsivity

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The design and development of solar-blind photodetectors utilizing ultrawide bandgap semiconductors have garnered significant attention due to their extensive utility in specialty commercial sectors. Solar-blind photodetectors that display excellent photosensitivity, fast response time and are produced using cost-effective fabrication steps would fulfill the performance demands in relevant applications. Herein, we report highly textured Sn-doped Ga₂O₃ thin film metal-semiconductor-metal type deep-UV photodetectors using a commercially scalable magnetron sputtering method. Commercially achievable growth and fabrication steps are chosen intentionally to demonstrate an economically viable photodetection strategy without compromising the device performance. In-depth structural, morphological, chemical, and optical characterization is reported to optimize the configuration for further device fabrication and testing. Under transient triggering circumstances, a fast response time of around 500 ms is reported, accompanied by a responsivity of approximately 60.5 A/W. The detectivity, external quantum efficiency, and photo-to-dark current ratio values are reported as 1.6×10^{13} Jones, 2.8×10^4 %, and 17.4, respectively. The overall device

performance cost-effective fabrication process for solar-blind UV photodetection using Sn-doped Ga_2O_3 is promising. The approach holds promise for significant implications toward the development of electronics capable of functioning in extreme environments and exhibits substantial potential for enhancing low-cost UV photodetector technology.

G 11. Study of Microplastics in Water: Formation and Raman Spectroscopy via Sonication of Polyethylene Terephthalate

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Microplastics (MPs) are plastic particles smaller than 5 mm in size. Several studies have shown that they are widespread in the ocean, polar glaciers, and deep-sea sediments. These MPs can release toxins and additives that damage the aquatic environment and affect marine organisms and human health. As a result, researchers worldwide are interested in studying the contamination of microplastics in the marine ecosystem and the generation of micro and nanoplastics in aquatic environments. This is mainly attributed to the fragmentation of plastics caused by natural processes such as abrasion, photolysis, and biotic factors, as well as by industrial activities. In this study, we examined the formation of microplastics (MPs) in water, mimicking the behavior of plastics in the real world. This investigation will assist in understanding the behavior of MPs at the air-water interface. Microplastics were generated in water through the spraying of Polyethylene Terephthalate (PET) in varying amounts with vigorous mixing. The use of ultrasonic mixing resulted in a decrease in particle sizes. The solutions were then analyzed using Raman Spectroscopy and Scanning Electron Microscopy (SEM). This approach offers a simple method for creating specific size distributions of microparticles, facilitating further research on these plastic particles in water.

Keywords: Microplastics, Polyethylene Terephthalate, Raman Spectroscopy, and Scanning Electron Microscopy,

G12. Supercapacitive Properties of Pulsed Laser Deposited $\text{Ba}(\text{Fe}_{0.7}\text{Ta}_{0.3})\text{O}_{3-\delta}$ Thin Films Deposited on Ni Foil

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The development and research into the area of semiconducting metal oxides (SMO) is continuously growing and adapting to the wide uses of SMOs in domestic and industrial applications. Being able to incorporate nano scale supercapacitors into modern devices would allow for greater power requirements to be fulfilled with a smaller storage solution. $\text{Ba}(\text{Fe}_{0.7}\text{Ta}_{0.3})\text{O}_{3-\delta}$ (BFTO) has been studied as a sensor in high temperature applications. The study of thin film of this material will allow it to be used in much smaller applications, including potential on chip applications. In this work, BFTO thin films have been deposited using pulsed laser deposition (PLD) on Ni substrates ranging from

room temperature to 600 °C in a partial pressure of 50 mTorr of Oxygen. Microstructural characterization of BFTO at 600 °C revealed crystalline size of about 21nm, with uniform distribution of spherically shaped grains 40-100 nm in size. As electrodes for micro supercapacitors, BFTO thin films deposited at 600 °C displayed a specific capacitance of 400 mF cm⁻² at a current density of 1 mA cm⁻² and retained 94% capacitance over 3000 cycles with good structural stability. BFTO may be able to be used in a wide variety of applications such as power storage or flexible electronics.

G13. Understanding and control of the surface oxidation layers in Nb thin films.

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Surface oxides formed on various metals significantly impact their properties and stabilities. In superconducting qubits based on niobium (Nb) thin films, these native oxide layers can affect both decoherence and stability. In this study, we use Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) to assess the influence of different treatments on the surface oxidation layers of Nb thin films. Chemical mechanical planarization (CMP) and accelerated neutral atom beam (ANAB) methods are used to tailor and control the surface oxidation. Our TEM results show that engineered oxide layers formed by both CMP and ANAB lead to a significant thickness reduction compared to the native oxide. Scanning transmission electron microscopy and energy-dispersive X-ray spectroscopy (STEM-EDS), along with X-ray photoelectron spectroscopy (XPS), reveal an oxidation gradient within both the native and surface engineered oxides. The top layer predominantly contains Nb⁵⁺ (Nb₂O₅), with various sub-oxides present towards the oxide-metal interface. Our ToF-SIMS depth profiling studies confirm the presence of an oxygen content gradient, and further reveal an enhanced resistance of the CMP and ANAB-formed oxides to subsequent oxidation. In addition, we show that an interfacial layer containing hydrogen (H) and hydroxide (OH) species is present at the Nb oxide-metal interface. The origin and impact of this H and OH trapped layer is further understood by *in situ* experiments and density functional theory (DFT) calculations. Such findings ultimately suggest the importance of employing surface engineering techniques paired with advanced analytical techniques towards understanding the physicochemical changes occurring at complex oxide/metal interfaces.

G14. Investigating the Growth Mechanism of ZIF-8 Thin Films via Chemical Bath Deposition for Enhanced Gas Sensing

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Metal-organic frameworks (MOFs) are a versatile class of crystalline materials composed of metal ions and organic ligands, known for their high surface area, tunable porosity, and diverse functionality¹. Among them, zeolitic imidazolate frameworks (ZIFs) like ZIF-8 stand out due to their inherent stability and ease of synthesis. ZIF-8, formed by the coordination of zinc ions with 2-methylimidazole ligands, exhibits a robust zeolitic structure¹. Understanding the nucleation and growth mechanisms of ZIF-8 is essential for tailoring its properties for specific applications.

This study used a chemical bath deposition (CBD) process to fabricate ZIF-8 film with controllable thickness. We systematically explored the growth mechanism of ZIF-8 thin films on functionalized substrates. Advanced characterization techniques, including scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), and Time-of-flight secondary ion mass spectrometry (ToF-SIMS), alongside in-situ growth monitoring, were employed to investigate the morphology, crystalline orientation, and molecular coordination of material/substrate interface.

Furthermore, the controllable ZIF-8 film was applied to quartz crystal microbalance (QCM) to develop a gravimetric gas sensor device. We enhanced CO₂ adsorption capability in gas measurement studies by increasing the ZIF-8 CBD deposition cycles. Additionally, this work reports the lowest limit of detection for CO₂ using the ZIF-8/QCM sensor.

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G15. Economically Competitive Production of Oleo-Furan Sulfonate Detergents from Furfural and Fatty Alcohols

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Oleo-furan sulfonates (OFS) are advanced detergents synthesized from fatty acids and furanic derivatives, presenting a sustainable alternative to petrochemical-based detergents with enhanced performance characteristics. The conventional production method via the acylation of furan by fatty acid anhydrides faces thermodynamic limitations due to the low equilibrium constant of acid dehydration to anhydrides. Our study introduces an innovative synthesis pathway leveraging the dehydrogenative aldol condensation of fatty alcohols with furfural, followed by transfer hydrodeoxygenation using isopropanol as a hydrogen donor.

The initial step employs hydrotalcite catalysts, where basic sites facilitate transfer dehydrogenation and aldol condensation reactions, achieving a 70% yield of α , β -unsaturated furanic aldehyde in a liquid-phase batch process, with no significant catalyst degradation over five recycles. In the subsequent synthesis step, the aldehyde undergoes hydrodeoxygenation (HDO) over a ruthenium-based catalyst – a combination of Ru/C for localized hydrogen production and RuO₂ hydrate for the reverse Mars-van Krevelen HDO step – at 180°C under both inert nitrogen (N₂) and hydrogen (H₂)

atmospheres. Remarkably, short reaction times show higher oleo-furan yields under H₂-HDO conditions. However, at extended reaction times, the inert N₂ atmosphere surpasses the H₂ atmosphere in oleo-furan production. This phenomenon is attributed to the reduction of the RuO₂ catalyst to Ru during the reaction, deactivating it for HDO. This finding offers a promising route to achieve high oleo-furan yields through HDO without relying on H₂.

The subsequent sulfonation of the oleo-furan intermediates produces OFS surfactants with good detergency properties. Technoeconomic analysis of the OFS production process indicates advanced economic potential compared to traditional methods, featuring the viability of this sustainable and efficient synthetic pathway.

G 16. *In-Situ* X-Ray Absorption Spectroscopy (XAS) Characterization of Molecular Catalysts for Photoelectrochemical and Photochemical CO₂ Reduction Reactions.

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The challenges posed by climate change necessitate a reevaluation of our approach to energy production. The rising level of carbon dioxide (CO₂) in the environment are contributing to greater global warming threats, underscoring the need for sustainable solutions. Electrochemical CO₂ reduction reaction (CO₂RR) has emerged as one of the promising ways to combat climate changes and simultaneously store energy in the form of value-added chemicals, like carbon monoxide (CO) and methanol. Further improvements had been made to harvest sunlight to drive this reaction. This is called photo-electro-chemical (PEC) CO₂RR, which decreases the dependencies of nonrenewable energy sources. Our research has shown that p-Si semiconductor protected by a film of TiO₂, which is further functionalized with (3-aminopropyl)triethoxysilane (APTES) and coated with cobalt phthalocyanine (CoPc) on graphene oxide, has emerged as the best performing catalyst and photocathode for PEC CO₂RR. However, its mechanism to promote the PEC is unknown. In this study, we investigate the changes of catalyst using in-situ X-ray absorption spectroscopy (XAS) during the production of CO and methanol via PEC CO₂RR. Specifically, we focus on elucidating the changes in oxidation states, electronic structures, and coordination numbers of cobalt within CoPc, as it serves as the active center of PEC CO₂RR. Our findings underscore the dynamic changes observed in CoPc's properties during the production of CO and methanol, shedding light on crucial aspects of its catalytic behavior. These insights are important for designing new catalysts to enhance PEC CO₂RR technologies, especially considering the ongoing exploration of a family of CoPc with different ligands for CO₂RR.

G 17. Characterization of Oxide Nanoparticles Dispersed in Laser-Melted Metallic Specimens

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The chemical composition and structural characteristics of oxide nanoparticles embedded in metallic matrices are crucial for understanding their impact on material properties.¹ This study investigates the oxide nanoparticles formed during the laser melting of yttrium titanate (Y₂Ti₂O₇) with 316L stainless steel (SS). Using Scanning Electron Microscopy (SEM), Energy Dispersive X-ray Spectroscopy (EDS), and Transmission Electron Microscopy (TEM), we characterized the nanoparticles in the resulting Oxide Dispersion Strengthened (ODS) alloy.

Our findings reveal that, while oxide nanoparticles were successfully incorporated into the metallic matrix, the stoichiometry of yttrium and titanium deviated from the initial composition post-laser melting. Notably, the proportion of yttrium was reduced compared to titanium, but no evidence of yttrium loss was observed during laser printing. Despite this compositional change, incorporating these nanoparticles significantly enhanced the specimens' microhardness. Additionally, varying the amount of yttrium added resulted in different microhardness outcomes, with a higher concentration of oxide nanoparticles correlating with increased microhardness.

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G 18. Continuous-flow Synthesis and Characterizations of FeCrAl-Al₂O₃ Composite Microparticles

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This research focuses on the synthesis and microstructural characterization of FeCrAl-Al₂O₃ composites. The primary objective is synthesizing these composites and achieving a bi-continuous phase in their microstructure after laser fusing. We synthesized spherical FeCrAl-Al₂O₃ composites with controlled size and composition by adjusting flow rates and material content using a UV-assisted microfluidic system. By engineering these composite powders, we can improve the uniformity of material distribution and reduce powder denudation while printing complex structures using metal additive manufacturing technologies. The synthesized composites were subjected to laser fusing under varying laser conditions. The microstructures of the lasered composites were characterized using Scanning Electron Microscopy (SEM), Energy-dispersive X-ray Spectroscopy (EDS), and X-ray

Diffraction (XRD). Our key findings include the successful creation of spherical FeCrAl-Al₂O₃ composites and a detailed analysis of their microstructures post-laser fusing.

Furthermore, Al₂O₃ acts as a templating material, which can be selectively etched away, resulting in a highly porous FeCrAl structure with a large surface area. The significant impact of these findings lies in the potential to create porous FeCrAl foams, which can serve as catalytic scaffolds for jet fuel conversion and other applications. This research demonstrates the feasibility of using UV-assisted microfluidic synthesis to produce high-performance composite materials with tailored microstructures, advancing material science and engineering.

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G 19. High-throughput PbSe colloidal Quantum Dots (QDs) Synthesis via a Continuous Flow System

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In recent years, nano-sized materials have become a cornerstone of modern material science due to their unique electronic, photonic, magnetic, and chemical properties. The conventional synthesis approach is a batch reaction. However, batch reactors' disadvantages are widely discussed: lack of precise control over reaction conditions, limited reaction volume, and poor product quality control in large-scale synthesis. Over these problems, the interest in flow chemistry has increased over the last two decades. The benefits include more efficient mixing in multiphase systems, enhanced temperature control, scale-up potential, and better alignment with "green chemistry" principles related to efficiency and safety, making it a promising approach.

This study established a continuous flow system to continuously implement the hot injection procedure to create burst nucleation and control growth conditions. PbSe QDs were successfully synthesized after finding the right nucleation and growth conditions. The sizes of QDs can be tuned from 5nm to 12nm by adjusting the nucleation stage and growth stage temperature. The nucleation stage temperature is crucial to achieve small-size nanoparticle synthesis and narrower size distribution. The growth stage temperature is proven to impact the final particle size. The flow method synthesized QDs can be purified and compressed to make a radiation detector. Our work demonstrates an efficient way to study the nanoparticles' growth mechanism without changing the chemistry and a promising approach to achieve automated and scale production.

Keywords: Flow synthesis, PbSe QDs, nucleation, tunable size, automated synthesis

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G 20. Surface Comparison of ZIF8-Derived Zinc Oxide and Conventional Zinc Oxide Materials for Chemical Gas Sensing Applications

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Metal-organic framework (MOF)-derived metal oxide materials are gaining attention as a potential field of study for achieving high-performance chemiresistive gas sensors. MOFs are of particular interest in gas sensing due to their highly porous and large surface area nanostructures can have wide-ranging applications in not only gas sensing but other fields of study as well. Zeolitic imidazolate frameworks (ZIFs) such as ZIF-8 are one such example of MOFs which can then be converted into its corresponding metal oxide such as zinc oxide (ZnO). ZnO is often used as gas sensing material for the detection of ammonia (NH₃) gas, but undoped ZnO often suffers from low sensitivity and selectivity when undoped, limiting the overall effectiveness of the resulting sensor^{1,2}. Calcination of ZIF-8 into ZnO provides better sensing features for the resultant ZnO material by inheriting some of the porous and large surface area structure from its MOF precursor which improves the overall responsiveness of gas detection³. Morphological features highlighting the ZIF-8-derived ZnO inheriting some of the structure of ZIF-8 can be explained as features that improve the result of ZnO material's porosity, making it a better candidate for the detection of gases including NH₃ and other gases³. This work aims to utilize advanced surface characterization techniques such as X-ray diffraction (XRD) and Scanning Electron Microscope (SEM) to analyze and confirm the successful conversion of ZIF-8 to ZnO as well as X-ray Photoelectron Spectroscopy (XPS) to investigate the available oxygen vacancy for both conventional ZnO and ZIF-8-derived ZnO. This comparative study underscores the significance of surface characterization in developing advanced ZnO materials with enhanced performance attributes.

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G 21. Dry Printing of Nanostructured Thin Films Enabled by Low-pressure Vapor Phase Microreactor Assisted Nanomaterial Deposition

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The Low-Pressure Vapor Phase Microreactor-Assisted Nanomaterial Deposition (LP-V-MAND) method is a dry printing approach that employs vapor phase deposition to deposit thin film materials on various type of substrates selectively. This technique allows for precise control over the morphology and size of deposited patterns, making it one of the valuable tools in the manufacturing processes for various electronic applications.

The ability to accurately control the deposition patterns and tailor the morphology of these materials holds immense potential for the fabrication of advanced electronic devices. Applications include but are not limited to, transistors, gas sensors, and photodetectors. These applications require precise patterned nanostructured thin films to meet the specifications necessary for these applications to function effectively. To date, deposition of high-k dielectric materials such as ZrO₂ and TiO₂ and conductive materials like PEDOT has been demonstrated using LP-V-MAND.

Our research dives into the fundamental aspects of this process, mainly focusing on the growth and nucleation of PEDOT for gas sensor fabrication and performance evaluation. Comprehensive characterization of the deposited materials has been carried out using X-ray photoelectron Spectroscopy (XPS), Scanning Electron Microscopy (SEM), X-ray diffraction (XRD), and Atomic Force Microscopy (AFM). These techniques have confirmed the quality and desirable properties of the thin films produced through LP-V-MAND.

By refining this LP-V-MAND technique, we aim to contribute to advancing dry printing of nanomaterial-based electronics, paving the way for more efficient and precisely engineered electronic devices. The insights gained from our work provide a foundation for further exploration and optimization of LP-V-MAND in various applications, highlighting its importance in thin film science and technology.

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G 22. Investigation of Cobalt Telluride Restructuring Under Oxygen Evolution Reaction Conditions

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Hydrogen represents one of the most attractive options for energy storage from renewables; it is the simplest and most abundant element on earth and has the highest energy density of any fuel. Driven by the goal of a zero-emission energy infrastructure by 2050, a green hydrogen economy is critical to enable a 100% renewable society.^{1,2} Currently, the greatest challenge for hydrogen production is the cost, which is not yet able to compete with conventional fossil fuels. Thus, a key direction in hydrogen energy research is focused on improving the efficiency and economic viability of hydrogen production technologies and materials. A promising pathway towards sustainable hydrogen production is water-based electrolysis, but a critical barrier for efficient water splitting is the high overpotential of the sluggish oxygen evolution reaction (OER) at the anode side of electrolyzer. Among non-noble metals, transition metal chalcogenides have emerged as excellent options due to their superior electrocatalytic performances and better electrical conductivity and lower cost compared to most metal oxides and pure precious metals.^{2,3} However, irreversible restructuring is often observed in metal chalcogenide systems under oxidative OER conditions, leading to new phases that can sometimes outperform the material in its pristine state and creating a knowledge gap on what the real active sites of the catalyst are.⁴⁻⁶ As such, it is critical to identify the real active sites of metal chalcogenides to enable the rational design of electrocatalytic materials. While most of the focus has been on metal sulfides and selenides, this project is thus centered on elucidating the restructuring mechanism and true active sites of cobalt telluride materials, which has previously been shown to have excellent electrocatalytic performance and stability while being hypothesized to be more active than its sulfur and selenide counterparts to the higher electronegativity of tellurides.²

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G 23. Perovskite Oxide $\text{SrCo}_{0.5}\text{Ir}_{0.5}\text{O}_3$ as an Anodic Catalyst for Proton Exchange Membrane Water Electrolysis.

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Hydrogen, as a versatile energy carrier, offers significant potential for meeting the growing demand for clean and sustainable energy. Proton exchange membrane water electrolysis (PEMWE) has emerged as a promising technology for hydrogen production via the oxygen evolution reaction (OER). However, the slow kinetics of the OER at the anode side pose a challenge to achieving high energy conversion efficiency and hinder the commercialization of water electrolysis systems. In this study, we explore the application of the advanced $\text{SrCo}_{0.5}\text{Ir}_{0.5}\text{O}_3$ (SCIO) perovskite as an OER electrocatalyst in PEMWE, focusing on its electrochemical performance and durability. The SCIO perovskite catalyst was synthesized and characterized using surface-sensitive techniques (e.g., X-ray photoelectron spectroscopy) to evaluate its effectiveness as an anode electrocatalyst using rotation disk electrode (RDE) and applied at lab-scale PEM electrolyzer. Our findings highlight the potential of SCIO perovskite as an anode electrocatalyst for PEM water splitting. Further research and optimization are essential to fully realize the capabilities of SCIO perovskite catalysts and their scalability for commercial-scale PEMWE systems.

Keywords: Proton Exchange Membrane Water Electrolysis, Oxygen Evolution Reaction, Electrocatalyst, Perovskite, Metal oxides

G 24. A standardized methodology for the solid-state ion exchange of metal zeolite catalysts

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Single-site catalysts (SSCs) possess isolated active sites that allow for precise control over chemical reactions. The well-defined identity of SSCs ensures uniformity in the reaction environment at an atomic level. The isolated active sites of SSCs provide high selectivity and atom efficiency during reactions. Zeolites are aluminosilicates with highly ordered pore structures ranging from 2-10 Å in diameter. Zeolites are attractive supports for SSCs as their anionic framework stabilizes cationic metals in confined pores via ion-exchange.

Zeolite-based SSCs have found applications in the direct conversion of methane to methanol, a “holy-grail” reaction in catalytic chemistry, using copper zeolite SSCs (e.g., Cu-MOR). Specific copper active sites in Cu-MOR provide a high selectivity in the hydroxylation of methane to methanol. The most common synthesis method to obtain Cu-MOR and other zeolite-based SSCs is the aqueous-phase ion-exchange (APIE). While many successful zeolite-based SSCs have been produced from APIE, some significant shortcomings must be noted. First, APIE requires a large amount of post exchange filtering and drying steps. The waste liquid from the exchange and filtering steps, spent liquor containing

metal precursors, must be dealt with in an environmentally acceptable manner. Next, solvation shells formed around the metal cation during APIE increase the size of the incoming structure which precludes efficient exchange within the zeolite pore. Finally, many transition metals undergo complexations with water at moderate pH conditions forming diverse hydroxides (e.g. V, Fe, W) which is counterproductive in generating uniform active sites. For these reasons, an alternative synthetic approach is desired to obtain zeolite-based SSCs that are compatible with a wider set of catalytic transition metals.

A promising alternative to APIE is solid state ion-exchange (SSIE). During SSIE, a gas metal precursor (e.g., FeCl₂) and proton-form zeolite (e.g., H-MOR) are mixed and heated under an inert gas environment. The protonic sites (H⁺) in the zeolite are replaced with Fe cations and volatile HCl is formed and purged from the system. Originally developed in the 1970's, SSIE has become a lost art with only a handful of publications over the last 20 years. The most recent comprehensive review of SSIE surfaced in 2008. Recent literature has narrowed the focus of SSIE to copper catalysts (mostly for methane hydroxylation to methanol). The present work aims to revisit and formalize the exchange mechanisms and the active site identity of zeolite catalysts generated by SSIE. This work will broaden the synthetic scope of SSIE to a range of high-activity transition metals. Methods employed during SSIE synthesis include mass spectrometry and pH measurements to quantify the extent of cation exchange. For post-exchange analysis, SEM-EDS was used to verify the metal loading and to confirm the lack of metal agglomerates on the zeolite surface. XRD also demonstrated the lack of nanoparticle/agglomerate formation. High resolution argon physisorption provided a molecular fingerprint of the micropore structure and established the physical location of metal sites within the zeolite pore.

G 25. Machine learning-guided accelerated discovery of structure-property correlations in lean magnesium alloys for biomedical applications

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Magnesium alloys are emerging as promising alternatives to traditional orthopedic implant materials thanks to their biodegradability, biocompatibility, and impressive mechanical characteristics. However, their rapid in-vivo degradation presents challenges, notably in upholding mechanical integrity over time. This study investigates the impact of high-temperature thermal processing on the mechanical and degradation attributes of a lean Mg-Zn-Ca-Mn alloy, ZX10. Utilizing rapid, cost-efficient characterization methods like X-ray diffraction and optical microscopy, we swiftly examine microstructural changes post-thermal treatment. Employing Pearson correlation coefficient analysis, we reveal the relationship between microstructural properties and critical targets (properties): hardness and corrosion resistance. Additionally, leveraging the least absolute shrinkage and selection operator (LASSO), we pinpoint the dominant microstructural factors among closely correlated variables. Our findings underscore the significant role of grain size refinement in strengthening and

the predominance of the ternary $\text{Ca}_2\text{Mg}_6\text{Zn}_3$ phase in corrosion behavior. This suggests that achieving an optimal blend of strength and corrosion resistance is attainable through fine grains and reduced concentration of ternary phases. This thorough investigation furnishes valuable insights into the intricate interplay of processing, structure, and properties in magnesium alloys, thereby advancing the development of superior biodegradable implant materials.

G26. Influence of Fluorination and Oxygenation Sources on the Thermal Atomic Layer Etching of MoS₂

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Atomic layer etching (ALE) has emerged as a pivotal technique in the precise fabrication of two-dimensional (2D) materials, particularly molybdenum disulfide (MoS₂), which holds promise in the semiconductor industry due to its high mobility in monolayer form. The ability to precisely etch amorphous and crystalline MoS₂ films provides a pathway for controlling thickness, which is critical to achieving desired electrical and optical properties. Previous studies used MoF₆ and H₂O in thermal ALE of MoS₂. Here, we report studies of alternate sources of fluorination and oxygenation and evaluate their impact on thermal ALE of MoS₂. Oxygen sources include water and ozone and fluorine sources include HF/Pyridine and MoF₆. Etch rates, uniformity, and surface chemistry post ALE were characterized using spectroscopic ellipsometry, atomic force microscopy, and X-ray photoelectron spectroscopy. Preliminary results indicate etch per cycle values of 0.5 Å/cycle for MoF₆+H₂O at 200 C, 0.32 Å/cycle for HF+H₂O at 250 C, and 0.26 Å/cycle for HF+O₃ at 250 C. Additionally, ALE processes were combined with ALD to demonstrate thickness control for achieving few-layer MoS₂.

G 27. Demonstration of reliable electron beam lithography in a scanning electron Microscope

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Electron beam lithography (EBL) is a critical technique for the fabrication of nanoscale structures, that uses an accelerated beam of electron to pattern features down to 10nm on substrates coated with an e-beam sensitive resist, surpassing the capabilities of traditional lithography. In previous studies it has been demonstrated that EBL can also be done using scanning electron microscopy (SEM) to develop metallic nanostructures [1] and photonic components such as micro-ring resonator, directional couplers [2] and Mach-Zehnder interferometers. Higher performance metrics, such as the quality factor (Q-factor) for micro-ring resonators and coupling efficiency for directional couplers, require precise control of the dimensions and geometries of these components. Here, we show a reliable alternative to generate nanoscale patterns using the electron beam in an SEM column. In this study, resolutions down to 200 nm with a writing field ranging from 30-50 μm have been achieved with an accelerating voltage of

20-30 keV, beam current of 30-50 pA and dose in the range of few μC . Our results demonstrate the flexibility and accuracy of EBL using SEM and highlights its significance in developing advanced photonic devices.

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G 28. Direct Growth of Molybdenum Disulfide from Metal Contacts via Atomic Layer Deposition

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As current silicon-based transistor devices begin to approach the fundamental material scaling limits of silicon, new designs and material integration methods are required to meet the ever-increasing demand for greater computing power and memory storage densities. Molybdenum disulfide (MoS_2) is one material in the two-dimensional materials class which is a potential replacement for silicon within next generation microelectronic devices to enable further device scaling due to its high electron mobility, even when in monolayer form. High quality MoS_2 is required for integration into microelectronic devices as even small concentrations of defects can significantly impact the electrical properties of the monolayer film. Synthesis of monolayer MoS_2 which is of sufficient quality for integration into microelectronic devices while maintaining processing temperatures that are within the allowable thermal budget of back end of line processing has proven difficult. In this work we demonstrate a method of growing crystalline MoS_2 directly from contact metals via atomic layer deposition (ALD) using molybdenum hexafluoride and hydrogen sulfide as the reactants. Several different contact metals including tungsten, molybdenum, nickel, and platinum were used for blanket studies to determine the ability to deposit crystalline MoS_2 at low temperatures. Raman spectroscopy was used to examine the crystallinity of the deposited films and x-ray photoelectron spectroscopy was utilized to determine the chemical composition of the deposited films. To obtain high quality MoS_2 test structures, contact metals were patterned to template direct ALD of MoS_2 . Following MoS_2 deposition the samples were again characterized using Raman spectroscopy and atomic force microscopy to determine the crystallinity and morphology of the resulting MoS_2 film.

G 29. Elucidating the Role of Additives and Microstructure on Lead Sulfation in Lead-Acid Batteries

Carinna Lapson, Ajay Karakoti, Shannon Lee, Vijayakumar Murugesan
Pacific Northwest National Lab

Lead-acid batteries have historically been a reliable and cost-effective energy storage option. These batteries consist of a Pb negative electrode, PbO_2 positive electrode, and a microporous separator, all

saturated with H_2SO_4 electrolyte. The common failure mechanism, typically referred to as hard sulfation, involves the irreversible large crystal growth of non-electroactive PbSO_4 on the surface of the anode and is not well understood. In commercial batteries, expanders such as BaSO_4 and lignosulfonates are used as additives to promote uniform nucleation of PbSO_4 leading to smaller PbSO_4 crystals to minimize hard sulfation. However, the effectiveness of such expanders is limited in absence of an in-depth understanding of the nucleation and growth mechanisms. We are developing 3D optical microscopy technique to study the effect of additives on the nucleation and growth of lead sulfate under varying electrochemical conditions. Clean lead electrodes with and without barite crystals were imaged to understand the mechanisms of PbSO_4 nucleation at grain faces and boundaries as a function of electrochemical cycling parameters.



Undergraduate Students Posters

UG1. Analyzing the Structure-Property Behavior of Salt Hydrates as Promising Materials for Thermal Energy Storage

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Several industrial processes experience significant heat losses, underscoring the need for development of systems that can efficiently capture and utilize this waste heat. Thermal energy storage systems offer a viable solution for capturing and utilizing industrial waste heat reducing overall heat loads and contribute towards the global objective of achieving carbon neutrality.

Salt hydrates, particularly strontium chloride hexahydrate ($\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$) and calcium oxalate monohydrate ($\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$), have emerged as promising material candidates for Thermochemical Energy Storage (TCES) systems that capture, and release heat based on their reversible hydration. Despite their potential, the physical and thermal properties of these salts have not been extensively tested over multiple dehydration and rehydration cycles. Such testing is crucial for understanding their long-term stability and performance in real-world applications. This study addresses this gap by studying the impact of multiple dehydration and hydration cycling on their structural, compositional, and functional properties using multimodal analysis.

The thermal properties were monitored using Thermogravimetry-Differential Scanning Calorimetry (TG-DSC), to test the impacts of cycling on the structural stability and extent of hydration. Additionally, Fourier Transform Infrared Spectroscopy (FTIR) and Powder X-ray Diffraction (PXRD) were employed to analyze changes in chemical bonding and crystal structure, respectively. Optical microscopy was utilized to observe the effects due to expansion and contraction of the structure due multiple hydration and dehydration cycles. The knowledge gained from these multimodal characterization techniques about the stability and performance of $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$ and $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ as TCES materials will be presented.

UG2. Solid State Chemistry for the Synthesis and Characterization of Ternary Metal Chlorides

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Material discovery is crucial for the advancement of technology in various applications (*e.g.*, scintillation detection, thermoelectrics, energy storage, etc.). Using solid state chemistry techniques, such as typical “shake and bake” methods, we focus on the synthesis and structure/property characterization targeting new ternary metal chlorides. Synthesis of these hygroscopic chlorides requires the use of a glovebox to avoid hydration and decomposition of the materials. Additionally, tuning the chemical composition and structures allows for tuning of the resultant properties (melting/decomposition temperatures, ionic conductivity, magnetism, etc.). Structural and property

characterizations via X-ray diffraction (XRD), electrochemical impedance spectroscopy (EIS), thermogravimetric – differential scanning calorimetry (TG-DSC), and scanning electron microscopy – energy dispersive X-ray spectroscopy (SEM-EDS) of various ternary chlorides will be discussed.

UG3. Viscosity and Self-Diffusion Coefficients of Generalized Lennard-Jones Substances

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The transport properties of viscosity coefficient η and self-diffusion coefficient D for a pure gas are commonly estimated using the Chapman-Enskog kinetic theory of gases[1][2]. This involves calculating the collision integrals, $\Omega^*(l,s)$, based on the potential energy function describing the interaction between gas molecules. This potential energy function is often modeled by the Lennard-Jones (LJ) 6-12 potential. Previous works have developed a generalized Lennard-Jones potential (gLJ)[3][4], including a third parameter, β , and taking the form

$$V(r; \epsilon, r_m, \beta) = \epsilon \left[\frac{\beta}{6} \left(\left(\frac{r_m}{r} \right)^{12} - \left(\frac{r_m}{r} \right)^6 \right) - \left(\frac{r_m}{r} \right)^\beta \right]$$

A three-parameter potential has the ability to be more accurate than the standard LJ potential and is easier to fit than other potentials with larger parameter spaces, such as the Mie potential. This work aims to relate the gLJ to D and η . While well defined in some other potentials, the relationship between r_m and the collision diameter, σ , is not defined in previous literature. Here we determine the ratio $\sigma^* = \sigma/r_m$ for a given β using numerical root-finding methods. Additionally, we calculate the collision integrals $\Omega^*(1,1)$ and $\Omega^*(2,2)$ for gLJ substances, using methods which previously found values for the Modified Stockmayer potential[2]. These triply-nested integrals must be evaluated through quadrature.

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UG4. Exploring CO₂ Hydrogenation of Rhodium Bis(diphosphine) Complex in Protein Scaffolds

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Nature's enzymes have long championed chemical conversion reactions using several complex design elements, such as electronically tuned active sites and well-constructed secondary sphere coordination environments, often serving as inspiration for the development of robust catalysts. Development and rational design of artificial enzymes has shown to be a powerful tool for understanding these enzymes, allowing for the development of robust catalysts. We have previously demonstrated that a molecular complex, [RhI(PNglyP)₂]⁻, shows catalytic activity for hydrogenation of CO₂ to formate when covalently attached to a protein scaffold. Experimental and computational analysis of this constructed artificial enzyme suggest that a positioned positive charge near the active site is important for enhancement of catalytic activity while high solvent accessibility of the active site may result in slower catalytic activity. We aim to fully understand the role of the design principles necessary to achieve catalytic activity across different scaffolds. We utilized the Protein Data Bank (PDB) to identify stable and well-characterized protein scaffolds, followed by further refinement based on the ability to incorporate the molecular complex within a well-structured cavity. Scaffolds were modified for the selective covalent attachment of the rhodium complex by implementing cysteine residues in the identified cavities, as means to provide a well-defined secondary sphere environment around the metal center. The selected scaffolds were isolated and subjected to covalent attachment of the rhodium complex and screened for catalytic activity. One of the scaffolds exhibits successful incorporation of the rhodium molecular complex without disruption to the protein fold. High pressure 1H NMR demonstrates generation of formate with a turnover frequency of 0.06 ± 0.02 hr⁻¹ at 500 PSI of a 1:1 mixture of CO₂:H₂. Further studies are needed to determine the position of the rhodium molecular complex within the protein scaffold, with further rational design to the secondary sphere in order to investigate the effect of various design principles on catalytic activity.

UG5. Secondary metabolites in bioenergy plant root exudates: chemical characterization and microbial utilization

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Sorghum (*Sorghum bicolor*) is a bioenergy crop of interest to the Department of Energy. Understanding how sorghum interacts with its environment is important to optimizing its growth for biofuel production while also using fewer resources. The roots of all plants exude organic compounds called root exudates, which include compounds called secondary metabolites that are not involved in plant growth but affect the plant's interactions with its surroundings, for example, by attracting microbes or inhibiting the germination of competing plant species. If these can be isolated and characterized, secondary metabolite functions can be applied to optimizing plant-microbe

interactions for growth. Root exudates are complex mixtures of compounds and are difficult to separate and analyze; thus, most remain uncharacterized. Separation of exudate extracts was achieved using liquid chromatography and crystallization, followed by microcrystal electron diffraction, mass spectrometry, and nuclear magnetic resonance spectroscopy. To investigate the interactions between sorghum and its surroundings, soil microbes were cultured on various sorghum secondary metabolites to compare catabolism pathways. Serine hydrolases involved in secondary metabolite utilization were then characterized using activity-based protein profiling. Identification of root exudate compounds and characterization of the microbial utilization of these secondary metabolites will result in an enriched understanding of sorghum-microbe interactions.

UG6. Doping effect on electronic and electrochemical properties of high entropy oxide thin films

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Abstract: Earth-abundant transition-metal perovskite (ABO₃) oxides, with their high compositional flexibility and electronic tunability, are promising electrocatalysts for water splitting, a low-cost method to produce clean Hydrogen. Recent work found that certain perovskite oxide systems, such as Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3- δ} , La_{1-x}Sr_xCoO_{3- δ} , and La_{1-x}Sr_xNiO_{3- δ} , exhibit electrochemical activity comparable to or even greater than benchmark electrocatalysts based on platinum group elements. However, these oxide systems suffer from low stability, undergoing surface amorphization, cation leaching, and phase transformations under operating conditions. Recently, high entropy oxides (HEOs), which feature at least five atoms at the same lattice site in near-equimolar amounts, have shown great potential to combine high performance and stability for applications such as energy storage and catalysis. This project will utilize epitaxial perovskite HEO thin films with precise control over composition, phases, and strain states as a platform to yield mechanistic insights into the effect of element doping on the electronic and electrochemical properties of HEOs.



High School Student Posters

HS 1. Controlling Agricultural Pollution: 'Root' for Success

Aashrita Bhamidimarri

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Intensive agricultural production to meet global food demands require frequent irrigations and fertilization to maintain moisture and nutrients in soils. This causes water runoff, soil sedimentation, nutrient leaching, pollutions and eutrophication of water bodies leading to human, environmental, and economic losses globally. Diverse root systems from mixed crops can address this problem better than monocrops by improving soil hydraulic properties, soil health and prevent sedimentation by binding soils. A greenhouse experiment laid out in a randomized complete block design with four replications and five treatments (corn, wheat, soybean, mix of these species, and control) within a replication was conducted to test this hypothesis. Results showed that soil sedimentation, measured as turbidity of the drained waters, was lowest in corn and highest in control (2.75 vs 22.75%). Soils of mixed crops had fastest water infiltration rate (8.63 vs. 4.87 mm/s), and highest organic matter content (0.37 vs. 0.28%) compared to control. Cation exchange capacity was highest in soils of mixed treatment and lowest in soybean (5.5 vs 4.7 Meq/100g). Algal growth on the drained waters, an indicator of nutrient pollution, was 41% less in mixed treatment compared to control (432.25 vs 729 mg).

Although roots from monocrops improved soil sedimentation and hydraulic properties compared to control, this study showed that the diversity of roots from mixed crops not only improved soil hydraulic properties, but also improved soil health and drained water quality.

Recommendation of crop mixes based on roots can control agricultural pollution and benefit producers and environment equally.

HS 2. Sibylla: The Microscopists Toolkit

Todd, R., Thallapally, S, Cruz, E., Overman, N, Olszta, M.

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Science should be about the development of thoughts and theories pertaining to the exploration of new endeavors, not about formatting and data layouts. While data presentation and science communication are paramount to disseminating good science to all levels of society (e.g., general public versus technical conferences), most scientists lack the tools and sufficient metaphorical palettes to do so. Currently, most microscopists/scientists spend hours laying up figures/data because of the lack of software developed specifically aimed at creating annotated figures. This research centers on developing such a software that will provide microscopists and scientists with a toolkit that will allow quick and standardized creation of annotated figures. This work will greatly improve the productivity of all science communication, thereby leaving more time for science and less time spent agonizing over scale bar placement.

HS 3. Nano Cartographer: Data Visualization and Analyzation

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A vital part of science includes notetaking and keeping pictures/data organized and easy to understand. Pictures from electron microscope are one of the most crucial pieces of evidence for microscopists everywhere. However, without organization of this data, microscopists are having a hard time sharing their data and aiding their colleagues in comprehending the data. When collaborating with other microscopists, their peers have no idea how the data/pictures are organized, as it is all forced into folders on a single hard drive. As such, other microscopists are challenged to find the data they are looking for, and sometimes might have to waste time asking the microscopist who created the folder/data set. With Nano Cartographer, microscopists are given a “digital notebook”, that saves their notes, data, and annotations. Nano Cartographer provides a standard notetaking method, making it easier for other microscopists to access and understand the data. Nano Cartographer also allows scientists to add their thoughts and their understanding of the data, to revisit later or to aid other microscopists in their endeavor. This will greatly reduce the time it takes to access data and be a valuable tool to understand and analyze data as well.

HS 4. Outbreak Minimization Solutions and Applications

Daniel Gomez

St Stephen's Academy

Preventing and slowing the spread of adverse processes such as epidemic outbreaks and environmental contamination events are critical for public health. This can be achieved through techniques such as vaccination and ecosystem protection or remediation. However, practical limitations on the number of vaccines available and/or the cost of ecosystem protection necessitate optimization strategies. In this work, we reviewed a mathematical programming approach for epidemic intervention based on the Time Aware Influence Maximization Problem (TAIM) that identifies nodes and interfaces that maximize vaccination effectiveness in a network. We prove the efficacy of our algorithm using common representative databases that demonstrate their effectiveness. In addition, we propose this strategy as a plausible tool to address environmental contamination problems where a contaminant’s susceptibility to transfer across interfaces (i.e. air-to-water) could be used to predict effective nodes for ecosystem protection or remediation. Our results demonstrate that our algorithm can significantly reduce the impact of adverse events, showcasing its potential in both epidemic and environmental contamination remediation.

HS 5. A Eye Intelligence: The Future of Disease Detection Through the Eyes

Advaitha Motkuri

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The project presents a groundbreaking approach to enhance human health through the eye with the integration of artificial intelligence (AI) technology through a smartphone attachment. By leveraging the power of AI algorithms, our innovative system aims to detect and diagnose various diseases, including diabetes (diabetic retinopathy), glaucoma, and age-related macular degeneration, through retinal imaging captured by a smartphone attachment. This project addresses the universal need for accessible and cost-effective methods of detecting diseases through the eye, ensuring that individuals from all backgrounds have access to reliable screening methods regardless of their location or resources. Through rigorous testing and validation, this system demonstrates promising results in terms of accuracy, efficiency, and usability. The project represents a significant advancement in preventive care through the eyes, offering a scalable solution that has the potential to revolutionize the way diseases are detected and managed globally.

HS 6. Making Bioplastics from Banana Peels!

Srithan Thallapally

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Petroleum-based plastic is a major issue in today's world. Petroleum-based plastics are 99% fossil fuels, and 75% of all greenhouse gas emissions are made from fossil fuels. Therefore, an increase in petroleum-based plastics can be directly tied to an increase in greenhouse gasses produced. In this way, petroleum-based plastics not only affect the ocean and marine life but also the air and climate change. The purpose of this project is to use an already known way of creating bioplastics from banana peel waste and replace petroleum-based plastics with more environmentally friendly bioplastics. Bioplastics are currently being investigated as an alternative to petroleum-based plastics and also a more efficient way of reducing food waste produced by humans. In this experiment, glycerol and sorbitol were used as plasticizers, because of their ability to hydrogen bond to the starch molecules and create a film. Based on my experiments, the bioplastics produced with glycerol were more flexible but sacrificed their tensile strength compared to sorbitol. However, the opposite was true with the sorbitol, as my experiments showed that the sorbitol-based bioplastics had higher tensile strength but were not very flexible. These different characteristics can be applied in the different areas that plastic is present in, such as packaging for sorbitol-based plastic or grocery bags for glycerol-based plastic. In the future, I would like to use AI/ML tools for the expansion of this project to optimize the bioplastic formation and increase its effectiveness.

HS7. Investigating the Quality of Biodiesel Synthesized from Used Cooking Oils

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Biodiesel, an alternative to fossil-derived diesel, has many advantages and is produced from used oils using a transesterification reaction. In a transesterification reaction, the triglyceride molecules of oil

break down into glycerin and three fatty acid esters (biodiesel). This process for generating biodiesel is relatively simple and cost-effective; however, quantifying the purity of diesel is commonly done by determining its Cetane number, a gold standard, but it is costly and cumbersome. Biodiesel contains oxygenated species (esters) and variable unsaturation; hence cetane numbers cannot be directly used to quantify biodiesel quality. In this project, I used a transesterification reaction to produce seven different biodiesels from used oils (Figure 1). My goal in this project was to investigate various characterization techniques that are easily accessible to analyze the quality of biodiesel. I used proton NMR and IR measurements to determine the quality of biodiesel. The ratio of ester protons to unsaturation protons was used to estimate the number of double bonds of freshly prepared and as well air-treated biodiesels. NMR results revealed that the biodiesel derived from restaurant frying oil is stable to oxidation and ranked the best. Kinematic viscosity measurements of biodiesels are between 4.7 to 6.5 at 20 C. In general, the viscosity of biodiesels decreased with temperature. I also investigated the copper corrosion test, carbon residue test, and flash point of biodiesel to rank the seven biodiesels. Biodiesels derived from restaurant oil have the most balanced levels of unsaturation to ester and are rated the best of all biodiesels.

HS8. The Backbone of Innovation: Financial Operations

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The Financial Operations Division at Pacific Northwest National Laboratory (PNNL) is quintessential for scientific success at the lab. Financial Operations keeps PNNL financially stable and efficient by handling cost accounting, paying bills, paying employees, receiving payments, managing treasury, and ensuring compliance across all functions within finance. Guaranteeing that PNNL has the funds and resources needed for research supports innovation and leads to incredible scientific breakthroughs. Under Financial Operations, our team focused on the following teams: Accounts Payable, Travel, and Payroll, which together make up the services group of Financial Operations. Our work in Accounts Payable helped to increase accessibility to financial information within internal PNNL staff, and it ensured that vendors were paid on time. Through Travel, our work tracked expenses of employees on PNNL-related travel, as well as audited the reimbursement process for PNNL interviewees nationwide. Lastly, our work in Payroll audited vendor transactions and the Finance Manual system. The goal of our oral report is to delve deeper into the specifics of Financial Operations and how it relates to the greater context of scientific research. The combined enterprise of both the Research and Finance sectors maintains that PNNL continues to be a leader in scientific research and innovation.



General Posters

P1. Cryo-XPS for high vapor pressure samples and minimizing x-ray induced damage in sensitive samples.

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Traditional XPS measurements take place in ultra-high vacuum (UHV) conditions, which are not possible when trying to analyze materials with high vapor pressure. To eliminate issues with these types of samples, cryogenic temperatures are often needed. XPS is surface sensitive, so cryogenic treatment of specimens requires careful preparation so as not to adsorb water vapor onto the sample surface and obscure the chemical information from the true sample surface. This allows for investigations of materials systems not previously pursued in traditional XPS systems, which will be shown on example aqueous chemical solutions.

Besides simply controlling vapor pressure, cryogenic treatment of samples can also reduce the amount of chemical damage caused by x-ray illumination of sensitive samples. Lithium sulfur battery materials, of great current interest in the community, exhibit chemical changes over short exposure to x-rays during normal analysis. Cryogenic treatment of these same materials will be shown to dramatically minimize the damage, allowing careful analysis of chemical bonding without structural changes over times much longer than that necessary for the analysis to take place.

P2. Catalytic chemistry of acetic acid and acetic anhydride on magnetite (001)

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Acetic acid reactions on catalysts are of interest for applications in biomass upgrading through carbon-carbon coupling reactions to produce value-added chemicals. The Fe₃O₄(001) surface is of interest due to its ability to stabilize single transition metals up to elevated temperatures, serving as a model single-atom catalyst. Here, we employ a combination of X-ray photoelectron spectroscopy (XPS), low energy electron diffraction (LEED), and temperature programmed reaction spectroscopy (TPRS) to investigate the reactivity of acetic acid and acetic anhydride on the Fe₃O₄(001) support. XPS shows that formic acid deprotonates at low temperatures (~100 K), forming an acetate intermediate and a protonated lattice oxygen (hydroxyl). LEED images demonstrate that the Fe₃O₄(001) reconstruction is lifted at 0.5 ML of acetic acid (1 ML = 1 acetate per Fe atom). TPRS data reveals acetic acid and acetic anhydride largely decompose into CO, CO₂, and water at a peak

temperature centered at ~ 607 K. Ketene and recombinative acetic acid are produced as minor products at ~ 587 K. Comparison with HCOOH and DCOOH, where CO and CO₂ products desorb at lower temperatures, suggests the rate-limiting step for acetic acid and acetic anhydride decomposition to CO and CO₂ on Fe₃O₄(001) is the carbon-carbon bond scission step. In the case of ketene formation, the limiting step likely resides in the C-H scission steps. Further, XPS, acquired as a function of flash temperature along the TPRS, reveals no shift in binding energy for C1s peaks, indicating the intermediate species after acetate activation are short-lived. This study explains the complex interaction of acetates with the Fe₃O₄(001) and enables future studies to investigate acetate interactions with transition metal-supported single atoms.

P3. Non-destructive Depth Profiling of Multilayer Films Utilizing XPS/HAXPES

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X-ray photoelectron spectroscopy (XPS) has long been preferred for its precision and reliability in discerning nanometer thick films on silicon substrates. However, a challenge arises when using surface sensitive soft X-ray sources, as the areas of interest are often concealed beneath capping or oxide layers. While higher energy X-ray beams have facilitated the detection of photoelectron signals from deeper layers, most of this analysis has been conducted at synchrotron radiation facilities. Recent advancements in laboratory based hard X-ray photoelectron spectrometers (HAXPES), such as the PHI Genesis, have opened new avenues for the routine examination of subsurface layers of technological devices.

The poster highlights recent advancements in combined XPS/HAXPES laboratory instrumentation. It showcases the merging of angle resolved XPS and HAXPES data to assess thickness and composition of thin film structures using StrataPHI analysis software. Recent applications demonstrate its effectiveness in investigating semiconductors, nanoelectronics, and energy storage devices. Benefits of the XPS/HAXPES laboratory instrument include non-destructive probing of concealed interfaces in addition to the ability to conduct compositional studies beyond the probing depth limitation of soft X-rays.

P4. Effects of binders on the electrochemical performance of hard carbon anode in sodium ion batteries

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Sodium-ion batteries (SIBs) have recently become a potential candidate for replacing lithium-ion batteries (LIBs) because of their cost-effective and the wide distribution of sodium on the earth's crust. A long the way of SIBs development, the recent full-battery configuration demonstrated by Faradion (UK) shows the competitive energy level as the lithium-ion battery using LiFePO₄. Further achieving the practical high-energy batteries requires critically the control of the high mass loading process besides the nature of active materials. By this way, binders play a vital role in affecting not only the mechanical properties but also the electrochemical performance of the electrodes. In

particular, the binder helps to maintain the good contact between electrode materials and the current collector, ensure the continuous electronic contact, and create the surface film to prevent the parasitic reaction during the cycling process. Here, we deeply explored the effect of five common binders such as: the water-based binders (CMC, PAA, PANa) and the NMP-based binders (PVDF, PVDF-HFP) on the electrochemical performance of the Na//HC half-cells. Among them, CMC-based electrode is outstanding which delivered a high capacity of 304.5 mAh/g and high-capacity retention (91.9% after 100 cycles). Meanwhile, PVDF-HFP is the worst binder with a poor capacity retention of 20,3% after 100 cycles. These results were confirmed by EIS analysis and XPS analysis. Although the surface composition after cycling is not much differentiated between the five binders, the evolution of SEI resistance in CMC was quickly stabilized, while it increased dramatically in PVDF-HFP binders after a few initial cycles. Such hard carbon with CMC binder strongly impacts the sodium full cell of HC/NMC with an initial capacity of 135.7 mAh/g and capacity retention of 62.7% after 100 cycles at 50 mA/g.

Keywords: sodium-ion batteries, hard carbon, binder, full cell, cycling performance.

P5. Do different XPS systems give the same result?

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Literature analyses indicate a growing use of XPS in multiple disciplines and increasing observations of faulty analysis. To ensure reliable results it is important that care paid to XPS data acquisition and analysis. Our laboratory has instruments from three vendors, and it may be necessary to collect data from the available instrument. Users increasingly export data for analysis using alternative software. It is useful to know the consistency of data collected on “identical” samples collected on different systems and analyzed using “native” and other software packages. This paper describes a “simple” test of data collection on three different systems and analysis using the native software for each system and analysis when naively “blindly” exported to a non-native analysis package. Copper foil was the test specimen for which survey and high-energy spectra were collected using Kratos Axis DLD Ultra, Thermo-Fischer NEXSA, and Phi Quantera spectrometers. Using both survey and narrow window data the analyses included: i) comparison of Cu 3p and Cu 2p peak ratios, ii) Cu 3p and Cu 2p atom ratios using native software and iii) when exported to CasaXPS. We also compared the wide scan spectra shapes to the ideal Cu spectra provided by the National Physical Laboratory to obtain an approximate instrument response function. Although simple in concept, these comparisons were found to be less than straightforward. High count rate survey spectra ratioed to the ideal spectra produced unexpected variations in the instrument response functions. These ratios made more sense when count rates were reduced by lowering the X-ray intensity of decreasing the pass energy. Cu 3p and Cu 2p peak ratios were determined using peak intensities after removal of an iterated Shirley background between 58.0 eV and 91.0 eV for Cu 3p and 920.0 eV to 970.0 eV for Cu 2p. Because of variations in the instrument transmission functions, raw peak ratios among the three spectrometers differed by > 2. However, native software analysis on each instrument produced similar amounts of Cu to roughly $\pm 5\%$. Note that sensitivity factors are more established for Cu 2p peaks than for Cu 3p peaks which may account for some variation. Naive transfer of data for analysis by non-native software was found to produce results significantly different expected. This can be due to sensitivity factors applied or complications related to the instrument response function. These issues can be corrected but require care and verification or incorrect results will result.

