Science for our Nation's Energy Future

Energy Frontier Research Centers
Energy Innovation Hubs
Computational Materials and Chemical Sciences Projects

Principal Investigators' Meeting

September 18-20, 26, 2023
Virtual Meeting

U.S. DEPARTMENT OF ENERGY | Office of Science

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2023 EFRC-HUB-CMS-CCS PI MEETING AGENDA

September 18th – September 20th, and September 26th, 2023
All sessions virtual, Posters in Gather Space

DAY 1 – September 18th, 2023: Plenary Session

12:00 pm – 4:00 pm Eastern

12:00 – 12:05 pm	**Welcome from the Office of Science** *Dr. Linda Horton, Associate Director for the Office of Basic Energy Sciences*
12:05 – 12:20 pm	**Remarks from the Undersecretary for Science and Innovation** *Dr. Geraldine Richmond, Undersecretary for Science and Innovation*
12:20 – 1:00 pm	**Current and Future Energy Landscape – U.S. Energy Information Administration** *Dr. Joseph DeCarolis, U.S. Energy Information Administration (EIA)*
1:00 – 1:45 pm	**Team Science Highlights from BES** *EFRC Leadership Team*
1:45 – 2:00 pm	**Break**
2:00 – 2:50 pm	**Connections Across DOE: Clean Energy Transitions** *Panelists* • Eric Hsieh, *Office of Electricity* • Diana Bauer, *EERE Advanced Materials and Manufacturing Technologies Office* • Sunita Satyapal, *EERE Hydrogen and Fuel Cell Technologies Office* • Jennifer Wilcox, *Office of Fossil Energy and Carbon Management* *Moderator: John Vetrano, Office of Basic Energy Sciences*
2:50 – 3:00 pm	**Break**
3:00 – 3:50 pm	**Creating Equitable and Inclusive Research Communities** *Panelists* • Noel Blackburn, *Brookhaven National Laboratory* • Natalie Holder, *SLAC National Accelerator Laboratory* • Charla Lambert, *Cold Spring Harbor Laboratory* • Melissa McDaniels, *University of Wisconsin–Madison* and *the Center for the Improvement of Mentored Experiences in Research (CIMER)* *Moderator: Julie Carruthers, Office of Scientific Workforce Diversity, Equity, and Inclusion*
3:50 – 4:00 pm	**Poetry of Science Art Contest Winners**
4:00 pm	**Adjourn**

DAY 2 – September 19th, 2023

Advanced Manufacturing; Hydrogen; Separations; Solar

12:00 pm - 4:30 pm Eastern

12:00 – 12:05 pm	**Sign-On, Day 2 Welcome** Introductions and Welcome
12:05 – 12:35 pm	**Lightning Talks Session I (Zoom)**
12:35 – 12:45 pm	**Break (10 minutes)**
12:45 – 2:15 pm	**Poster Session I (GatherTown)**
2:15 – 2:45 pm	**Lightning Talks Session II (Zoom)**
2:45 – 2:55 pm	**Break (10 minutes)**
2:55 – 4:25 pm	**Poster Session II (GatherTown)**
4:25 – 4:30 pm	**Lightning Talk Winners Announcement**
4:30 pm	**Adjourn**

DAY 3 – September 20th, 2023

Energy Storage; Environmental Management; Nuclear; Subsurface; Water

12:00 pm - 4:30 pm Eastern

12:00 – 12:05 pm	**Sign-On, Day 3 Welcome** Introductions and Welcome
12:05 – 12:35 pm	**Lightning Talks Session I (Zoom)**
12:35 – 12:45 pm	**Break (10 minutes)**
12:45 – 2:15 pm	**Poster Session I (GatherTown)**
2:15 – 2:45 pm	**Lightning Talks Session II (Zoom)**
2:45 – 2:55 pm	**Break (10 minutes)**
2:55 – 4:25 pm	**Poster Session II (GatherTown)**
4:25 – 4:30 pm	**Lightning Talk Winners Announcement**
4:30 pm	**Adjourn**

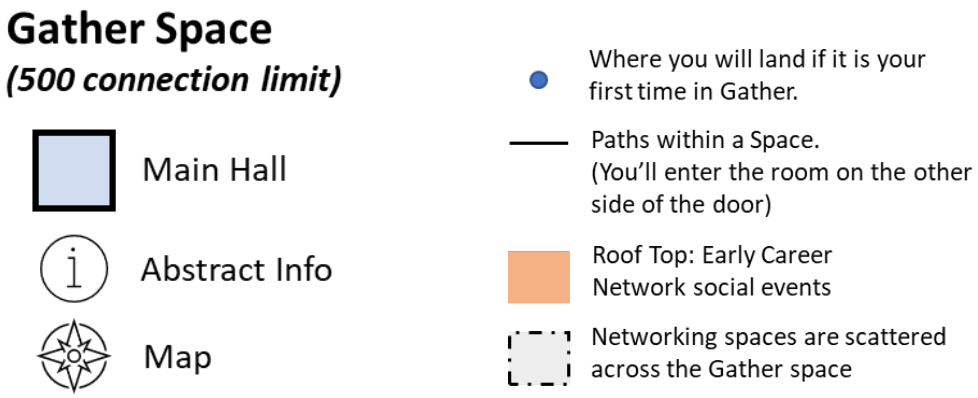
DAY 4 – September 26th, 2023

Microelectronics; QIS

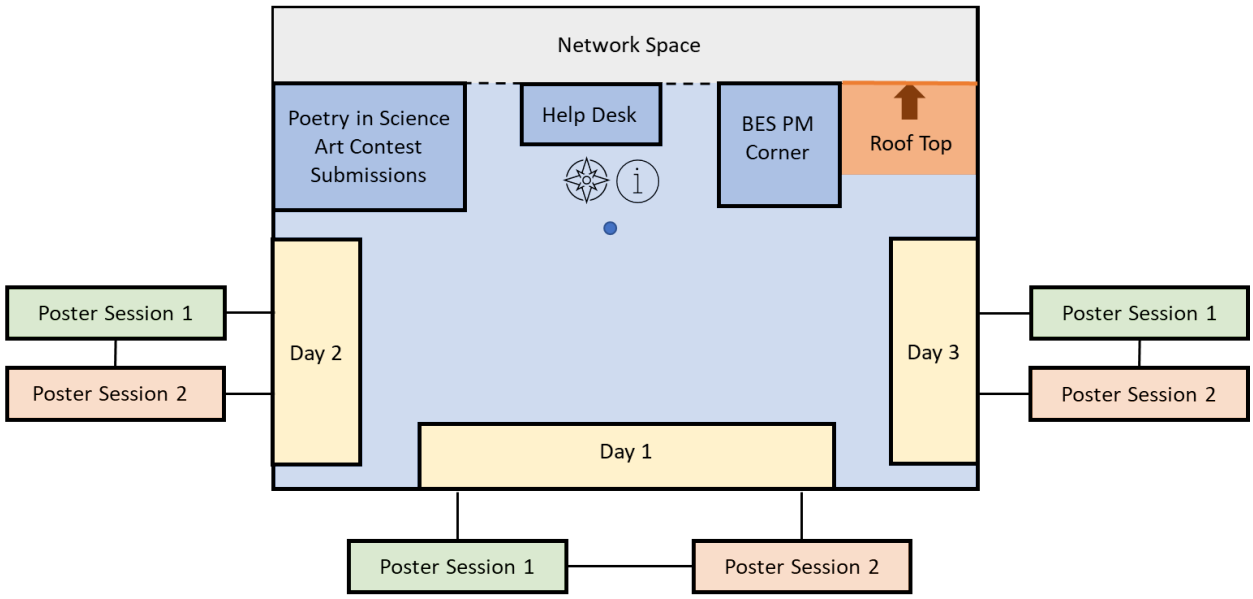
12:00 pm - 4:30 pm Eastern

12:00 – 12:05 pm	**Sign-On, Day 4 Welcome** Introductions and Welcome
12:05 – 12:35 pm	**Lightning Talks Session I (Zoom)**
12:35 – 12:45 pm	**Break (10 minutes)**
12:45 – 2:15 pm	**Poster Session I (GatherTown)**
2:15 – 2:45 pm	**Lightning Talks Session II (Zoom)**
2:45 – 2:55 pm	**Break (10 minutes)**
2:55 – 4:25 pm	**Poster Session II (GatherTown)**
4:25 – 4:30 pm	**Lightning Talk Winners Announcement**
4:30 pm	**Adjourn**

GATHER SPACE



Map to 2023 EFRC-Hub-CMS-CCS PI Meeting Gather Space



LIGHTNING TALK ABSTRACTS

Day 1 – September 19, 2023

Lightning Talk Session 1

I-T1-1: SPEEDING UP MATERIALS SYNTHESIS BY MANIPULATING TRANSPORT

[EFRC-GENESIS]

Gabrielle E. Kamm[1], John J. Ferrari[1], Guanglong Huang[2], Eymana Maria[2], Danrui Hu[1], Simon M. Vornholt[2], Rebecca D. McAuliffe[3], Gabriel M. Veith[3], Katsuyo S. Thornton[2], Wenhao Sun[2], Karena W. Chapman[1]
[1]Stony Brook University, [2]University of Michigan, [3]Oak Ridge National Laboratory.

Presenter: Gabrielle E. Kamm

Caption: (from left) Gabrielle Kamm, John Ferrari and Eymana Maria

The discovery of new materials is a bottleneck in the development of next generation technologies. While we can predict hypothetical materials (and their properties!), at present, we cannot predict how to synthesize them. GENESIS is exploring how materials synthesis is governed by the flow of energy and atoms across multiple length scales to enable predictive synthesis of next generation materials.

For solid state synthesis of inorganic materials, reactions evolve from the interfaces between reactive precursors, as atoms move within and between particles, on the nanometer- and micron-scales. Using in situ synchrotron scattering we interrogate these non-equilibrium synthesis pathways experimentally to resolve how the composition, structure, and heterogeneity of multi-component reactions evolve over multiple length scales, following a free-energy pathway.

For model reactions that produce $LiFeO_2$, anode material Li_4Ti5O_{12}, and $Fe_2[MoO_4]_3$, we explore how changing the reaction architecture and reactive interface density on the particle-scale impacts the relative reaction kinetics – this allows us to distinguish the how different transport pathways limit the reaction. We use in situ X-ray scattering and phase-field simulations to identify how reaction microstructure on different length scales can control reactivity in the solid state. Our results challenge the view that solid-state reactions are necessarily slow and represent a key step towards predicting and controlling these reactions. Optimizing architecture to decouple reaction temperature, time, and yield may allow reactions to be tailored to control phenomena such as transition-metal migration and inter-site mixing seen in layered transition metal oxides.

Affiliated poster: [I-S1-43] Speeding up materials synthesis by manipulating transport on different length scales.

I-T1-2: ACCELERATING ENERGY-EFFICIENT ADVANCED MATERIALS DISCOVERY: DEGRADABLE PDCPD THERMOSETS

[EFRC – REMAT]

Yasmeen S. AlFaraj[1], Anna A. Cramblitt[2], Somesh Mohapatra[1], Yuyan Wang[1], Avni Singhal[1], Benjamin Suslick[2], Jeff Moore[2], Nancy Sottos[2], Rafael Gomez-Bombarelli[1], Jeremiah A. Johnson[1]
[1]Massachusetts Institute of Technology, [2]University of Illinois Urbana-Champaign

Presenter: Yasmeen AlFaraj

Energy efficient manufacturing of thermoset polymers and polymer-based composites with realistic end-of-life strategies presents one of the most significant scientific and societal challenges for this century. The Regenerative Energy-Efficient Manufacturing of Thermoset Polymeric Materials (REMAT) EFRC seeks to develop materials, methods, and models to achieve regenerative thermoset polymers with generation-invariant thermomechanical properties over several lifecycles. These goals are pursued in tandem with thermos- and photochemical reaction-diffusion processes for regenerative thermoset polymers with fabrication rates, energy consumption, and materials performance that equal or exceed state-of-the-art additive manufacturing methods. The industrial thermoset polydicyclopentadiene (pDCPD) was identified as a suitable beachhead material for exploration: due to dicyclopentadiene's high energy density, an energy-efficient polymerization method called frontal ring opening metathesis polymerization (FROMP) can be employed to convert it into pDCPD. FROMP utilizes a small external energy input to form a self-propagating reaction "front" and harnesses subsequent exothermic reactions to cure the thermoset. Here, we highlight success in forming pDCPD using frontal polymerization techniques with materials properties comparable to its batch-cured counterpart. Additionally, the REMAT EFRC also focuses on establishing a small molecule cleavable comonomer additive library for the facile deconstruction and recycling/upcycling of pDCPD. Importantly, chemical materials design is an arduous process, and the inclusion of low loadings of small molecule additives can impact the thermomechanical properties of the bulk materials. Hence, we employ data-driven design methods and high-throughput experimental techniques to accelerate the identification of optimal additives resulting in chemically deconstructable thermosets without compromising the resultant thermomechanical properties.

Affiliated poster: [I-S1-47] Circularizing High-Performance FROMP Thermosets with Chemistry.

I-T1-3: A TANDEM PHOTOELECTROCHEMICAL/PHOTOTHERMAL SYSTEM FOR CO_2 REDUCTION TO LIQUID FUELS

[Hub – LiSA]

Aisulu Aitbekova,[1,2] Kyra Yap,[1,3] Matthew Salazar,[1,2] Magel Su,[1,2] Tobias A. Kistler,[1,4] Peter Agbo,[1,4] Theodor Agapie,[1,2] Jonas C. Peters,[1,2] Thomas F. Jaramillo,[1,3] Alexis T. Bell,[1,4] Harry A. Atwater[1,2]
[1]Liquid Sunlight Alliance, [2]California Institute of Technology, [3]SLAC National Accelerator Laboratory, [4]Lawrence Berkeley National Laboratory

Presenter: Aisulu Aitbekova

Tandem processes are a promising approach to generating solar fuels and chemicals. However, only a few studies report the successful operation of such integrated systems due to a requirement for simultaneous optimization of each step. We have developed a two-step photoelectrochemical-photothermal system to convert CO_2 into multicarbon (C4-C6 hydrocarbons) products**.** In the first step of the process, CO_2 reduces to ethylene in a photovoltaic-electrochemical cell. Here we focus on a catalyst design and show how functionalizing a copper electrode with molecular additives enhances ethylene formation and suppresses hydrogen generation via water splitting. The working hypothesis for this selectivity change is the inhibited proton transfer through hydrophobic molecular additive films, which results in diminished hydrogen evolution reaction rates. In the second step, ethylene oligomerizes into butenes inside a photothermal reactor with a selective solar absorber. Operating such a reactor under sunlight requires maximizing the light-to-heat conversion and minimizing heat losses. We accomplish this goal by simultaneously optimizing the absorber's optical properties, the reactor's geometry, and insulation. The heat required to run this reaction is provided by sunlight. The optimized reactor reaches a temperature of 100 °C (under 3-sun intensity), sufficient to drive an industrially relevant ethylene oligomerization reaction to convert ethylene into C4-C6 hydrocarbon solar fuels. Moreover, we demonstrate that this process works using a diluted ethylene stream gas directly produced by a CO_2 electrolysis cell that produces ethylene. Overall, we successfully perform solar-driven conversion of CO_2 into valuable products through combined catalyst design and reactor engineering.

Affiliated poster: [I-S1-12] Tandem Photoelectrochemical/ Photothermal System for CO_2 Reduction to Liquid Fuels

I-T1-4: CIRCULAR POLYOLEFINS: DESIGN PRINCIPLES FOR SUSTAINABLE PLASTICS

[EFRC – CPI]

Sam Marsden[1], María Ley-Flores[1], Riccardo Alessandri[1], Isabella Vettese[1], Zubin Kumar[1], Archit Chabbi[2], Juan J. de Pablo[1], Stuart J. Rowan[1]

[1]University of Chicago; [2]Rice University

Presenter: María Ley-Flores

Caption: (from upper left) Sam Marsden, Isabella Vettese, and Zubin Kumar (from lower left) María Ley-Flores, Riccardo Alessandri, and Archit Chabbi

Polyolefins represent the largest fraction of global plastic waste generation. Most current recycling efforts focus on mechanical recycling of plastics, often leading to performance losses and short usage cycles. In recent years, chemical recycling technologies have emerged as promising solutions to deconstruct polymers into small molecules for a wide range of applications, including as feedstocks for new polymers. However, due to the high energetic cost of breaking down the carbon-carbon σ bond, progress in polyolefin chemical recycling has been particularly challenging. To address this issue, our study explores a series of circular polyolefins featuring cleavable moieties based on ester, anhydride, and carbonate functionalities to incorporate controllable degradation through glycolysis or hydrolysis. The main objective of this work is to develop structure-property relationships that facilitate the prediction of properties for these candidate polymers. By integrating experimental studies and molecular simulations, we have identified trends in the thermophysical properties of these candidate polymers in the melt, which are relevant for processing applications, and compared them to the performance of commercial polyethylene. Furthermore, our findings have provided valuable insights into how these cleavable bonds impact the crystallinity of the polymers. This research contributes to advancing our understanding of circular polyolefins and their potential as sustainable alternatives to polyethylene, paving the way for more efficient and sustainable recycling practices.

Affiliated poster: [I-S1-15] Closing the Loop: Structure-Property Relationships in Circular Polyolefins

I-T1-5: CHARACTERIZATION OF BACTERIAL MICROCOMPARTMENT SHELL FORMATION THROUGH DENATURANT-INDUCED SHEET DISMANTLING AND SUBSEQUENT SHELL SELF-ASSEMBLY

[EFRC - CCBC]
Kyleigh Range[1], Joshua MacCready[2], Markus Sutter[1,2], Sam Snyder[3], Arinita Pramanik[1], Nina Ponomarenko[3], Daniel Ducat[2,4], Paul Ashby[1], Michaela TerAvest[4], Corie Ralston[1]
[1]Lawrence Berkeley National Laboratory; [2]Michigan State University; [3]Argonne National Laboratory

Presenter: Kyleigh Range

Caption: Kyleigh Range, an undergraduate at Cal State East Bay

Bacterial microcompartments (BMCs) are proteinaceous organelles, found amongst many prokaryotes, that play a vital role in enhancing enzyme efficiency through enzyme-substrate colocalization and preventing the accumulation of harmful organic compound intermediates in the cytosol. The bounding membrane of BMCs is a protein shell. One goal of the CCBC is to characterize the mechanisms by which the shell proteins assemble dynamically in vitro, and to design methods to control shell self-assembly from the constituents: hexamers (BMC-H), pentamers (BMC-P) and trimers (BMC-T). Many BMC-H avidly self-assemble into “sheets” upon purification. Here, we will describe the use of denaturant to dismantle hexamer sheets and reconstitute the resulting hexamer proteins with other shell constituents in controlled ratios to produce intact shells. The method enables the characterization of the kinetics of shell self-assembly, encapsulation of abiotic cargo, and will be used to design and construct various engineered shells with defined cargo for eventual applications in biofuel synthesis and carbon sequestration.

Affiliated poster: [I-S1-42] Bacterial microcompartment shell orthogonality in cells and *in vitro* assembly.

I-T1-6: AUTOMATING MODEL SPACE SELECTION IN FRAGMENT-BASED MULTIREFERENCE METHODS

[CCS – Exascale]

Matthew R. Hermes[1], Valay Agarawal[1], Laura Gagliardi[1], Cong Liu[2], Christopher Knight[2], Rishu Khurana[2]
[1]*University of Chicago;* [2]*Argonne National Laboratory*

Presenter: Matthew R. Hermes

Partitioning active spaces into products of localized subspaces, as in frameworks such as the localized active space (LAS), cluster mean-field, rank-one basis, or active-space decomposition, is a powerful tool for reducing the otherwise exponential computational cost of multireference electronic structure theory calculations. However, the methodological price that must be paid for such a framework is that over the top of the infamous "active space selection problem", a new "model space selection problem" is layered. Utilizing a complete product space basis reproduces the exponential cost explosion that one is trying to avoid, so a reduced basis should be used, but how can such a reduced basis be generated in a manner that is both sufficiently flexible to address all relevant regions of chemical space and sufficiently automated that problem-specific fine-tuning does not dominate all results? Here, we present the localized active space state interaction singles (LASSIS) method, which consists of a straightforward set of heuristics for automatic generation of model spaces spanning localized active spaces with varying numbers of orbitals and electrons and various spin multiplicities. We show *via* test calculations on a variety of systems that LASSIS robustly improves upon the quantitative accuracy of the single-product LASSCF reference state at low cost, with negligible additional user input.

Affiliated poster: [I-S1-33] Automating model space selection in fragment-based multireference methods.

I-T1-7: EFFICIENT AND SCALABLE, HIGH-FIDELITY GREEN'S FUNCTION THEORY OF ELECTRONIC STRUCTURE AND RESPONSE FUNCTIONS

[CCS – QuestC]

Peyton Cline[1], Mushir Thodika[1], Casey Eichstaedt , Dimitar Pashov[2], Brian Cunningham[3], Myrta Gruening[3], Mark van Schilfgaarde[1]

[1]National Renewable Energy Laboratory, [2]King's College London, [3]Queen's University Belfast

Presenter: Mark van Schilfgaarde

Traditionally electronic structure methods in chemistry focus on wave function methods for high fidelity and density-functional methods for scale. A less common approach, Green's function theory, is intermediate between the two. With suitable methodological developments, Green's function theory can approximate the fidelity of the best quantum chemical approaches while scaling much better with system size. Further, it provides a natural route to make response functions. Questaal is a Green's function based electronic structure method with a self-consistent low-order diagrammatic theory at its core, called the Quasiparticle Self-Consistent *GW* approximation. It is the self-consistency, combined with diagrams beyond the traditional *GW* approximation, that offer high fidelity. With next-generation machine architectures, such an approach offers a promising route to accurately describe both eigenstates and response functions for systems intermediate in size between small molecular systems and large, including photocatalysis, and optical properties of 1D and 2D materials. We present work in progress to evaluate the total energy much more efficiently than quantum-chemical methods, but with good accuracy, to reformulate the theory in real space; and to achieve optimal efficiency, present a new basis called Jigsaw Puzzle Orbitals, which are both compact like traditional Gaussian orbitals, but much more complete for a given hamiltonian rank. We demonstrate the fidelity achievable with optical excitations and response functions in a wide range of weakly and strongly correlated systems.

Affiliated poster: [I-S1-48] A sufficient diagrammatic theory for excitons in strongly correlated materials.

I-T1-8: STABLE SOLID MOLECULAR HYDROGEN ABOVE 900K FROM A MACHINE-LEARNED POTENTIAL TRAINED WITH DIFFUSION QUANTUM MONTE CARLO

[CMS – QMC-HAMM]

Hongwei Niu,[1] Yubo Yang,[2,3] Scott Jensen,[3] Markus Holzmann,[4] Carlo Pierleoni,[5] and David M. Ceperley[3]
[1]Harbin Institute of Technology; [2]Flatiron Institute; [3]University of Illinois Urbana-Champaign; [4]University Grenoble Alpes; [5]University of L'Aquila

Presenter: Scott Jensen

We survey the phase diagram of high-pressure molecular hydrogen with path integral molecular dynamics using a machine-learned interatomic potential trained with Quantum Monte Carlo forces and energies. Besides the HCP and C2/c-24 phases, we find two new stable phases both with molecular centers in the Fmmm-4 structure, separated by a molecular orientation transition with temperature. The high temperature isotropic Fmmm-4 phase has a reentrant melting line with a maximum at higher temperature (1450K at 150GPa) than previously estimated and crosses the liquid-liquid transition line around 1200K and 200GPa.

Affiliated poster: [I-S1-02] Stable solid molecular hydrogen above 900K from a machine-learned potential trained with diffusion Monte Carlo.

I-T1-9: ELECTROCATALYTIC PROPERTIES OF PULSED LASER-DEPOSITED TITANIUM DIOXIDE AND TITANIUM OXYNITRIDE THIN FILMS GROWN ON PHOTO-ADSORBING SINGLE CRYSTAL SUBSTRATES WITH DIFFERENT ORIENTATIONS

[EFRC – CEDARS]
Sheila Cherono[1], Ikenna Chris-Okoro[1], Swapnil Shankar Nalawade[1], Austin Reese[2], Brady Bruno[2], Jacob Som[2], R. Soyoung Kim[3], Johannes Mahl[3], Junko Yano[3], Ethan Crumlin[3], Jin Suntivich[2], Tanja Cuk[4], Bishnu Bastakoti[1], Y.Yun[1], Shyam Aravamudhan[1], Dhananjay Kumar[1]
[1]North Carolina Agricultural and Technical State University; [2]Cornell University; [3]Lawrence Berkeley National Laboratory; [4]University of Colorado at Boulder

Presenter: Sheila Cherono

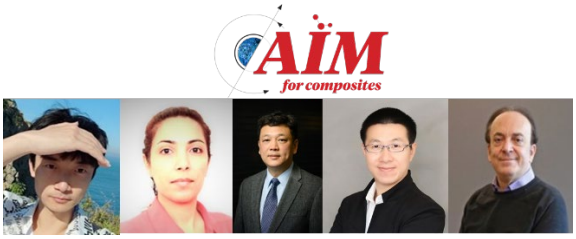
Caption: Sheilah Cherono, PhD Student, CEDARS, NCAT

This research focuses on the growth of (photo)electrocatalytic titanium dioxide (TiO_2) and oxynitride (TiON) films epitaxially grown on single crystal substrates at different orientations. The films were grown using pulsed laser deposition (PLD), which has many advantages, including fast response time, energetic evaporants, and congruent evaporation. These advantages were used to determine the optimal growth conditions, which, when combined with careful substrate selection, led to oxide and oxynitride films with well-defined strain and well-controlled vacancies. Furthermore, since PLD can transfer the composition of the target having elements with vapor pressures as different as 10^6 from each other, it can enable the incorporation of non-Ti cations into TiO_2 and TiON (photo)electrocatalytic films. Soft X-ray absorption spectroscopy at the Ti L-edge, O K-edge, and N K-edge was collected on the TiON samples to obtain information regarding the electronic structure. We use these controls afforded by PLD to tailor the band edges of semiconductors to evaluate the creation and evolution of water-splitting intermediates as a function of potential and/or photo triggers. We use this capability to examine the hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) mechanisms on oxide and oxynitride catalysts.

Affiliated poster: [I-S1-05, I-S1-21, I-S1-35] Stimulated Absorption and Emission from Diverse TiO_2 Crystal Facets during the Oxygen Evolution Reaction.

I-T1-10: PREDICTING TRANSIENT RESPONSE OF COMPOSITES SUBJECT TO DYNAMIC LOADING USING DEEP NEURAL OPERATOR LEARNING

[EFRC – AIM for Composites]
Minglei Lu[1], Elham Kiyani[2], Gang Li[1], Zhen Li[1], George Karniadakis[2].
[1]Clemson University; [2]Brown University



Presenter: Zhen Li

Caption: AIM Team

Additive manufacturing allows fabrication of composites with complex 3D structures directly from computer-aided designs. The mechanical properties of these composites, especially response to dynamic loading, highly depend on their 3D structures. In general, for each specified 3D structural design, it could take hours or days to perform either finite element analysis (FEA) or experiments to test the mechanical response of composites to a given dynamic load. To accelerate the physics-based prediction of composite properties for various structural designs, we employ a deep neural operator (DNO) to learn the transient response of composites under dynamic loading as surrogate of physics-based FEA models. Results demonstrate that the trained DNO can act as surrogate of physics-based FEA to predict transient mechanical response in terms of reaction force and stress distribution of the composites to various strain loads, which can reduce the computational cost from hours of FEA to a fraction of a second at an accuracy of 98%. The learned neural operator is able to provide extended prediction of the composites subject to new strain loading patterns at a reasonably well accuracy. Such superfast and accurate prediction of mechanical properties of composites could significantly accelerate the material design processes for desired mechanical properties. Furthermore, we will showcase a physics-informed machine learning framework augmented with symbolic regression for discovery of new governing equations of composites from data, where the equations have explicit mathematical forms that can be easily understood and interpreted by humans.

Affiliated poster: [I-S1-24] Predicting transient response of composites subject to dynamic loading using deep neural operator learning.

I-T1-11: MECHANISTIC INSIGHTS OF RUO2-MEDIATED BUTENE ELECTROSYNTHESIS

[EFRC– CD4DC]

Joseph Hupp,[1] Chibueze V Amanchukwu,[2] Anna Wuttig,[2] Ksenija D Glusac[3], Laura Gagliardi[2], Gautam Stroscio,[2] Arturo Sauza de la Vega,[2] Hannah Fejzic,[2] Reginaldo J. Gomes,[2] Špela Kunstelj,[2] Biki Behera[3]
[1]*Northwestern University;* [2]*The University of Chicago;* [3]*Unviersity of Illinois at Chicago*

Presenter: Špela Kunstelj

The valorization of biogenic carbon sources provides an alternative and sustainable synthetic route to access petroleum-derived feedstocks. Non-Kolbe oxidation of valeric acid, sourced from a hydrolysis product of cellulose, enables the electrosynthesis of butene, currently accessed as a by-product of petroleum refining. However, the key scientific challenge lies in tuning the selectivity of non-Kolbe electrolysis as numerous products are accessible at extreme oxidative potentials, including the competitive oxygen evolution reaction (OER), i.e., the oxidation of the solvent. Thus, the practical utilization of non-Kolbe reactions for selective butene electrosynthesis requires a mechanistic understanding of the branchpoints that limit butene Faradaic efficiencies. This work studies the reaction conditions and mechanisms involved that enable higher Faradaic efficiencies for butene while limiting OER, using the current state-of-the-art electrode material for butene electrosynthesis, RuO2.

Affiliated poster: [I-S1-17] Study and Development of MOF-Coated Electrodes for Electrocatalysis.

I-T1-12: ENHANCED METHANOL PRODUCTION FROM PHOTOELECTROCHEMICAL CO2 REDUCTION VIA INTERFACE AND MICROENVIRONMENT TAILORING

[Solar Hub – CHASE]

Bo Shang[1], Fengyi Zhao[2], Yuanzuo Gao[1], Jing Li[1], Conor L. Rooney[1], Colton Sheehan[3], Oliver Leitner[1], Langqiu Xiao[3], Thomas E. Mallouk[3], Tianquan Lian[2], Hailiang Wang[1]
[1]Yale University; [2]Emory University; [3]University of Pennsylvania

Presenter: Hailiang Wang

Recent research has shown that immobilizing cobalt phthalocyanine (CoPc) molecules onto semiconductor results in conversion of CO_2 into CO and methanol. In our prior work, we explored a planar SI-T1-iO_2 substrate modified with a molecular linker and a hybrid catalyst of graphene oxide/CoPc. Although this photocathode demonstrated the ability to achieve a 6-electron reduction of CO_2 to methanol with a faradaic efficiency (FE) of 8%, the current density and stability were limited, likely due to the weak interaction between Si and GO/CoPc. The crucial interface and microenvironment between the semiconductor light absorber and the catalyst have not been adequately investigated and optimized. Several challenges hinder the integration of the catalyst on Si, including stabilizing the catalyst layer on the Si surface through linking or assembly, designing an efficient catalyst loading method for optimal light transmission, passivating the native Si surface to prevent competing hydrogen evolution reactions, and creating a hydrophobic local environment to tailor the selectivity towards methanol. In this work, we present a novel approach by designing a silicon micropillars array structure coated with a super-hydrophobic carbon fluoride layer for CO_2 reduction to methanol. The results show a remarkable methanol faradaic efficiency of up to 20% and a partial current of 3.4 mA cm^{-2}, which is 17 times higher than the planar Si without the microstructures. Our study opens a new route of interface and microenvironment tailoring in improving the efficiency of CO_2 photoelectrocatalytic reduction processes, and sets the benchmark for efficient photoelectrocatalytic CO_2 reduction to liquid fuels.

Affiliated poster: [I-S1-46] CO_2 Reduction to Methanol on Silicon Photoelectrodes via Molecular Catalysis.

I-T1-13: INTERACTIVE DYNAMIC ENERGY ANALYSIS (IDEA): A NEW TOOL FOR PREDICTING CATALYTIC REACTION PATHWAYS THROUGH JOINT DENSITY-FUNCTIONAL THEORY

[EFRC – CABES]
Colin R. Bundschu, Mahdi Ahmadi, Juan Felipe Méndez-Valderrama, Héctor D. Abruña, Tomás A. Arias (Cornell University)

Presenter: Colin Bundschu

We introduce a new tool for the ab initio study of reaction pathways called Interactive Dynamic Energy Analysis (IDEA), and we apply this novel approach to the study of the alkaline oxygen reduction reaction (ORR) on spinel materials. This reaction holds significant promise for reducing or even eliminating the need for costly platinum group metals (PGMs) in alkaline fuel cells, a development that could be pivotal in advancing this technology. Understanding the underlying mechanism is key to making further progress. Through our first-principles IDEA analysis, we have been able to challenge the traditionally assumed pathway for the reaction. We provide convincing evidence that the previously accepted pathway is incorrect and reveal the true reaction pathway on Co_3O_4. Finally, the IDEA tool enables us to rapidly comprehend how to optimize the resulting reaction by introducing epitaxial strain.

Affiliated Poster: [I-S1-20] Interactive Dynamic Energy Analysis (IDEA): A New Tool for Predicting Catalytic Reaction Pathways through Joint Density-Functional Theory.

Lightning Talk Session 2

I-T2-1: HIGH-THROUGHPUT POTENTIAL-DEPENDENT MODELING OF THE ELECTROCHEMICAL NITROGEN REDUCTION REACTION

[CCS – BEAST]

Cooper Tezak,[1] Nicholas Singstock,[1] Abdulaziz Alherz,[1] Derek Vigil-Fowler,[2] Christopher Sutton,[3] Ravishankar Sundararaman,[4] Charles Musgrave.[1]

[1]Univeristy of Colorado Boulder, [2]National Renewable Energy Laboratory, [3]University of Couth Carolina, [4]Rensselaer Polytechnic Institute.

Caption: Cooper Tezak

Presenter: Cooper Tezak

We showcase the capability enabled by the BEAST CCS collaboration for high-throughput first-principles electrochemistry, including accurate solvation and explicit bias dependence, using the nitrogen reduction reaction (NRR), a promising route to carbon-free ammonia synthesis. Current electrocatalysts do not catalyze NRR at practical temperatures. The failure to design effective NRR catalysts is partly due to the limited understanding of the NRR mechanism and poor description of the effects of bias and the solvent on the reaction energies. We modeled 30 transition metal catalyst surfaces using grand-canonical DFT to identify and understand the bias dependence of the NRR rate limiting steps. We use Φ_{max}, a grand canonical analogue to the thermodynamic screening descriptor G_{max}, which approximates the apparent activation barrier of a reaction network, to quantify catalyst activity accounting for applied bias. This approach yields a thermodynamic activity "volcano" diagram that qualitatively differs from those predicted by models that use simplified proton-coupled electron transfer mechanisms to approximate the effect of the applied potential. We find that NH3 desorption limits NRR activity for materials at the top of the volcano and truncates its peak at increasingly reducing potentials. This approach is transferable to other materials and electrocatalysis systems where both electrochemical and chemical steps are modeled under an applied bias. We used this approach to generate a dataset of >500 metal-adsorbate combinations to enable the machine learned prediction of electrocatalyst properties, including with beyond-DFT methods in ongoing work in the BEAST collaboration.

Affiliated poster: [I-S2-47] High-Throughput Potential-Dependent Modeling of the Electrochemical Nitrogen Reduction Reaction.

I-T2-2: AUTOMATED GENERATION OF MICROKINETICS FOR HETEROGENEOUSLY CATALYZED REACTIONS CONSIDERING CORRELATED UNCERTAINTIES

[CCS – ECC]

Bjarne Kreitz, C. Franklin Goldsmith
Brown University

Presenter: Bjarne Kreitz

We showcase the capability enabled by the BEAST CCS collaboration for high-throughput first-principles electrochemistry, including accurate solvation and explicit bias dependence, using the nitrogen reduction reaction (NRR), a promising route to carbon-free ammonia synthesis. Current electrocatalysts do not catalyze NRR at practical temperatures. The failure to design effective NRR catalysts is partly due to the limited understanding of the NRR mechanism and poor description of the effects of bias and the solvent on the reaction energies. We modeled 30 transition metal catalyst surfaces using grand-canonical DFT to identify and understand the bias dependence of the NRR rate limiting steps. We use Φ_{max}, a grand canonical analogue to the thermodynamic screening descriptor G_{max}, which approximates the apparent activation barrier of a reaction network, to quantify catalyst activity accounting for applied bias. This approach yields a thermodynamic activity "volcano" diagram that qualitatively differs from those predicted by models that use simplified proton-coupled electron transfer mechanisms to approximate the effect of the applied potential. We find that NH3 desorption limits NRR activity for materials at the top of the volcano and truncates its peak at increasingly reducing potentials. This approach is transferable to other materials and electrocatalysis systems where both electrochemical and chemical steps are modeled under an applied bias. We used this approach to generate a dataset of >500 metal-adsorbate combinations to enable the machine learned prediction of electrocatalyst properties, including with beyond-DFT methods in ongoing work in the BEAST collaboration.

Affiliated poster: [I-S2-41] Automated Generation of Microkinetics for Heterogeneously Catalyzed Reactions Considering Correlated Uncertainties.

I-T2-3: FUNCTIONALIZED IONIC LIQUID ELECTROLYTE CONTROLS CO_2 ELECTROREDUCTION PRODUCT SELECTIVITIES AND OVERPOTENTIALS OVER TRANSITION METALS

[EFRC – 4C]
Saudagar Dongare[1], Oguz K. Coskun[1], Louise Berben[2], Manu Gautam[3], Bijandra Kumar[4], Joshua Spurgeon[3], Robert Sacci[5], Anastassia N. Alexandrova[6], and Burcu Gurkan[1]
[1]Case Western Reserve University; [2]University of California, Davis; [3]University of Louisville; [4]Elizabeth City State University; [5]Oak Ridge National Laboratory; [6] University of California, Los Angeles

Presenter: Saudagar Dongare

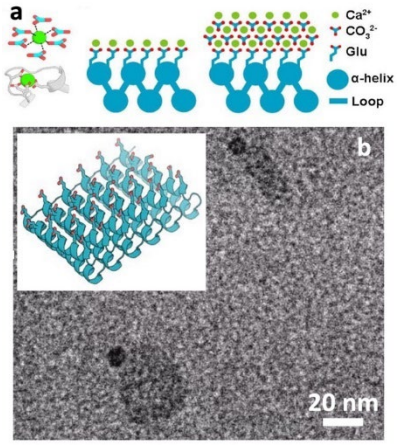
Caption: (From upper left) Saudagar Dongare, Oguz K. Coskun, Manu Gautam; (From middle left) Louise Berben, Bijandra Kumar, Joshua Spurgeon; (From lower left), Robert Sacci, Anastassia N. Alexandrova, and Burcu Gurkan

Electrochemical CO_2 reduction (ECO_2R) is an attractive technology platform to convert CO_2, a greenhouse gas, to fuels and other commodity chemicals considering its modularity and mild operational conditions. Despite the wide research efforts in the development of selective and stable catalysts in aqueous electrolytes, ECO_2R remains challenging due to competition from the hydrogen evolution reaction and high overpotentials needed to drive the conversion reaction. Novel electrolytes such as those based on ionic liquids (ILs) have the potential to synergize reactive carbon capture and conversion due to their tunability in CO_2 solubility, selectivity, and reduction potentials. However, the electrolyte effects on ECO_2R, specifically in the presence of functionalized ILs, is not well understood. In particular, the role of the common imidazolium cation has been a matter of debate. Here, we present the interfacial liquid behavior and the specific surface species as examined by in-situ surface enhanced Raman spectroscopy (SERS), electron paramagnetic resonance (*EPR*), static and dynamic electrochemical impedance spectroscopy (dEIS), differential electrochemical mass spectrometry (DEMS), and Density Functional Theory (DFT) calculations on Ag, with ongoing working including Cu electrode. A systematic study of structures was synthesized to probe the role of the cation, anion, and the generated carbamate and carboxylate species from absorption of CO_2 by the ILs on ECO_2R. A superior selectivity for CO_2-to-CO reaction on Ag at lowered overpotentials was achieved compared to non-aqueous electrolytes and unfunctionalized ILs. C_{2+} products including C_4 were possible with Cu. Not only imidazolium but also the pyrrole anion were found to co-catalyze ECO_2R by enabling high concentrations of CO_2 at the interface and stabilizing reaction intermediates, thus enabling a mechanism for tuning selectivity and overpotentials.

Affiliated poster: [I-S2-01] Functionalized Ionic Liquid Electrolyte Controls CO_2 Electroreduction Product Selectivities and Overpotentials Over Transition Metals

I-T2-4: DIRECTING POLYMORPH SPECIFIC CALCIUM CARBONATE FORMATION WITH DE NOVO DESIGNED PROTEIN TEMPLATES

[EFRC – CSSAS]
Fatima Davila-Hernandez[1]
[1]*University of Washington*



Presenter: Fatima Davila-Hernandez

Caption: a - Schematic illustrating concept for a flat helical repeat protein designed de novo to template the organization of Ca^{2+} and CO_3^{2-} ions into a crystalline motif in order to drive crystal nucleation, b - Frame from an in situ TEM movie showing the nucleation of calcite (dark gray) adjacent to supramolecular assemblies (light gray) of Ca^{2+} ions and designed proteins having the structure shown in the inset.

Organisms generate biominerals with unique physical properties by controlling the nucleation, growth, and assembly of inorganic crystals. An ability to achieve similar outcomes synthetically would enable the construction of complex hybrid materials and provide a potential strategy for carbon dioxide reduction technologies. The sequences of native biomineral-associated proteins and their effects on mineralization are well characterized for some systems, but the three-dimensional structures of the protein-mineral interfaces that enable such exquisite control are largely unknown. We hypothesized that heterogeneous nucleation of calcium carbonate could be achieved by a structured flat molecular template that pre-organizes calcium ions on its surface. To test this hypothesis, we designed helical repeat proteins displaying regularly spaced carboxylate arrays on their surfaces and found that both protein monomers and protein-Ca^{2+} supramolecular assemblies directly nucleate nano-calcite with non-natural (110) or (202) faces. The nanocrystals then assemble by oriented attachment into calcite mesocrystals. In contrast, in the absence of the designed proteins, vaterite forms first and grows uncontrollably to micron size, before dissolving as calcite crystals with the commonly expressed faces subsequently nucleate and grow. We find further that nanocrystal size can be tuned by varying the length of the designed protein templates, while variations in template surface chemistry impact the resulting crystal polymorph. Thus, bio-mineralization can be programmed using *de novo* protein design, providing a route to next-generation hybrid materials.

Affiliated poster: [I-S2-26] Directing Polymorph Specific Calcium Carbonate Formation With De Novo Designed Protein Templates.

I-T2-5: COMBINING X-RAY SCATTERING AND OPTICAL SPECTROSCOPY TO CHARACTERIZE ION AND SOLVENT INTERCALATION IN Π-CONJUGATED POLYMERS AND THEIR IMPACT ON OPTOELECTRONIC FUNCTION

[EFRC – SPECS]
Spencer Yeager[1]
[1]*University of Arizona*

Presenter: Spencer Yeager

Conjugated (semiconducting) polymers (CPs) show promise as materials for photocathodes as the chemical and physical properties can be tailored to selectively drive fuel-forming reactions such as H_2 evolution. The nanometer-scale chemio-physical behavior of donor-acceptor heterojunctions in contact with an electrolyte is still a significant knowledge gap that must be addressed in order to carry out efficient photoelectrochemical processes that lead to fuels. In this work we investigate a proof-of-concept all-polymer photocathode with a platinum co-catalyst electrodeposited to facilitate proton reduction. We investigate the catalytic function, durability, and transient dynamics of this material system in contact with aqueous electrolytes of varying pH to establish a fundamental understanding of how electrolyte penetration into the junction forms "interphase" regions, impacts charge generation, transport, recombination, and catalytic activity. Operando Raman scattering experiments provided much needed chemical insights via peak shifts whilst transient absorption spectroscopy and time-resolved microwave conductivity provide insight into associated changes in optoelectronic function. We find that this blend of polymers is suitable for photo-induced generation of H_2 from H_2O, with no added energy source, other than AM1.5 solar illumination, with current densities and quantified rates of H_2 formation that suggest that optimized versions of these platforms could eventually compete with some well-established inorganic (hard) material platforms. Future work will include efforts to understand the molecular scale issues that limit both efficiency and durability, and quantification of yields of H_2 and introduction of non-platinum cocatalysts (selectively) to lower activation energies in water splitting reaction and reduce rates of competitive side reactions.

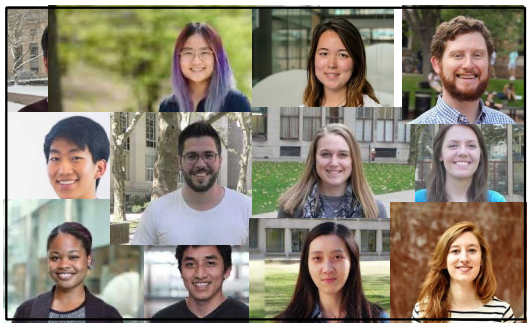
Affiliated poster: [I-S2-45] Correlating electronic disorder to structural dynamics in conjugated polymers.

I-T2-6: PHOTOCATALYSIS IN A NEW LIGHT: A BIOHYBRID APPROACH FOR IMPROVED REACTIVITY WITH TUNABLE LOW-ENERGY LIGHT EXCITATION

[EFRC – BioLEC]

Paul T. Cesana[1], Beryl X. Li[2], Claire G. Page[2,3], Samuel G. Shepard[4], Stephen I. Ting[2,5], Dvir Harris[1], Stephanie M. Hart[1], Courtney M. Olson[1], Megan A. Emmanuel[2], Jesus I. Martinez Alvarado[2], Minjung Son[1], Talia J. Steiman[2], Felix N. Castellano[4], Abigail G. Doyle[2,5], Todd K. Hyster[2,3], David W. C. MacMillan[2], Gabriela S. Schlau-Cohen[1]

[1]Massachusetts Institute of Technology; [2]Princeton University; [3]Cornell University; [4]North Carolina State University; [5]University of California, Los Angeles



Presenter: Paul T. Cesana

Caption: Student and post-doc authors of this work, left to right, as listed in author list.

Photocatalysts convert light into chemical reactivity, yet are light-limited and often require blue-to-UV excitation. In photosynthesis, light capture and reactivity have been optimized by separation into distinct sites. Inspired by this molecular architecture, we synthesized biohybrid photocatalysts by covalent attachment of a light-havesting component to a reactive component. Spectroscopic investigation using pump—probe spectroscopy and fluorescence lifetime measurements found that absorbed energy was efficiently transferred to the reactive component, and the utility of the biohybrids was demonstrated via an increase in product yields using test reactions. This generalizable biohybrid strategy has been broadly demonstrated with photosynthetic proteins or dyes as the light-harvesting component and transition metal photocatalysts or photoenzymes as the reactive component, and it can be readily implemented in future applications.

Affiliated poster: [I-S2-12] Photocatalysis in a New Light: A Biohybrid Approach for Improved Reactivity with Tunable Low-Energy Light Excitation.

I-T2-7: A MULTISCALE COMPUTATIONAL FRAMEWORK FOR BIOMOLECULAR ENERGY TRANSDUCTION: FROM ELECTRONS TO THE MESOSCALE

[CCS – CMSET]

[1]Scott Kaiser, [1]Sahithya Sridharan Iyer, [1]Daniel Beckett, [1]Siva K. Dasetty, [3]Tomasz Skora, [2]Garnet K. L. Chan, [3]Tamara Bidone, [1]Andrew Ferguson, [1]Gregory A. Voth
[1]University of Chicago, [2]California Institute of Technology, [3]University of Utah

Presenter: Scott Kaiser

Caption: (left to right) Scott Kaiser, Sahithya Sridharan Iyer

Many of the most challenging energy transduction processes to model accurately involve molecular systems that couple degrees of freedom over a wide range of time and length scales. Striking examples involve chemical reactions where the catalysis is activated by localized electronic and atomic factors that are themselves coupled to the slow macromolecular dynamics taking place over much larger distances and timescales, e.g., the turnover of microtubules involving large conformational rearrangements, which is controlled by the GTP hydrolysis of β-tubulin. We develop exascale-ready software capable of bridging varied length and time scales. Leveraging modern advances in GPU technology, the Chan group has optimized a multigrid DFT implementation which improves upon the CP2K QM/MM method by a factor of two. The approach is implemented in a full QM/MM workflow with PySCF and LAMMPS, and is employed in QM/MM studies of GTP hydrolysis in microtubules. Connecting to the all-atom scale, the Ferguson group is addressing the fundamental challenge of slow relaxation dynamics in microtubules using a neural network-based equation free approach, which allows an all-atom configuration to 'leap forward' in time. The method is implemented to extrapolate 4 μs of all-atom data for a 40 million atom microtubule system collected by the Voth group to longer time and length scales, allowing for the exploration of converged equilibrium properties. To access even longer length and time scales, a granular space coarse graining method was developed and implemented with GPU acceleration in LAMMPS, achieving a significant performance increase over a CPU implementation.

Affiliated poster: [I-S2-25, I-S2-54] A Multiscale Computational Framework for Biomolecular Energy Transduction: From Electrons to the Mesoscale.

I-T2-8: XYLAN PLAYS A CRITICAL ROLE IN PATTERNED SECONDARY CELL WALL FORMATION

[EFRC – CLSF]
Sarah A. Pfaff, Edward R. Wagner, Ying Gu, Daniel J. Cosgrove
The Pennsylvania State University

Caption: Sarah A. Pfaff

Presenter: Sarah A. Pfaff

Numerous cellular processes act in a coordinated manner to deposit patterned secondary cell walls (SCWs). Arabidopsis protoplasts, transiently transformed with *VND7* overexpression, were used to investigate the role of xylan in patterned SCW formation. Cellulose and xylan patterns were examined with fluorescence labeling and confocal microscopy. Protoplasts with shortened xylan backbones (*irx9-2*, *irx14*, and *endo*-1,4-β-xylanase-treated) produced distorted SCWs bands with coincident cellulose and xylan patterning. Protoplasts isolated from the mutant *esk1*, where cellulose-xylan interactions are limited[1], also produced distorted SCWs but, uniquely, the cellulose and xylan patterns did not coincide.

Our research shows that SCW patterning in the regenerated wall is disrupted by altered xylan structure. We propose that a cellulose-xylan network is established during early wall synthesis which acts as a scaffold to direct subsequent microtubule-independent cellulose deposition[2]. Short-chain xylans do not properly tether cellulose microfibrils[3], which results in polymer drift, yielding an indistinct scaffold that is reinforced in later synthesis. When cellulose and xylan do not interact, their patterns remain misaligned during SCW formation. We are continuing to investigate whether the SCW influences cytoskeletal remodeling, which would affect the sites of cellulose synthase and xylan delivery later in wall development. Finally, we present SCW-regenerating protoplasts as a novel platform to research the deposition of xylem vessel-type SCWs.

Affiliated poster: [I-S2-07] Xylan Plays a Critical Role in Patterned Secondary Cell Wall Formation.

I-T2-9: CATALYTIC CHEMICAL RECYCLING OF POST-CONSUMER POLYETHYLENE

[EFRC – iCOUP]

Shilin Cui[1], Alejandra Arroyave[2], Andrew L. Kocen[1], Jaqueline C. Lopez[1], Anne M. LaPointe[1], Massimiliano Delferro[2], Geoffrey W. Coates[1]
[1]Cornell University; [2]Argonne National Laboratory

Presenter: Shilin Cui

We report a new approach to transform post-consumer polyethylene into a new polymer with chemical recyclability, while retaining its original material properties. The incorporation of cleavable linkages into polyolefin backbones allows the polymer to be depolymerized into telechelic segments capable of repolymerization to achieve chemical recyclability.

In our initial studies, we developed catalysts for the copolymerization of propylene and butadiene to incorporate internal C=C bonds into a polypropylene backbone and subsequently used catalytic metathesis and transesterification to transform the copolymer into a chemically recyclable ester-linked polypropylene. In the case of post-consumer high-density polyethylene (HDPE), catalytic dehydrogenation using an Ir-POCOP catalyst yielded the HDPE with different degrees of backbone unsaturation at varied reaction time. Cross-metathesis converted the partially unsaturated HDPE into telechelic macromonomers. The direct repolymerization of these macromonomers by transesterification resulted in a brittle material due to the low weight-average molecular weight. Partial aminolysis with trifunctional linkers increased the overall functionality, and subsequent transesterification generated a polymer with comparable thermal and mechanical properties to the starting post-consumer HDPE. Depolymerization of the repolymerized material was catalyzed by an organic base to regenerate the telechelic macromonomers. A follow-up study used a “Trojan Horse” approach to induce masked unsaturation into a polyethylene chain by copolymerization of ethylene and a functional oxa-norbornadiene monomer. The partially unsaturated PE was generated by a retro-Diels-Alder reaction at elevated temperature.

Affiliated poster: [I-S2-33] Catalytic Chemical Recycling of Post-Consumer Polyethylene.

I-T2-10: EXPLORING SYMMETRY BREAKING AND STRUCTURAL DIMENSIONALITY ENGINEERING IN HOIPS: UNRAVELING EMERGENT SPIN, ELECTRONIC, AND OPTICAL PROPERTIES

[EFRC – CHOISE]
Yi Xie,[1] Jack Morgenstein,[1] Gabrielle Koknat,[1] Nicholas J. Weadock,[2] Junxiang Zhang,[2] Heshan Samuditha Weerasinghe Hewa Walpitage,[3] Peter C. Sercel,[4] Alan Phillips,[5] Naidel A. M. S. Caturello,[6] John Colton,[7] Xiaoping Wang,[8] Ruyi Song,[1] Benjamin G. Bobay,[1] Jeffrey Blackburn,[5] Matthew C. Beard,[5] Zeev Valy Vardeny,[3] Seth Marder,[2] Michael F Toney,[2] Volker Blum,[1] and David B. Mitzi[1]
[1]Duke University; [2]University of Colorado Boulder; [3]University of Utah; [4]Center for Hybrid Organic Inorganic Semiconductors for Energy; [5]National Renewable Energy Laboratory; [6]Federal University of ABC; [7]Brigham Young University; [8]Oak Ridge National Laboratory

Presenter: Yi Xie

Hybrid organic-inorganic perovskite (HOIP) semiconductors enable remarkable compositional, structural, and dimensional versatility owing to the broad flexibility in selecting single or mixed organic cations within the HOIP framework. Consequently, novel structural dimensionality, varying degrees of distortions and symmetry breaking, and associated impacts on optoelectronic properties can be targeted. One of our current works demonstrates a chiral-chiral mixed-cation system wherein a controlled small amount (<10 %) of dopant chiral cation can be doped into a chiral 2D HOIP system to modulate the structural symmetry from a higher symmetry (*C*2) to the lowest symmetry state (*P*1) and impact the spin-related, chiroptical, and thermal properties. However, an understanding of the microscopic mechanisms behind the structural distortions and symmetry breaking has remained elusive. Temperature-dependent neutron diffraction was therefore performed for a new PbI_4^{2-}-based 2D HOIP, wherein a thermally-induced structural transition leads to inversion symmetry breaking and a substantial spin splitting (~33 meV). A precise estimation of H atom positions unveiled the templating effect of organic cations by investigating how organic-inorganic hydrogen-bonding tailors the perovskite structure and modulates spin-related properties. Moreover, we developed novel HOIPs exhibiting an intermediate structural dimensionality (between 1D and 2D) with varying widths of the inorganic ribbons, suggesting the potential to tune quantum confinement and modulate exciton properties. The tunable perovskite structures and their associated structure-sensitive properties underlie a deeper comprehension of the structure-property relationship and therefore benefit future semiconductor design and prospective application in energy harvesting, light-emission, spin-control, and ferroelectricity.

Affiliated poster: [I-S2-11] Exploring Symmetry Breaking and Structural Dimensionality Engineering in HOIPs: Unraveling Emergent Spin, Electronic, and Optical Properties.

I-T2-11: MECHANISMS THAT GOVERN LONG-TERM STABILITY OF ZIF-8-BASED POROUS LIQUIDS

[EFRC – UNCAGE-ME]

Matthew J. Hurlock,[1] Matthew S. Christian,[1] Jessica M. Rimsza,[1] and Tina M. Nenoff[1]

[1]*Sandia National Laboratories*

Presenter: Matthew J. Hurlock

Caption: (Left) Matthew J. Hurlock and (Right) Matthew Christian

To address the challenges of traditional CO_2 sorbent materials a new class of porous materials was recently developed that combines the porosity of solids with the fluidity of liquids. These new "porous liquids" (PLs) are formed from stable combinations of a ridged-porous host and a solvent that is excluded from the pore space resulting in permanent internal porosity. Type 3 PLs are formed by combining bulk solvent with nanoporous-solid sorbents such as metal–organic frameworks (MOFs). Type 3 PLs based on ZIF-8 (zeolitic imidazole framework) exploit the framework hydrophobicity to allow for solvation in aqueous solvents without solvent adsorption. However, solid ZIF-8 is known to degrade in the presence of water and CO_2, and the long-term stability of ZIF-8 in aqueous PLs is unknown. In a recently published study, using combined experimental and computational approaches, the stability of a ZIF-8 PL formed from a water-organic solvent system was examined and the degradation mechanisms identified. The PL was stable in air for several weeks, while aging in a CO_2 atmosphere caused formation of a secondary phase from degradation of ZIF-8. Atomistic simulations identified a multi-step, multi-component degradation mechanism of the PL that arose from increased solvent reactivity caused by the high pH of the PL. Experimental structural evaluation of the PL solvent system was used to validate the computational findings. Together this work lays out an evaluation strategy to identify the long-term stability of PLs for carbon capture. SNL is managed and operated by NTESS under DOE NNSA contract DE-NA0003525.

Affiliated poster: [I-S2-27] Type 3 Porous Liquid Design Based on Pore Accessibility and Framework Stability.

I-T2-12: TEMPORAL EVOLUTION OF NANOMATERIALS STRUCTURE AND FUNCTION DURING HYDROGEN EVOLUTION INDUCTION PERIOD FOR STATE-OF-THE-ART PT-LOADED RH-DOPED $SrTiO_3$ NANOPARTICLES

[EFRC – EPN]

Zejie Chen[1], Wenjie Zang[1], Justin T. Mulvey[1], Pushp Raj Prasad[1], Jocienne N. Nelson[2], Akihiko Kudo[3], Xiaoqing Pan[1], Joseph P. Patterson[1], A. Alec Talin[2], Shane Ardo[1]
[1]University of California Irvine; [2]Sandia National Laboratories; [3]Tokyo University of Science

Presenter: Zejie Chen

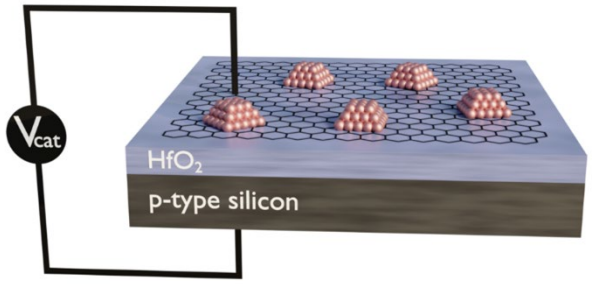
Caption: (from upper left) Zejie Chen, Wenjie Zang; (from lower left) Justin T. Mulvey, Pushp Raj Prasad, Jocienne N. Nelson

A main effort of EPN EFRC is to use correlative microscopy techniques to understand, predict, and control the activity, selectivity, and stability of solar water splitting nanoreactors in isolation and as ensembles. A common observation across many nanomaterials platforms is an induction period for H_2 evolution that is apparent during in-situ photodeposition of cocatalysts on nanoparticles. Conventional wisdom suggests that the induction period is due to photoreduction of partially oxidized cocatalysts. Support for this hypothesis comes from ex-situ X-ray photoelectron spectroscopy measurements correlated with H_2 evolution activity measured on the tens-of-minutes timescale using traditional gas chromatography systems. Instead, we are elucidating details of the induction period during in-situ cocatalyst photodeposition using high temporal resolution (20 seconds) in-line mass spectrometry coupled with high spatial resolution scanning transmission electron microscopy. State-of-the-art Rh-doped $SrTiO_3$ nanoparticles loaded with Pt shortly before, at, and shortly after the induction period were collected from the photocatalytic reactor and examined using scanning transmission electron microscopy. Results indicate that there are four different types of Pt-$SrTiO_3$ interfaces formed during the induction period. This subtle change in the Pt-$SrTiO_3$ interface could potentially provide insight into causes of efficient charge separation and electron transfer to active Pt sites on the photocatalyst surface. Furthermore, electron tomography measurements are conducted to reproduce the distribution of different Pt-$SrTiO_3$ interfaces on a single Rh-doped $SrTiO_3$ nanoparticle. Finally, single nanoparticle current–voltage curves and electron-beam-induced-current measurements are being used to differentiate the electronic properties of the four types of Pt-$SrTiO_3$ interfaces.

Affiliated poster: [I-S2-51] Development of a Diverse Correlative Microscopy Platform for Advanced Characterization of Solar Water Splitting Nanoreactors in Isolation and as Ensembles.

I-T2-13: CENTER FOR PROGRAMMABLE ENERGY CATALYSIS

[EFRC – CPEC]
Paul J. Dauenhauer[1]
[1]*University of Minnesota*



Presenter: Paul J. Dauenhauer

Caption: A catalytic condenser modulates the charge density of metal nanoclusters to alter surface reactions.

The catalytic conversion of small molecules to energy carriers such as hydrogen, methanol, or ammonia can be accelerated via the use of dynamic catalysts that are forcibly oscillated with time. Using both dynamic light and charge, the reaction pathways and associated energy profiles are modulated on the time scale of the surface reaction to transition reactions between rate-limiting reaction steps. Charge condensation was modulated on Pt nanoclusters via the catalytic condenser architecture (inset picture), which stabilizes electrons or holes in the active metal/graphene top film. The mechanisms and kinetics associated with variable charge density are examined by density functional theory. Charge condensation in metal nanoclusters heterogeneously accumulates at edge and corner sites, altering the binding energy and transition states of carbon- and nitrogen-containing adsorbates. Linear scaling relationships of molecular adsorption and reaction associated with charge condensation versus periodic trends provide quantitative prediction of the effects of charge modulation and reaction control. These controllable kinetic effects were explored experimentally via vacuum experiments, continuous flow reactions, and spectroscopy. Fundamental insight into the mechanisms of surface reactions occurring on catalysts that change with time is enabling tunable input programs that direct catalyst changes for improved catalytic activity and selectivity.

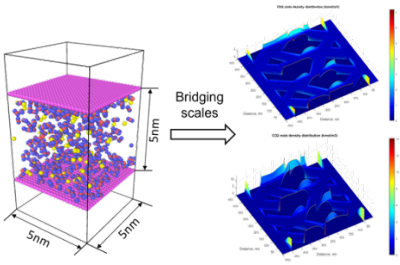
Affiliated poster: [I-S2-56] Design and Characterization of Catalytic Condensers.

Day 2 – September 20, 2023

Lightning Talk Session 1

II-T1-1: COUPLED PHASE BEHAVIOR AND TRANSPORT IN COMPLEX CONFINED NANOPOROUS NETWORKS

[EFRC – CMC-UF]
Lingfu Liu[1], Nijat Rustamov[1], Saman Aryana[1]
[1]*University of Wyoming*



Presenter: Lingfu Liu

Caption: (left) A Schematic of a nano-slit containing a CH_4-CO_2 mixture, (right) Mole density distribution of the mixture in a confined pore network.

Confinement has a profound impact on the phase behavior, flow, and transport of gases due to copious interactions between the gas molecules and those of the confining solid. Shale systems are an example of a natural environment with an abundance of nanoconfined features interspersed with much larger features in complex geometric configurations that make classical homogenization techniques ineffective. This poster reviews our work as part of the CMC-UF on the intricate micro and meso-scales physics, including our contributions to computational tools bridging these scales to gain insight into macro-scale and system-level behavior in shale and tight subsurface formations. We will discuss using fluidic systems to investigate flow behavior in complex pore networks, the limitations of these systems due to the need to incorporate nano-sized features, and our developed numerical infrastructure as an alternative to lab experiments. Our numerical experiments utilize finely tuned, optimized implementations of the lattice-Boltzmann (LB) method, coupled with intermolecular force representations, capturing phase behavior and adsorption under confinement. Once tuned against molecular simulation data, LB implementations simulate the impact of confinement, adsorption, and complex geometries on gas storage and flow in complex confined pore networks. Our ongoing work involves exploring artificial intelligence to scale up the computational domains we can simulate, aiming to reach sizes akin to macroscale Representative Elementary Volumes.

Affiliated poster: [II-S1-37] Coupled phase behavior and transport in complex confined nanoporous networks.

II-T1-2: WHY DOES DISSOLVING SALT IN WATER DECREASE ITS DIELECTRIC PERMITTIVITY

[CCS – CSI]

Chunyi Zhang[1,2], Shuwen Yue[1], Athanassios Z. Panagiotopoulos[1], Michael L. Klein[2], Xifan Wu[2]
[1]Temple University; [2]Princeton University

Presenter: Chunyi Zhang

The static dielectric permittivity of sodium chloride solution decreases as more salt is dissolved. This phenomenon is referred to as dielectric decrement. For nearly one century, this phenomenon has been widely explained by dielectric saturation theory, which invokes saturation in the dielectric response of the individual solvent water molecules. However, the dielectric saturation theory lacks the collective dipolar response picture of water. Moreover, the local electric field induced by ions should be calculated using quantum mechanics instead of a classical description. In this work, we elucidated the microscopic origin of dielectric decrement in salt water at the level of quantum mechanics by employing state-of-the-art neural network methods and density functional theory. Our simulated dielectric permittivity as a function of solute concentration agrees well with the experimental results. The present results unambiguously determine that the dielectric decrement should mostly be attributed to the suppressed dipolar correlation among solvent water molecules as the solute concentration increases. Specifically, around the solvated ions, the tetrahedral H-bond structure is replaced by approximately spherical hydration shells. The intrusion of these hydration shells interrupts the H-bond-induced correlations among the molecular dipoles, resulting in the observed dielectric decrement.

Affiliated poster: [II-S1-36] Why does dissolving salt in water decrease its dielectric permittivity.

II-T1-3: PROBING HIGHER ORDER PHONON ANHARMONICITY IN CERAMIC NUCLEAR FUELS UNDER TEMPERATURE AND PRESSURE EXTREMES

[EFRC – TETI]

Saqeeb Adnan[1], Amey Khanolkar[2], Marat Khafizov[1], Chris Marianetti[3], Michael Manley[4], David H. Hurley[2]
[1]The Ohio State University; [2]Idaho National Laboratory; [3]Columbia University; [4]Oak Ridge National Laboratory

Presenter: Saqeeb Adnan

Nuclear energy stands as one of the primary contributors to America's carbon-free energy portfolio. Nuclear reactors require fuels capable of enduring intense radiation and temperature conditions, where enhanced thermal energy transport is critical for maximizing reactor efficiency and safety. Anharmonic lattice vibrations dictate how atoms in a crystalline lattice interact with each other and play a pivotal role in the thermophysical properties of the solid. Since thermal transport in ceramic nuclear fuels is mostly governed by lattice vibrations (phonons), understanding anharmonic interactions of phonons at extreme temperatures and pressure is important for developing an accurate understanding of fuel behavior at operating conditions. Under extreme pressure and temperature, the lattice anharmonicity reveals itself through changes in lattice volume and phonon-phonon interactions. We monitor these anharmonic effects through measurements of phonon properties at temperatures up to 1000°C and pressure up to 20 GPa. Investigation of the zone-centered optical phonons through Raman spectroscopy and the acoustic phonons through time-domain Brillouin scattering enables us to measure the changes in the phonon frequency and lifetimes as a function of temperature and pressure. The experimentally obtained phonon properties serve as a benchmark for validating first-principles phonon calculation that go beyond the lowest-order perturbative treatment of phonon anharmonicity. This can lead to the development of mechanistic models that can accurately predict the thermophysical properties of nuclear fuels in extreme environments.

Affiliated poster: [II-S1-25] Beyond 3rd order anharmonicity.

II-T1-4: EXPERIMENTAL OBSERVATIONS OF CHEMO-MECHANICAL COUPLING DURING CARBON MINERALIZATION IN FRACTURES

[EFRC – GMCS]

Chelsea Wren Neil[1], Haylea Nisbet[1], Uwaila Iyare[1], Yun Yang[1], Bill Carey[1], Hari Viswanathan[1], Peter Kang[2]
[1]Los Alamos National Laboratory; [2]University of Minnesota

Presenter: Chelsea Wren Neil

To demonstrate the viability of long-term geologic carbon dioxide (CO2) sequestration in mafic and ultramafic rocks, it is crucial to understand the complex interplay between geochemical changes, triggered by reaction between rock and injected CO2, and geomechanical changes, such as fracture formation and propagation, which will expose new reactive mineral surfaces and allow for prolonged CO2 injection. In particular, we must learn how the CO2 mineralization reaction will progress within both flowing and dead-end fractures and how this reaction will impact the rock structure through reaction-driven cracking, dissolution and weakening of the rock matrix, and changes to frictional forces between rock surfaces. In this poster, we present the current and ongoing research at Los Alamos National Laboratory, where we are applying advanced experimental tools to fill these knowledge gaps. These tools include Raman spectroscopy to characterize reacted surfaces, high temperature-pressure microfluidics for in situ observation of reaction in flowing fractures, and scanning electron microscopy observation of fracture propagation in single crystal olivine to investigate reaction-driven cracking. Preliminary results show that fracture properties, including surface roughness and aperture, impact the quantity and characteristics of reaction products including magnesite and iron oxides. Additionally, precipitation of magnesite within preexisting olivine fractures, as well as dissolution pit formation on the olivine crystal surface, was observed.

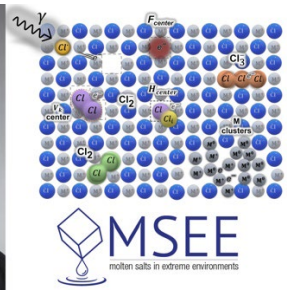
Affiliated poster: [II-S1-05] Experimental Observations of Chemo-Mechanical Coupling during Carbon Mineralization in Fractures.

II-T1-5: ADVANCES IN THE EFFECTS OF IONIZING RADIATION ON THE STABILITY AND REACTIVITY OF MOLTEN SALTS

[EFRC – MSEE]

Alejandro Ramos-Ballesteros[1,2], Kazuhiro Iwamatsu[3], Santanu Roy[4], Ruchi Gakhar[1], Phillip Halstenberg[5], Michael E. Woods[1], Bobby Layne[3], Jay A. LaVerne[2] , Simon M. Pimblott,[1] James F. Wishart[3], and Gregory P. Holmbeck[1]

[1]Idaho National Laboratory, [2]University of Notre Dame, [3]Brookhaven National Laboratory, [4]Oak Ridge National Laboratory, [5]University of Tennessee, Knoxville



Presenter: Alejandro Ramos-Ballesteros

Caption: (left) Alejandro Ramos-Ballesteros, (right) Radiation-induced defects in solid chloride salts.

Molten salts are proposed as liquid fuels and coolants in a new fleet of nuclear reactors with operational and safety advantages over present reactor designs. Salt mixtures containing monovalent and divalent metal cations are of particular interest because of their tunable Lewis acidity-basicity that can be used to control the solubility of dissolved metal ions in the reactor. However, these salt mixtures will be exposed to intense, multi-component ionizing radiation fields within the reactor environment, leading to unanticipated changes in the physical and chemical properties of the system. Consequently, understanding the underlying chemical effects of radiolysis on the salt is essential for the reliable, efficient, and sustainable operation of molten salt reactors. Assembling this fundamental understanding necessitates the identification of initial and steady-state salt radiolysis products and characterizing their respective chemistries over multiple time and distance regimes. To this end, we have employed solid (gamma ray) and molten (electron pulse) salt irradiation techniques to isolate these species and interrogate their chemical behavior with a combination of electron paramagnetic resonance, diffuse reflectance, and integrated transient optical absorption spectroscopy techniques. Here we present our most recent findings on radiation-induced processes in complex salt mixtures, including: *(i)* the radiolytic reduction of uranium trichloride; *(ii)* the aggregation of nickel nanoparticles in irradiated lithium potassium-zinc chloride eutectic; and *(iii)* the influence of magnesium and potassium cation ratios on the transient behavior of the solvated electron in molten chloride mixtures.

Affiliated poster: [II-S1-18] Advances in the Effects of Ionizing Radiation on the Stability and Reactivity of Molten Salts.

II-T1-6: STRUCTURE AND SOLVATION DYNAMICS OF DEEP EUTECTIC SOLVENTS

[EFRC – BEES2]
Desiree Mae Prado[1], Rathiesh Pandian[1], Ibrahim Alfurayj[1], Xiaochen Shen[1], Carla Fraenza[2], Stephanie Spittle[3], William Brackett[3], Bryce Hansen[4], Kaylie Glynn[4], Yong Zhang[5], Brian Doherty[6], Robert Savinell[1], Steve Greenbaum[2], Joshua Sangoro[4], Edward Maginn[5], Mark Tuckerman[6], and Clemens Burda[1]
[1]Case Western Reserve University; [2]Hunter College of CUNY; [3]University of Tennessee, Knoxville; [4]The Ohio State University; [5]University of Notre Dame; [6]New York University

Presenter: Desiree Mae Prado

Deep eutectic solvents (DESs) are mixtures of hydrogen bond donor (HBD) molecules and hydrogen bond acceptor (HBA) molecules that are characterized by a significant depression of the melting point compared to that of its individual constituents. With their versatile properties, DESs hold great promise as next-generation electrolytes for electrochemical energy storage solutions. In this study, we investigate the influence of varying the HBA, HBD, HBA/HBD molar ratios, and co-solvents on the structure and dynamics of DES ethaline, a 1:2 molar ratio mixture of choline chloride (ChCl) and ethylene glycol (EG). When examining the influence of HBA/HBD molar ratio, femtosecond transient absorption spectroscopy reveals two distinct time components. Both components indicate that solvation dynamics are enhanced with increasing ChCl composition up to 16.67 mol% but are slowed down for 33 mol% ChCl. Additionally, molecular dynamics simulations shed light on the role of co-solvents, specifically water molecules, in DESs. Higher concentrations of water co-solvent promote longer Grotthuss mechanism chain lengths within the DES. The H_3O^+ ion, briefly stabilized by Cl^-, interacts with ethylene glycol, indicating a disruption of the hydrogen bond network in the DES. Our results reveal that substituting ChCl with ChF as the HBA enhances the relaxation dynamics of DES. The ^{19}F-NMR spectrum of ethalineF unveils two distinct chemical environments surrounding the fluoride ion, namely EG···F (freely dissolved F^- in EG) and Ch···F (choline-bound F^-). Consequently, by altering the O-H spacing and alkyl chain length of EG, it becomes possible to fine-tune the polarity and solvation dynamics of DESs.

Affiliated poster: [II-S1-15] Structure and Solvation Dynamics of Deep Eutectic Solvents

II-T1-7: EXPERIMENTALLY-INFORMED STATE DEPENDENT ATOMIC FORCES IN REAL FLUID ENSEMBLES

[EFRC – MUSE]
Brennon L. Shanks, Michael P Hoepfner
University of Utah

Presenter: Brennon L. Shanks

Predictive multiscale modeling and molecular thermodynamic theories are critical to provide needed insight into confined fluid properties due to a lack of available and consistent experimental data. However, several knowledge gaps exist in the development of such predictive models. Firstly, atomistic simulations have demonstrated poor representation of local fluid structure and are predominantly benchmarked to available macro-fluid properties (e.g., density). Secondly, atomistic simulations are time-consuming and efficient equations of state approaches are desired. In this poster, we first present a novel solution to the century-old "inverse problem" where experimental neutron diffraction measurements are used to extract accurate pair potentials to improve the prediction of local atomic forces and properties. We demonstrate by analyzing experimental diffraction results that the forces between atoms in krypton fluids varies as a function of state and are less attractive and more deformable as the temperature increases. These measurements enable potentially transformative new applications of neutron scattering to improve molecular modeling directly and provide a novel pathway to assess local atomic forces in real fluid ensembles. We then discuss a representative investigation to explore the translation of atomic simulations to equation of state modeling for binary mixtures of methane-heptane and CO2-heptane using Monte Carlo simulations. The results reveal a decrease in the critical points of the mixtures and enable optimization of equation of state approaches. Coupled together, these studies highlight the need for additional and fundamental development of accurate pair potentials and approaches and simulation methods to reliably predict fluid properties and phase behavior in confinement.

Affiliated poster: [II-S1-31] Improvement of Atomistic Modeling for Confined Fluid Properties: Translating from the Statistical to Continuum Scale.

II-T1-8: REDUCING THE ENERGY BARRIER FOR PROTON TRANSPORT IN POLYMERS UNDER ANHYDROUS CONDITIONS

[EFRC – FaCT]

Zitan Huang[1], Michelle Lehmann[3], Michael Hickner[2], Tomonori Saito[3], Ralph Colby[1]
[1]Penn State University; [2]Michigan State University; [3]Oak Ridge National Laboratory

Presenter: Zitan Huang

Proton exchange membrane fuel cells are a promising technology that would enable our vehicles to be powered by a clean renewable energy source. For efficient performance, these fuel cells need to operate under anhydrous conditions, however this significantly reduces proton mobility. Our goal is to understand the underlying mechanisms and molecular interactions that facilitate proton hopping transport in anhydrous systems through a combined experimental and computational approach. We have developed a Python script to search molecular databases for potential proton-hopping molecules. We have also compiled our own database of proton conducting polymers in non-aqueous systems. The results of this, along with new compounds created using the cheminformatics package RDKit are used to perform DFT analysis. The results of this will be fed into a machine learning system for identification of targets for synthesis and experimental testing.

Concurrently, we have evaluated the ionic conductivity and other dielectric properties of pure azole molecules and azole-phosphonic acid mixtures using broadband dielectric spectroscopy (BDS). The measurements show that pure azole molecules have a high conductivity after melting, and that their conductivity, dielectric properties, and viscosity are all similar in the melt state. Then the conductivity for several azole-phosphonic acid mixtures were investigated using BDS. The azole-phosphonic acid mixtures exhibited a much higher conductivity than that of the pure azole molecules due to the additional proton provided by the acid. The mixtures show conductivity values in the range of 100 mS/cm.

Affiliated poster: [II-S1-35] Reducing the energy barrier for proton transport in polymers under anhydrous conditions.

II-T1-9: NEW REACTIVE FORCE FIELDS EXPLORE MOLECULAR REACTIVITY IN CONCENTRATED ELECTROLYTES

[EFRC – IDREAM]
Maxime Pouvreau[1], Qing Guo[2], Hsiu-Wen Wang[3], Gregory K. Schenter[1], Carolyn I. Pearce[1,4], Aurora E. Clark[2,1], Kevin M. Rosso[1]
[1]Pacific Northwest National Laboratory; [2]University of Utah; [3]Oak Ridge National Laboratory; [4]Washington State University

Presenter: Maxime Pouvreau

Caption: Maxime Pouvreau. A new reactive force field will be used to study aluminate oligomerization and the early-stage nucleation of solid phases.

Reactive force fields (RFFs) offer a fast alternative to density functional theory for exploring chemical reactions in complex systems. The extreme conditions of super-concentrated solutions in next-generation energy systems mandate enhanced efficiency because of their slow molecular motions. IDREAM has developed a new RFF that decreases computational cost by an order of magnitude, while reaching the same time and spatial scales as non-reactive force fields. The model was force-matched on ab initio molecular dynamics data and applied to a fundamental problem inhibiting the processing of legacy highly radioactive wastes stored in tanks at Department of Energy sites, i.e., the unpredictable behavior of aluminum in sodium hydroxide solutions. The accuracy of the model was extensively verified against multimodal synchrotron and neutron data obtained from user facilities, e.g., radial distribution functions, as well as computed free energy profiles for oligomerization and formation energies. The model allows simulation of early-stage aluminum hydroxide nucleation, which is experimentally challenging as it involves ultrafast changes in both aluminum coordination number and connectivity, complicating the molecular-scale interpretation of the transformation mechanism. The functional form of the RFF is being continually developed to model both solid-state and solution chemistry with the same level of accuracy. Through parameterization, the RFF will be transferable to other systems involving main group metals, silicon, magnesium, or calcium, so that nucleation and surface reactivity can be efficiently modeled in other materials relevant to energy science research.

Affiliated poster: [II-S1-41] Nucleation of Aluminum Hydroxide Polymorphs from Alkaline Sodium Aluminate Solutions.

II-T1-10: MECHANOCHEMICAL PHENOMENA AT THE ALKALI METAL/SOLID ELECTROLYTE INTERFACE

[EFRC – MUSIC]
Catherine Haslam[1], S. Sandoval[2], B. Vishnugopi[3], J. Sakamoto[1], D. Mitlin[4], P. Mukherjee[3], M. McDowell[2]
[1]University of Michigan; [2]Georgia Institute of Technology; [3]Purdue University; [4]University of Texas, Austin

Presenter: Catherine Haslam

The primary impetus to develop solid-state batteries is the enabling of alkali metal anodes. Supplanting conventional graphite with Li metal anodes, dramatic improvements in energy density (1,200 Wh/l) can be achieved. However, owing to its reactivity with air, manufacturing with Li metal can be costly and complicated. Recently, it has been shown that Li metal anodes can be made after cell assembly using a state-of-the-art lithiated cathode where Li is electroplated. Currently, the nucleation and growth of the Li anode formed through this process is controlled by a mechano-electrochemical phenomenon. MUSIC integrates expertise in solid ion conductors, solid-state electrochemistry, metallurgy, and solid-state mechanics to develop a fundamental understanding of mechano-electrochemical phenomena that control the initial plating and subsequent cycling behavior of *in situ* formed Li anodes. Using sulfide and oxide electrolyte model systems, it was shown that the integration of these alloy layers, regulate and homogenize Li-ion flux at the electrode-electrolyte interface. Moreover, it was shown that alloy layers can regulate Li nucleation that emulates uniform Li-electrodeposition in liquids. These findings can help accelerate the commercialize solid-state batteries by simplifying and reducing the cost as well as increasing performance by minimizing Li metal excess in Li metal solid-state batteries.

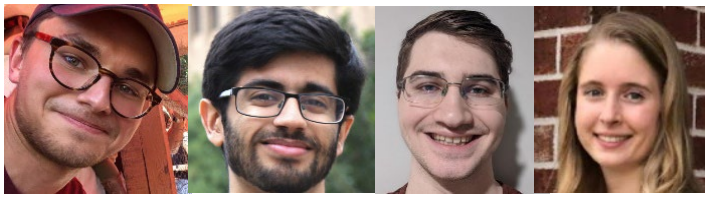
Affiliated poster: [II-S1-39] The Influence of Lithium Alloys and Compounds on Nucleation and Growth of Lithium at Solid-State Electrolyte Interfaces

Lightning Talk Session 2

II-T2-1: MECHANISMS UNDERLYING MIXED SALT PARTITIONING IN UNCHARGED POLY(ETHYLENE OXIDE)-BASED MEMBRANES

[EFRC – M-WET]

Everett S. Zofchak, Aubrey E. Quigley, Jordyn G. Yoh, Kevin K. Reimund, Nathaniel A. Lynd, Benny D. Freeman, Venkat Ganesan
University of Texas at Austin



Presenter: Everett Zofchak

(from left) Everett Zofchak, Rahul Sujanani, Nico Marioni, and Aubrey Quigley

Selective polymer membranes are critical in established and emerging water treatment processes (e.g., desalination, resource recovery). Many new applications require precise separation of specific ions (e.g., Li^+) from concentrated solute mixtures, yet current membranes exhibit limited ion-ion selectivity due to non-specific polymer-ion interactions. Additionally, our current understanding of ion transport in membranes is informed by single salt studies, yet separations are necessarily performed in complex mixtures. The design of highly selective membranes is hindered by poor understanding of the molecular interactions underpinning ion transport in polymers challenged with electrolyte mixtures. We performed experimental and computational studies to systematically probe the effects of hydration and mixed salt interactions on ion transport. Measurements in polymers exposed to humid air showed that ion transport rates depend weakly on water content at low water activity but depend strongly on water content at high water activity. Complementary simulations provided molecular level insights, suggesting ion transport is governed by polymer dynamics at low water content and by water dynamics at high water content. Mixed ion partitioning experiments performed at a fixed ionic strength facilitate comparison of single and mixed salt partitioning. Systematic deviations were observed between the single and mixed salt cases. Molecular dynamics simulations coupled with equilibrium thermodynamic modeling indicate these differences arise from: (1) differences in ion affinity for the membrane and (2) electrostatic interactions between ions in a predictable manner. Together, the synergistic combination of synthesis, characterization and simulations provide new fundamental insights for designing membrane materials for advanced ion separations.

Affiliated poster: [II-S2-35] Fundamental Design Principles of Highly Selective Membranes for Water Treatment.

II-T2-2: MODELING ION EXCHANGE IN FAUJASITES: A METHODS STUDY USING DENSITY FUNCTIONAL THEORY

[EFRC – CHWM]
An T. Ta[1], Ayoub Daouli[2], R. Seaton Ullberg[1], Vanessa Proust[3], Agnès Grandjean[3], Michael Badawi[2], Simon R. Phillpot[1]
[1]University of Florida, Gainesville, [2]University of Lorraine, [3]CEA, DES, ISEC, DMRC, Univ Montpellier

Presenter: An T. Ta

From left to right: An T. Ta, Ayoub Daouli, R. Seaton Ullberg, Vanessa Proust

Zeolites are popular candidates as capture materials for removing harmful cesium radionuclides (e.g., cesium-137) from used nuclear waste because of their relatively low cost, radioactive stability, and effective performance. Faujasites are among the zeolite types under consideration and are made up of two building units (sodalite and d6mr), which results in a framework that possesses specific exchange sites in its super and inner cages. In this study, approaches implementing various reference states (e.g., gaseous, implicit solvation, explicit solvation) were evaluated to determine the most appropriate technique for modeling ion exchange in faujasites using density functional theory (DFT). It was found that the consideration of both implicit and explicit solvation leads to the most reliable results. Exchange energies for Li^+, K^+, and Rb^+ with Na-X zeolites were considered and validated with available experimental data.

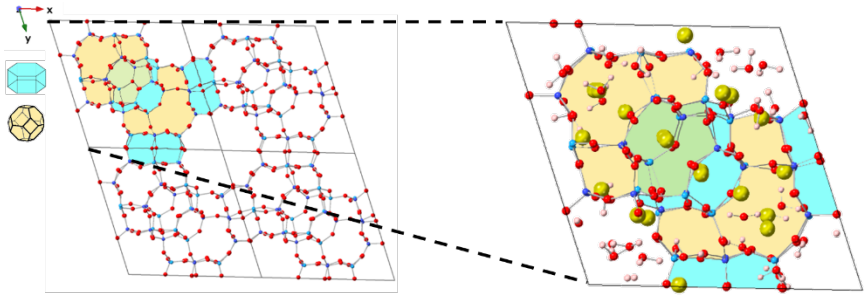


Figure 1. *Supercell of bare Na-X model (left) and primitive cell of explicitly solvated Na-X (right). Green regions denote a depiction of both sodalite and d6mr from the perspective shown. O atoms are shown in red, H atoms in pink, Al in blue, Si in cyan, and Na in yellow.*

Affiliated poster: [II-S2-32] Modeling Ion Exchange in Faujasites: A Methods Study Using Density Functional Theory.

II-T2-3: ION TRANSPORT IN MoS_2 NANOCHANNELS

[EFRC – AMEWS]
Eli Hoenig
University of Chicago

Presenter: Eli Hoenig

The design of synthetic channels with superior selectivity for any desired target ion remains a significant challenge due to limited understanding of the interplay between aqueous fluid containing the target and the solid interface. Two-dimensional (2D) materials offer new opportunities for controlling separation and selectivity, with interlayer spacings from angstroms to nanometers. We have created 2D platform channels with three complimentary classes of materials: transition metal dichalcogenides (TMDCs), phyllosilicate minerals, and MXenes. (i) ***TMDCs***: We have synthesized a confined angstrom-scale 2D channel based on MoS_2 functionalized with acetate, and we have observed anomalous and cooperative ion transport within this channel. Molecular dynamics (MD) simulations were also conducted to investigate the interplay between ions, revealing the significant role of long-range interactions in influencing counterion pairing. (ii) ***Phyllosilicate minerals***: We have devised a route to tunable ion-transport properties for vermiculite membranes (VMs) by the introduction of alkanediamine molecules to cross-link the layers, which also enhances membrane stability. (iii) ***MXenes***: We have designed hierarchically engineered MXenes with novel MXene morphologies, surface terminating groups, and hybrid organic-inorganic material systems; we have also investigated the role of material structure (across multiple length scales) impact separation properties. Based on this material platform and advanced characterization and modeling, we aim to elucidate the impact of various factors such as interlayer spacing, ion binding mode, dehydration, and electrostatic interactions on water and ion permeabilities and selectivities. These insights will provide constructive guidance for the precise design of selective 2D materials.

Affiliated poster: [II-S2-25] Functionalized confined two-dimensional channels for separation and selectivity

II-T2-4: REFRACTORY TRANSITION METAL OXIDES AS ELECTRODES IN LITHIUM-ION BATTERIES

[EFRC – SCALAR]
Ashlea Patterson,[1] Yunkai Luo,[2] Yucheng Zhou,[2] Laurent Pilon,[2] Bruce Dunn,[2] Ram Seshadri[1]
[1]University of California, Santa Barbara, [2]University of California, Los Angeles

Presenter: Ashlea Patterson

Refractory transitions metal oxides include oxides of metals such as zirconium (Zr), niobium (Nb) and molybdenum (Mo) that typically have high melting temperatures. These oxides, particularly of Nb, are also key components in oxide materials that can take up and release lithium rapidly in electrochemical energy storage systems, with voltages that make them suitable as anodes that can be paired with a high voltage cathode material. A large body of research from the SCALAR EFRC has emerged on these materials, including design principles for these compounds to function as high-power electrodes capable of fast charging/discharging, the role of crystal structure and composition in ensuring such fast charge/discharge, the role of metallicity and insulator-to-metal transitions with lithiation to enable current to be delivered quickly, the role of multielectron redox on the transition metal.

We will present recent work on new Wadley-Roth compounds from the Na–Nb–O family that are effective at high-rate, high-capacity redox and describe subtle compositional differences in certain bronze compounds with related structures that dramatically impact cycling stability and high-rate-performance.

An important aspect of SCALAR research that has informed our understanding of these anode oxide materials had involved of the use of calorimetry and entropy potential measurements as a function of lithiation and delithiation. These measurements permit distinct regimes in the electrochemistry to be identified even when there are no structural signatures.

Affiliated poster: [II-S2-41] Refractory Transition Metal Oxides as Electrodes In Lithium-Ion Batteries.

II-T2-5: NEW ROUTES TO HYDROGEN INCORPORATION IN $SrTiO_3$

[EFRC – HEISs]

Megan Burrill[1], Yea-Shine Lee[1], Roberto dos Reis[1], Zhi Li[1], Erica Truong[1], Guennnadi Evmenenko[1], James R. Rondinelli[1], Vinayak P. Dravid[1], Chris Wolverton[1], Yan-Yan Hu[2], Michael J. Bedzyk[1], Sossina M. Haile[1]
[1]Northwestern University; [2]Florida State University

Presenter: Megan Burrill

While proton incorporation in acceptor-doped $BaZrO_3$ and related perovskites has long been established, recent literature indicates that undoped titanate perovskites can incorporate hydride species, forming, for example, $SrTiO_{3-x}H_x$ (STO: H^-). Key to broadening the study of these materials is the development of a readily tuned synthesis approach. Here we pursue a two-step reduction process under hydrogen atmospheres, designed to first reduce the based material ($SrTiO_3$) and subsequently incorporate hydride anions. Thermogravimetric analysis (TGA) reveals that the first step successfully produces $SrTiO_{2.82}$. Electron energy loss spectroscopy following the second step suggests an impact of the processing steps on the Ti environment, indicating that either the Ti does not exhibit its ideal octahedral coordination or the average oxidation state lies between 3+ and 4+. ^1H solid-state NMR shows significant differences between pristine STO and STO: H^-, with a stronger peak in the latter at 1 ppm. Additionally, a peak at 5 ppm, tentatively attributed to surface H^+ species, is substantially lower in STO: H^- than in the (nominally) pristine material. The totality of the results suggests STO: H^- has been obtained.

Affiliated poster: [II-S2-24] Hydride Incorporation in $SrTiO_3$ and Computationally Predicted $xBaZrO_3$-(1-x)$SrTiO_3$.

II-T2-6: NANOFLUIDIC PLATFORMS FOR ADDRESSING KNOWLEDGE GAPS AT THE WATER-ENERGY NEXUS

[EFRC – CENT2]

Yu-Ming Tu[1], Rahul Prasanna Misra[1], Matthias Kuehne[2], Hananeh Oliaei[3], Cody L. Ritt[1], Samuel Faucher[1], Kyle Sendgikoski[4], Xintong Xu[5], John Cumings[4], Arun Majumdar[5], Narayana Aluru[3], Daniel Blankschtein[1], and Michael S. Strano[1*]

[1]Massachusetts Institute of Technology; [2]Brown University; [3]University of Illinois Urbana-Champaign; [4]University of Maryland; [5]Stanford University

Presenter: Yu-Ming Tu

Caption: (from left) Yu-Ming Tu, Rahul Prasanna Misra, Matthias Kuehne, and Cody L. Ritt

Fluids confined inside single digit nanopores (SDNs) with pore dimensions comparable to the size of the fluid molecules can exhibit thermodynamic properties, including phase transitions, which differ remarkably from those in the bulk phase. Here, we develop a high-throughput platform utilizing carbon nanotubes (CNTs) as SDNs to precisely characterize environmental coupling effects and investigate fluid phase transitions under strong confinement. Using local laser heating *in vacuum*, we discovered thermally reversible radial breathing mode (RBM) downshifts of CNTs by an extraordinary 10 to 15%, which is attributed to a reversible increase in damping and can be described using the harmonic oscillator model across 93 different Raman scans. Additionally, immersing CNTs opened by focused ion beam in water reveals phase transitions with concave-up trajectories dominated by the internal fluid desorption (adsorption) at high (low) temperatures. To model water phase transitions, we have developed an equation of state (EOS), aided by molecular simulations carried out in a hybrid statistical mechanical ensemble, where the confined water is maintained in quasi-chemical and thermal equilibrium with separate chemical potential and thermal reservoirs, respectively, under non-isothermal conditions. Importantly, this thermodynamic theory entails a self-consistent determination of the phase transition temperature as a function of the water-CNT interactions and CNT diameters, thereby enabling an accurate characterization of the enthalpy of phase change through fitting to the experimental data. Overall, our combined experimental and theoretical study demonstrates the exceptional promise of CNTs as precision systems for various nanofluidic applications at the water-energy nexus.

Affiliated poster: [II-S2-06] Nanofluidic Platforms for Addressing Knowledge Gaps at the Water-Energy Nexus.

II-T2-7: MULTISCALE NUCLEAR-ELECTRONIC ORBITAL QUANTUM DYNAMICS IN COMPLEX ENVIRONMENTS

[CCS – NEOQD]

Eleftherios Lambros[1], Aodong Liu[1], Mathew Chow[2], Sharon Hammes-Schiffer[2], Xiaosong Li[1]
[1]University of Washington; [2]Yale University

Presenter: Eleftherios Lambros

Multiscale descriptions of quantum dynamics are critically important for modeling and understanding complex chemical processes at the interface of energy conversion, storage, and transfer. The nuclear-electronic orbital (NEO) method provides an effective and elegant way to introduce nuclear quantization directly into quantum chemistry calculations, enabling the capture of zero-point energy, hydrogen tunneling, and other nuclear quantum effects not included in conventional electronic structure calculations. The NEO method is particularly useful for studying nonadiabatic processes, such as photoinduced proton transfer and proton-coupled electron transfer, which often occur in solution or in extended, heterogeneous environments. A multiscale treatment is required to accurately model the chemical complex of interest as well as its surrounding environment. In our work, the NEO method has been integrated into a solvent environment using both a simple, yet powerful polarizable continuum model (PCM) embedding, as well as an atomistic hybrid quantum mechanical/molecular mechanical (QM/MM) strategy. Our calculations demonstrate that the environment can quantitatively polarize the nuclear density, providing important insight into how energy-related proton transfer processes behave in solution. Furthermore, the NEO QM/MM approach, coupled with the state-of-the-art MB-pol water model, can capture atomically resolved solvent effects on the quantized nuclei and the coupled nuclear-electronic dynamics. These methods are implemented in ChronusQ, an open-source quantum chemistry package allowing the democratization of these advances towards US energy leadership. Finally, our outreach program develops a STEM educational pathway for students from University of Hawai'i to participate in a research experience for undergraduates in computational chemical sciences.

Affiliated poster: [II-S2-38] Multiscale Nuclear-Electronic Orbital Quantum Dynamics in Complex Environments.

II-T2-8: THE DUALITY IN DAMAGE: MULTI-SCALE INVESTIGATIONS INTO CORROSION AND IRRADIATION EFFECTS IN SALT-FACING NUCLEAR REACTOR MATERIALS

[EFRC – FUTURE]

Sean H. Mills[1,2], Ryan D. Hayes[1], Ho Lun Chan[3], Nathan Bieberdorf[1], Minsung Hong[1], Elena Romanovskaia[3], Alexandra M. Kennedy[1], Laurent Capolungo[4], Mark Asta[1], John R. Scully[3], Peter Hosemann[1], Raluca O. Scarlat[1], Andrew M. Minor[1,2]

[1]University of California Berkeley, [2]Lawrence Berkeley National Laboratory, [3]University of Virginia, [4] Los Alamos National Laboratory

Sean Mills, University of California, Berkeley

Presenter: Sean H. Mills

Structural materials used in nuclear reactor environments are exposed to coupled extremes including irradiation, high temperatures, and corrosive media that act synergistically to degrade materials and their functional performance. Achieving a fundamental understanding that connects corrosive processes with native and corroded alloy chemistry, microstructure, interfacial chemistry, pore morphology, and accumulating point defects is imperative to improving their durability. It is, however, challenging to predict how variations in alloying elements, salt chemistry, and atomistic point defects interact and lead to material failure across temporospatial scales. In this talk we highlight how scanning electron microscopy and transmission electron microscopy techniques combined with inductively coupled plasma optical emission spectroscopy and phase field modeling can reveal morphological and compositional dynamic changes associated with fluoride salt corrosion from the micro- to nano-scale in a model Ni-Cr binary alloy system, and how those changes result from mass transport and structural rearrangement in these highly non-equilibrium conditions.

Affiliated poster: [II-S2-13] Molten Salt Dealloying Corrosion of Metals: Mechanisms and Irradiation Effects.

II-T2-9: BATTERIES IN ACTION: OPERANDO CHARACTERIZATION FOR UNDERSTANDING TOWARDS THE DEVELOPMENT OF HIGH ENERGY, FAST CHARGING BATTERIES

[EFRC – m2M#S]

Calvin D. Quilty, Patrick J. West, Esther S. Takeuchi, Kenneth J. Takeuchi, David C. Bock, Amy C. Marschilok
[1]*Stony Brook University*

Presenter: Sean H. Mills

LiNi0.8Mn0.1Co0.1O2 (NMC811) is a commercially successful Li-ion battery cathode due to its high energy density and cyclability. Utilizing this system under fast charge and high potential charge conditions is of great interest as this will help facilitate widespread electric vehicle adoption; high potential charging leads to higher energy density and therefore longer vehicle range while fast charging is needed to enhance consumer acceptance. These aggressive charging conditions can lead to enhanced capacity fade, however. To design next-generation NMC811 batteries with higher energy that are capable of fast charging but without sacrificing cycle life, the origins of the capacity fade must be understood. Operando X-ray characterization techniques are critical for this endeavor as they allow for the acquisition of information about the evolution of battery materials in a functional battery without disassembly of the battery which can introduce artefacts into the data and obscure the fundamentally dynamic processes that occur in a battery during operation. A combination of operando XRD and operando hard XAS as well as soft XAS and SEM reveal that charging NMC to high potential leads to more structural distortions and particle fracture, as well as surface reconstruction that lead to increased capacity fading. On the other hand, fast charging does not induce additional structural distortion or surface reconstruction suggesting that the phenomena at the graphite anode may be more critical under fast charge. These findings show that obtaining higher energy density Li-ion batteries will require stabilizing the cathode at high potential while the greater focus for fast charging batteries should be on the anode.

References:

1. Quilty, C. D.; West, P. J.; Wheeler, G. P.; Housel, L. M.; Kern, C. J.; Tallman, K. R.; Ma, L.; Ehrlich, S.; Jaye, C.; Fischer, D. A.; Takeuchi, K. J.; Bock, D. C.; Marschilok, A. C.; Takeuchi, E. S., Elucidating Cathode Degradation Mechanisms in LiNi0.8Mn0.1Co0.1O2 (NMC811)/Graphite Cells Under Fast Charge Rates Using Operando Synchrotron Characterization. Journal of The Electrochemical Society 2022, 169 (2), 020545.

2. Quilty, C. D.; West, P. J.; Li, W.; Dunkin, M. R.; Wheeler, G. P.; Ehrlich, S.; Ma, L.; Jaye, C.; Fischer, D. A.; Takeuchi, E. S.; Takeuchi, K. J.; Bock, D. C.; Marschilok, A. C., Multimodal electrochemistry coupled microcalorimetric and X-ray probing of the capacity fade mechanisms of Nickel rich NMC – progress and outlook. Physical Chemistry Chemical Physics 2022, 24 (19), 11471-11485.

Day 3 – September 26, 2023

Lightning Talk Session 1

III-T1-1: Harnessing Solar Energy: Unleashing the Power of Strongly Correlated Materials

[CMS – NPNEQ]
Sangeeta Rajpurohit[1], Xavier Andrade[1]
[1]*Lawrence Berkeley Nat onal Laboratory*

Presenter: Sangeeta Rajpurohit

CMS NPNEQ center brings together expertise from ab-initio methods and tight-binding model-based approaches to develop and distribute an open-source exascale-compatible software for simulating non-adiabatic dynamics in solids across multiple time and length scales. We apply real-time simulations based on the tight-binding model rt-TDDFT (i.e. rt-TB-TDDFT), to study photocurrent dynamics in ferroelectris and have made remarkable progress in understanding the combined effects of interactions on the bulk photovoltaic effect (BPVE) in correlated solids. Our rt-TB-TDDFT methodology explicitly takes into account charge, spin, orbital, and lattice degrees, and includes all important interactions, such as Coulomb interaction between electrons, electron-phonon (el-ph) interactions, and Hund's coupling. This allowed us to elucidate the combined effects of interactions on the evolution and decay of the photocurrent on timescales beyond the reach of present non-perturbative ab-initio methods. The rt-TB-TDDFT simulations show the generation of strong phonon-assisted ballistic photocurrent in correlated ferroelectrics hosting optical phonons that are strongly coupled to electrons [1,2]. This photocurrent rises sharply across a photoinduced phase transition. Furthermore, our simulations demonstrate transient effects, such as THz oscillatory currents, their decay within picoseconds and current saturation current at higher light intensities, all of which are inaccessible using perturbative frequency domain techniques typically used for BPVE [1,2]. Our results illustrate a promising alternative way for controlling and optimizing the BPVE by utilizing phonon-assisted ballistic current and light-induced phase transitions.

Ref: 1) S. Rajpurohit, C.D. Pemmaraju, T. Ogitsu, L.Z. Tan. PRB, 105, 094307 (2022)
2) S. Rajpurohit, T. Ogitsu, L.Z. Tan. PRB (accepted)

Affiliated poster: [III-S1-08] Nonperturbative Studies of Functional Materials under Nonequilibrium Conditions.

III-T1-2: FLOSIC FOR COMPLEX ANION-SOLVENT SOLUTIONS

[CCS – FLOSIC]

Kushantha P. K. Withanage[1], Alexander I. Johnson[1], Mark R. Pederson[1] and Koblar A Jackson[2]
[1]The University of Texas at El Paso, [2]Central Michigan University

Presenter: Kushantha P. K. Withanage

Caption: Kushantha Withanage

Processes occurring in batteries, fuel cells, photovoltaics, and natural water-splitting complexes require computational capabilities that go beyond the most widely used density functional theory (DFT) methods and, specifically, that are able to treat ions in solution. The computational description of such processes must be able to correctly predict electron and ion transfer in solution or in the presence of dielectric media. However, due to unphysical self-interaction error (SIE), density functional approximations (DFAs) push electronic orbital energies well above experiment and may also predict wrong ordering of energy levels. The problem becomes especially severe in anionic systems, where positive DFA orbital energies incorrectly imply unbound electrons. In solution, electrons that should be tied to the anion can migrate, unphysically, onto neighboring solvent molecules Self-interaction corrected methods are needed. Recent developmental work aimed at improving the Fermi-Lowdin orbital self-interaction correction (FLOSIC) includes an implementation using complex orbitals (https://doi.org/10.1063/5.0091212), a quantum-learning method for automated determination of Fermi-Orbital Descriptors, (https://doi.org/10.1063/5.0135089) and significant new algorithms to enable simulations on a trianionic Cr complex, $[Cr(C2O4)^{]-3}$ embedded in a cluster of 117 water molecules. Our results in the latter calculation show that the HOMO of the trianion properly lies below the LUMO states of the water molecules. This poster presents a high-level view of why it is important to have automated methods for highly-charged ions in solution and introduces several new algorithms, encoded by the first author, that lead to a factor of 125 decrease in computer time required for FLOSIC calculations in the large-N limit.

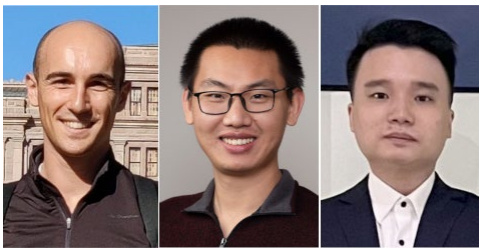
Affiliated poster: [III-S1-17] FLOSIC FOR COMPLEX ANION-SOLVENT SOLUTIONS.

III-T1-3: AB INITIO MANY-BODY THEORY OF POLARONS

[CMS – EPW]

Jon Lafuente-Bartolome[1,2], Chao Lian[1], Weng Hong Sio[1,2], Idoia G. Gurtubay[2], Asier Eiguren[2], Feliciano Giustino[1]

[1]The University of Texas at Austin, [2]University of the Basque Country at Bilbao, [3]University of Macau



Presenter: Feliciano Giustino

From left to right: Jon Lafuente-Bartolome, Chao Lian, Weng Hong Sio

Polarons are fascinating realizations of emergent quasiparticles resulting from the interaction between fermions and bosons. In crystals, polarons form when electrons or holes become dressed by phonons in the form of lattice distortions. In the presence of weak electron-phonon interactions, polarons behave like conventional Bloch waves with heavier effective masses. In the presence of strong interactions, on the other hand, polarons become localized wavepackets and profoundly alter the transport, electrical, and optical properties of the host material. In this poster we report on recent progress in *ab initio* calculations of polarons. In particular, (i) we review a methodology that enables the calculation of small and large polarons using density-functional perturbation theory and without resorting to cumbersome supercell calculations, as well as its implementation in the EPW code. (ii) We develop a generalization of this approach to a fully-fledged field-theoretic Green's function framework, and we show that for the prototypical Frohlich Hamiltonian our approach achieves an accuracy comparable to Feynman's celebrated path integral solution. (iii) We establish the link between polaron formation and the physics of phonon-induced band gap renormalization. We show how polaron formation and phonon-induced band structure renormalization, which traditionally have been considered as unrelated effects, are in fact complementary aspects of the same physical phenomenon and require a unified theoretical description. These developments bear significant implications on our current understanding of temperature-dependent band structures in semiconductors and insulators [Phys. Rev. Lett. 129, 076402 (2022); Phys. Rev. B B 106, 075119 (2022)].

Affiliated poster: [III-S1-10] Ab Initio Many-Body Theory of Polarons.

III-T1-4: SUPERFLUID DENSITY THROUGH A VAN HOVE SINGULARITY: Sr_2RuO_4 UNDER UNIAXIAL STRAIN

[EFRC – QSQM]

Eli Mueller[1,2], Yusuke Iguchi[1], Fabian Jerzembeck[3], Marisa L. Romanelli[4], Jorge O. Rodriguez[4], Clifford W. Hicks[5], Yoshiteru Maeno[6], Vidya Madhaven[4], Kathryn A. Moler[1,2]

[1]SLAC National Accelerator Laboratory; [2]Stanford University; [3]Max Planck Institute; [4]University of Illinois, Urbana-Champaign; [5]University of Birmingham; [6]Kyoto University

Presenter: Eli Mueller

Caption: (left to right) Eli Mueller, Marisa Romanelli, Jorge Rodriguez, Fabian Jerzembeck

Strontium ruthenate (Sr_2RuO_4) is an archetype in the field of unconventional superconductivity. The metallic normal state from which superconductivity condenses is among the simplest and best understood among unconventional superconductors. Yet, after nearly three decades of strenuous effort, the pairing mechanism of the superconducting state remains unresolved. In recent years, uniaxial compression has emerged as a powerful new probe of the physics of Sr_2RuO_4. Uniaxial strain tunes the Fermi surface through a Van Hove singularity (VHS), resulting in a dramatic enhancement of the superconducting critical temperature, T_c, that peaks around 3.5K at the VHS. Here, we perform scanning SQUID microscopy on samples under uniaxial compression to study the low temperature behavior of the London penetration depth, $\lambda(T)$, as the system is strain tuned through the VHS. Our measurements show an approximately 15% enhancement in the zero-temperature superfluid density under strain with a maximum that coincides with the peak in T_c. When tuned near the VHS, we observe a T^2 dependence of $\lambda(T)$ below $0.5T_c$ instead of a T-linear dependence expected for line nodes in the gap. These results provide new input for the development of theories of unconventional superconductivity in Sr_2RuO_4.

Affiliated poster: [III-S1-27] Superfluid density through a Van Hove singularity: Sr_2RuO_4 under uniaxial strain

III-T1-5: PREDICTIVE INVERSE DESIGN OF NEURONAL COMPONENTS

[EFRC – REMIND]
Timothy D. Brown,[1,2] Suhas Kumar,[1] Adelaide Bradicich,[2] R. Stanley Williams,[2] Patrick J. Shamberger[2]
[1]Sandia National Laboratories—Livermore; [2]Texas A&M University

Presenter: Thimothy D Brown

Caption: Timothy D. Brown

The most important aspect of building neuron-like electronic components is to be able to predictively design material properties based on required component behaviors. This process represents a substantial challenge because of the various material parameters and the extreme nonlinearities involved in the underlying materials, a requirement for neuron-like electrical properties (abrupt switching, self-oscillations, spiking, bursting, chaos, etc.). Predictive design is important because it is practically impossible to experimentally tune all the material parameters (thermal, electronic, thermodynamic, kinetic, etc.), manufacture hardware components based on the materials, and to efficiently navigate the substantial design space.

Here we build a compact predictive model, which bridges the knowledge gap by connecting fundamental phase transition processes in Mott insulators and spin transition systems to neuronal component-level behaviors. This model is capable of answering the question "will my material produce neuron-like behavior?" with only simple material properties, and without any elaborate component or network-level measurements. We will show how this computationally inexpensive model could help rapid screening of candidate materials across a diverse range of mechanisms (including complex oxides, coordination and intercalation compounds, etc.), and lead to useful predictions and discovery of neuronal materials.

Affiliated poster: [III-S1-19] Edge of Chaos in Phase Transition Materials.

III-T1-6: LEVERAGING THE RESILIENCE OF DIAMOND WITH ITS UNIQUE MATERIAL PROPERTIES TOWARDS NEXT GENERATION GRID INNOVATION

[EFRC – ULTRA]
Kelly Woo[1], Mohamadali Malakoutian[1], Matthias Muehle[2], Franz Koeck[4], Timothy Grotjohn[3], Stephen Goodnick[4], Robert Nemanich[4], Srabanti Chowdhury[1]
[1]Stanford University, [2]Fraunhofer USA Center, [3]Michigan State University, [4]Arizona State University

Presenter: Kelly Woo

For a smarter and a more resilient electricity grid, it is necessary to integrate multiple energy sources, manage various power storage capabilities, and meet the diverse electrical needs of modern society. Ultra-wide bandgap (UWBG) semiconductor and dielectric technology has been recognized for its ideal properties capable of operating at high power density and higher temperatures. Studying the fundamental phenomena in UWBG materials – including synthesis, defect and impurity incorporation, electronic structure at interfaces, and the interaction of electrons and phonons at high fields will enable smaller, more efficient energy conversion and control systems suitable at the grid-level. The study of these novel material properties was achieved through the characterization of Schottky, PIN and their combination that gives rise to a new type of junction called Schottky-PIND. Besides doping, extrinsically doped Diamond's interaction with light led to quantifiable photoconductivity responses, where deep doping and defect levels could be analyzed. Furthermore, the light-matter response phenomenon unleashed the potential of diamond-based photoconductive switches (PCSSs) which can utilize more accessible sub-bandgap excitation sources, in the visible or towards infrared range rather than in the deep UV, as was demonstrated in our studies. As there are increased efforts toward electrification, developing safer mechanisms like PCSSs for making and breaking high power circuits will be essential at high voltages. In ULTRA we established a path towards high-quality diamond material with both electrical and optical characterization techniques and demonstrated the vast potential of diamond's photoconductive behavior. These results set the platform for future studies for grid applications.

Affiliated poster: [III-S1-40] Design Optimization of UWBG Power Devices: A Co-Design Approach.

III-T1-7: TOWARDS ACCURATE POLARITONIC POTENTIAL ENERGY SURFACES WITH CAVITY QUANTUM ELECTRODYNAMICS COMPLETE ACTIVE SPACE CONFIGURATION INTERACTION THEORY

[CCS – MAPOL]
Nam Vu[1], Niranjan Govind[2], Jonathan Foley[1]
[1]University of North Carolina-Charlotte; [2]Pacific Northwest National Laboratory

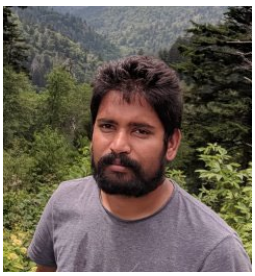
Presenter: Dr. Nam Vu

Polariton chemistry has attracted great attention as a potential route to modify chemical structure, properties, and reactivity through strong interactions between molecular electronic, vibrational, or rovibrational degrees of freedom. A rigorous theoretical treatment of molecular polaritons requires the treatment of matter and photon degrees of freedom on equal quantum mechanical footing. In the limit of molecular electronic strong or ultra-strong coupling to one or a few molecules, it is desirable to treat the molecular electronic degrees of freedom using the tools of *ab initio* quantum chemistry, yielding an approach we refer to as *ab initio* cavity quantum electrodynamics (ai-CQED), where the photon degrees of freedom are treated at the level of cavity quantum electrodynamics. Here, we present an approach called QED-CASCI to provide ground- and excited-state polaritonic surfaces with balanced description of strong correlation effects among electronic and photonic degrees of freedom. Such a method can provide value as a benchmark for lower-rank methods, and as a route to polaritonic potential energy surfaces and couplings that can be leveraged for ab initio molecular dynamics simulations of polariton chemistry.

Affiliated poster: [III-S1-04] Center for Many-Body Methods, Spectroscopies, and Dynamics for Molecular Polaritonic Systems.

III-T1-8: THEORETICAL RIXS INVESTIGATION OF THE INFINITE LAYERS NICKELATES

[CMS – Comscope]
Umesh Kumar[1], Corey Melnick[2], Gabriel Kotliar[1,2]
[1]Rutgers University; [2]Brookhaven National Lab



Umesh Kumar

Presenter: Umesh Kumar

The electronic structure of the recently discovered infinite-layer nickelates superconductors is not well understood. Using COMSUITE theoretical RIXS tools [1,2], we find that while the undoped nickelates at low energies are good cuprate analogs as found in earlier studies, upon doping these materials display significant multi-orbital effects, manifesting themselves in a softening of the RIXS signal at the Ni-L edge [3]. We compare our studies with existing experiments and highlight the importance of theoretical spectroscopy.

[1] *EDRIXS: An open source toolkit for simulating spectra of resonant inelastic x-ray scattering,* Y.L. Wang, G. Fabbris, M.P.M. Dean, and G. Kotliar, Computer Physics Communications 243, 151 (2019).

[2] PORTOBELLO: *Bringing Electronic Structure Codes into the Modern Software Ecosystem*, R. Adler, C. Melnick, G. Kotliar in preparation.

[3] U. Kumar, C. Melnick, G. Kotliar in preparation.

Affiliated poster: [III-S1-36] COMSUITE, a modern tool to predict physical properties of correlated materials combining electronic structure methods with dynamical mean field theory: applications to the topological superconductor, $FeSe_{0.5}Te_{0.5}$.

III-T1-9: FRAGILE SUPERCONDUCTIVITY IN A DIRAC METAL

[EFRC – IQM]
Chris J. Lygouras[1], Junyi Zhang[1], Jonah Gautreau[2], Mathew Pula[2], Sudarshan Sharma[2], Shiyuan Gao[1,3], Tanya Berry[1], Thomas Halloran[1], Peter Orban[1], Gael Grissonnanche[3], Juan R. Chamorro[1], Kagetora Mikuri[3], Dilip K. Bhoi[4], Maxime A. Siegler[1], Kenneth J.T. Livi[1], Yoshiya Uwatoko[4], Satoru Nakatsuji[1,4,5,6], B. J. Ramshaw[3,6], Yi Li[1], Graeme M. Luke[2,7], Collin L. Broholm[1,8], and Tyrel M. McQueen[1].
[1]Johns Hopkins University; [2]McMaster University; [3]Cornell University; [4]University of Tokyo; [5]CREST, Japan Science and Technology Agency; [6]Canadian Institute for Advanced Research; [7]TRIUMF, Vancouver, Canada; [8]NIST Center for Neutron Research.

Presenter: Chris Lygouras

Studying superconductivity in Dirac semimetals is an important step towards understanding quantum matter with topologically non-trivial order parameters. We report the properties of the superconducting phase in single crystals of the Dirac material $LaCuSb_2$ prepared by the self-flux method. Chemical and hydrostatic pressure drastically suppress the superconducting transition. Furthermore, due to large Fermi surface anisotropy, magnetization and muon spin relaxation measurements reveal Type-II superconductivity for applied magnetic fields along the **a**-axis, and Type-I superconductivity for fields along the **c**-axis. Specific heat confirms the bulk nature of the transition, and its deviation from single-gap *s*-wave BCS theory suggests multigap superconductivity. Our tight-binding model points to an anisotropic gap function arising from spin-orbital texture near the Dirac nodes, and provides an explanation for the appearance of an anomaly in specific heat well below T_C. Given the existence of superconductivity in a material harboring Dirac fermions, $LaCuSb_2$ proves an interesting material candidate in the search for topological superconductivity.

Affiliated poster: [III-S1-33] Fragile Superconductivity in a Dirac Metal.

III-T1-10: HARNESSING QUANTUM GEOMETRY FOR THE DETECTION AND MANIPULATION OF ANTIFERROMAGNETISM

[EFRC – CATS]
Jianxiang Qiu[1], Zumeng Huang[2], Junyeong Ahn[1], Zhe Sun[2], Anyuan Gao[1], Jian Tang[2], Houchen Li[1], Ashvin Vishwanath[1], Qiong Ma[2], Suyang Xu
[1]Harvard University; [2]Boston College

Presenter: Jianxiang Qiu

CATS has a goal to discover new transport and optical phenomena in magnetic topological materials. In particular, the interaction between polarized light and quantum topological materials is a highly intriguing topic in physics. In the magnetic topological insulator $MnBi_2Te_4$, CATS explored the light-matter-interaction in the antiferromagnetically coupled even-layers. Using circular polarized light, we report the surprising observation of helicity-dependent optical control of the fully compensated antiferromagnetic order for the first time. CATS has discovered that such optical control comes from the unique antiferromagnetic circular dichroism, which appears only in reflection but remains absent in transmission. As the antiferromagnetic spin texture breaks the inversion symmetry, it also leads to magnetic photocurrents that have been rarely studied before. CATS used linearly polarized light and found that it could generate an intrinsic photocurrent that was sensitive to external electric and magnetic fields. We explain these phenomena from the perspective of the unique quantum geometric properties in the material.

Affiliated poster: [III-S1-20] Quantum geometric detection and manipulation of the antiferromagnetic order.

III-T1-11: MANIPULATING MOLECULAR ENTANGLEMENT VIA INELASTIC SCATTERING OF ITINERANT ELECTRONS

[EFRC – M^{2}QM]

Christian Bunker, Silas Hoffman[1], Xuanyan Jiang[1], Eric Swizter[3], Shuang-Long Liu[1], Garnet Chan[6], Hai-Ping Cheng[1,8], George Christou[1], Arthur Hebard[1], Richard Hennig[1], Steve Hill[2,7], Mark Pederson[4], Talat Rahman[3], Michael Shatruk[2], John Stanton[1], Neil Sullivan[1], Samuel Trickey[1], Vivien Zapf[5], Xiaoguang Zhang[1], and Xiao-Xiao Zhang[1]

[1]University of Florida; [2]Florida State University; [3]University of Central Florida; [4]University of Texas El Paso, [5]Los Alamos National Laboratory; [6]California Technology Institute; [7]National Laboratory of High Magnetic Field, [8]Northeastern University

Presenter: Christian Bunker

The Center for Molecular Magnetic Quantum Materials aims to discover, develop, and deliver the pivotal materials physics and chemistry knowledge of molecular magnetic quantum materials essential for quantum information technologies. Our goal is to transform molecular magnets from promising building blocks into viable *quantum materials* that are useful both for coherent quantum information systems and for quantum electron-spin devices. Our research activities cover magneto-electric couplings and magneto-striction in magnetic and electric field, spin-spin coupling, entanglement and decoherence, and spin coupling and entanglement at surfaces and in junctions due to molecule-substrate interactions. Starting with synthesizing a suite of molecules with desired properties, M^{2}QM experimentalists probe spin entanglement and decoherence using electron paramagnetic resonance at and away from the clock transition, measure magnetization at high magnetic field, electric polarization in a magnetic field and *vice versa* to study molecules that demonstrate spatial-inversion-symmetry-breaking and/or spin-crossover behavior, and measure spin-dependent tunneling current across magnetic molecule vertical junctions. Our theory and computation team collaborates closely with experimental counterparts to advance understanding of control quantum behavior. As an example, we introduce a theoretical model of a molecular system hosting a few molecular spin qubits. These qubits can experience exchange interactions with itinerant electrons which allow inelastic scattering processes. In the context of quantum computing, such two-qubit interactions are necessary for implementing a universal set of quantum gates, but are difficult to control in molecular systems. We demonstrate that the entanglement between the qubits can be manipulated via the degrees of freedom of the itinerant electrons.

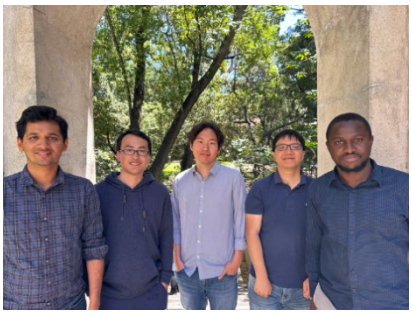
Affiliated poster: [III-S1-16] Molecular Magnetic Quantum Materials.

III-T1-12: DIVERSE NATURE OF EXCITONIC STATES IN TRANSITION METAL DICHALCOGENIDE MOIRÉ SUPERLATTICES

[CMS – C2SEPEM]

Mit H. Naik[1,2], Hongyuan Li[1,2], Chen Hu[1,2], Woochang Kim[1,2], Yusuf Shaidu[1,2], Ziyu Xiang[1,2], Jeffrey B. Neaton[1,2], Felipe H. da Jornada[3], Feng Wang[1,2], and Steven G. Louie[1,2]

[1]University of California at Berkeley; [2]Lawrence Berkeley National Lab; [3]Stanford University



Presenter: Mit H. Naik

(from left) Mit H. Naik, Hongyuan Li, Woochang Kim, Chen Hu and Yusuf Shaidu

Developing predictive, parameter-free methods and software tools to understand the science and applications of novel energy conversion and transfer processes in materials is a challenging quantum many-body problem, since in general excited-state phenomena are complex and accurate treatment of many-body interactions are essential. Here, we present some recent advances developed in our Center (C2SEPEM) using *ab initio* many-body field-theoretic techniques to address these challenges. We show recent progress in the development and validation of three open-source, production quality and highly scalable software packages – BerkeleyGW, StochasticGW and NanoGW – by combining novel theoretical concepts with advances in numerical methods and algorithms. For example, we demonstrate the capability of scaling unprecedented *GW* calculations to 10,000 electrons utilizing the entire Summit supercomputer at OLCF (more than 27,000 GPUs) achieving over 100 PFLOP/s of performance and time to solution to the order of minutes. Several breakthroughs in theory/method development and their applications are discussed. We developed a new *ab initio* time-dependent *GW* method to compute field-driven nonequilibrium and nonlinear excited-state phenomena including electron self-energy and excitonic effects. We showcase applications of this approach to understand novel Floquet-like band renormalization driven by excitonic field, and many-electron effects on second-harmonic generation. We developed new methods to describe exciton-phonon interactions and show that off-diagonal terms in the exciton-phonon coupling matrix elements are essential for predicting accurate exciton linewidths. Finally, we present a new pristine unit-cell matrix projection (PUMP) method to study excitons in large-area moiré superlattices. We predict moiré excitons that have a previously unidentified in-plane charge-transfer character.

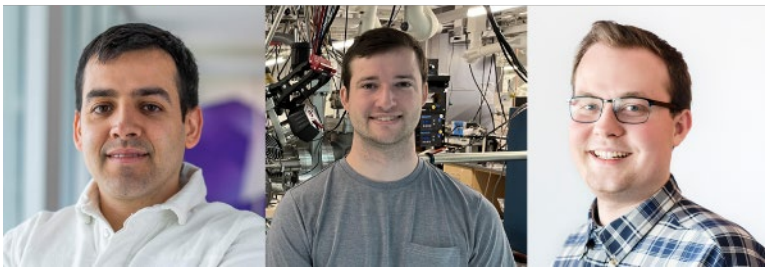
Affiliated poster: [III-S1-33] Many-Body Excited-State Phenomena in Materials: Methods and Applications.

Lightning Talk Session 2

III-T2-1: ATOMIC SCALE POLARIZATION SWITCHING IN NOVEL FERROELECTRICS

[EFRC – 3DFeM]

Sebastian Calderon V,[1] John Hayden,[2] Steven M. Baksa,[2] William Tzou,[1] Susan Trolier-McKinstry,[2] Ismaila Dabo,[2] Jon-Paul Maria,[2] Elizabeth C. Dickey[1]
[1]Carnegie Mellon University, [2]Pennsylvania State University



Presenter: Sebastian Calderon

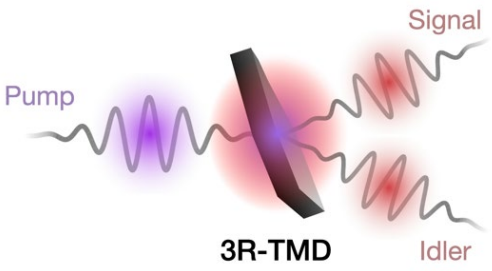
Caption: (from left) Sebastian Calderon, *John Hayden, Steven M. Baksa.*

Domain wall dynamics, including nucleation, motion, and pinning on structural defects define fundamental behaviors of ferroelectrics such as coercive bias, time dependent responses, nonlinearities, enhanced electromechanical and dielectric responses, amongst many others. Understanding the underlying mechanisms responsible for these fundamental behaviors is vital for the development of back-end-of-the-line compatible ferroelectric materials including $Hf_{1-x}Zr_xO_2$, $Al_{1-x}B_xN$, and $Zn_{1-x}Mg_xO$. Moreover, understanding the polarization dynamics in these materials requires probing these phenomena on the local level. Here, we apply a multimodal approach by implementing and cross correlating atomic force microscopy, scanning transmission electron microscopy, and various local optical techniques including nano-Fourier transform infrared spectroscopy, second harmonic generation, and photoluminescence. This allows us to leverage a variety of probe sizes ranging from 0.1 to 100 nm, to better understand how the functional properties are correlated with local intrinsic and extrinsic defects, ultimately enabling the further development of relevant materials. Furthermore, we develop and implement machine learning based scanning probe microscopy to investigate the correlation between local polarization hysteresis, nonlinearities with domain structures, and domain growth mechanisms, allowing for high-throughput characterization and understanding of local polarization phenomena. The combination of these advanced characterization techniques enables us to gain fundamental insight into the factors that affect ferroelectric switching and how ferroelectric domains nucleate and grow in $Hf_{1-x}Zr_xO_2$, $Al_{1-x}B_xN$, and $Zn_{1-x}Mg_xO$ material systems.

Affiliated poster: [III-S2-07] Developing local probes to understand polarization phenomena in wurtzite and fluorite ferroelectrics.

III-T2-2: LAYERED SEMICONDUCTORS ARE CHANGING THE GAME IN QUANTUM INFORMATION

[EFRC – Pro-QM]
Chiara Trovatello[1]
[1]*Columbia University*



Presenter: Chiara Trovatello

Caption: Generation of entangled photon pairs from a layered semiconductor (3R-TMD).

Nonlinear optics lies at the heart of classical and quantum sources of radiation which are essential for both fundamental spectroscopy and optical information processing. For example, one photon at frequency ω can annihilate into two lower energy photons, resulting in an entangled photon pair: the basic building block of a quantum computer. The maximum efficiency of a nonlinear process is achieved by minimizing the wave vector mismatch, at the so-called phase matching condition (Δk=0). Typical phase-matched nonlinear crystals have moderate nonlinearities (1-20 pm/V), but can achieve high conversion efficiencies (10-2-10-1) due to their large thickness (millimeter/centimeter). However, such macroscopic thickness does not easily lend itself to on-chip integration. Here we aim to miniaturize nonlinear crystals, achieving phase matching in engineered stacks of layered semiconductors such as non-centrosymmetric transition metal dichalcogenides, which possess huge nonlinear susceptibilities of 100-1000 pm/V and promise the same efficiencies of bulk crystals within micron-thicknesses. Bridging macroscopic and microscopic nonlinear optics will enable new on-chip technologies including nonlinear waveguides, nano-lasers, and entangled photon sources. More generally, miniaturized quantum light sources promise to impact the future of secure quantum information, creating entirely new digital protocols and technologies, and enabling significant advances in computing speed and energy efficiency.

Affiliated poster: [III-S2-17] Bridging macroscopic and microscopic nonlinear optics.

III-T2-3: LONG-RANGE, NON-LOCAL SWITCHING OF SPIN TEXTURES IN A FRUSTRATED ANTIFERROMAGNET

[EFRC – NPQC]

Shannon C. Haley[1,2], Valeria Rosa Rocha[1,2], Eran Maniv[3], Tessa Cookmeyer[1,2], Susana Torres-Londono[1], Meera Aravinth[1], Joel Moore[1,2], Robert J. Birgeneau[1], James G. Analytis[1,2]
[1]University of California, Berkeley; [2]Lawrence Berkeley National Laboratory; [3]Ben-Gurion University of the Negev

Presenter: Hossein Taghinejad

Antiferromagnetic spintronics is an emerging area of quantum technologies that leverage the coupling between spin and orbital degrees of freedom in exotic materials. Spin-orbit interactions allow spin or angular momentum to be injected via electrical stimuli to manipulate the spin texture of a material, enabling the storage of information and energy. In general, the physical process is intrinsically local: spin is carried by an electrical current, imparted into the magnetic system, and the spin texture will then rotate in the region of current flow. In this study, we show that spin information can be transported and stored ``non-locally'' in the material Fe_xNbS_2. We propose that collective modes can manipulate the spin texture away from the flowing current, an effect amplified by strong magnetoelastic coupling of the ordered state. This suggests a novel way to store and transport spin information in strongly spin-orbit coupled magnetic systems.

Affiliated poster: [III-S2-13] Long-range, Non-local Switching of Spin Textures in a Frustrated Antiferromagnet.

III-T2-4: THERMODYNAMICS OF NON-LINEAR OPTICAL RESPONSES OF FERROELECTRICS

[CMS – COMMS]

Aiden Ross[1], Rui Zu[1], Anna Morozovska[2], Venkatraman Gopalan[1], Long-Qing Chen[1]
[1]Penn State University, [2]Ukraine Academy of Sciences.

Caption: (left) Aiden Ross, (right) Rui Zhu

Presenter: Aiden Ross

Ferroelectric materials are prime candidates for non-linear photonic devices such as high-speed photonic modulators and quantum photonic integrated circuits owing to their excellent non-linear optical properties. However, there is a lack of a general theoretical framework to predict and understand the non-linear optical properties of ferroelectrics and their associated couplings to polarization, stress, and strain that are critical to their integration into photonic devices. We are developing a thermodynamic formulation to extend the widely used Landau-Ginzburg-Devonshire theory to accurately predict and optimize the optical properties of ferroelectrics. We separate the contributions of the ferroelectric soft mode and bound electrons to the total polarization and incorporate electro- and elasto-optical couplings. Our preliminary results on BaTiO3 demonstrate the capability of a newly developed thermodynamic energy function to accurately describe the experimentally measured temperature-dependent birefringence and electrooptic (Pockels) effect. The constructed thermodynamic model provides a new powerful tool to understand, predict, and engineer optical phenomena in ferroelectrics. In particular, the proposed theoretical framework will form the thermodynamic foundation for the phase-field model of non-linear optical properties of mesoscale ferroelectrics under development by our collaborating team with respective expertise in the phase-field method, advanced numerical algorithms, and non-linear optical properties of crystals.

Affiliated poster: [III-S2-21] Thermodynamics of Non-linear Optical Responses of Ferroelectrics.

III-T2-5: NON-LOCAL INTERACTIONS IN HYDROGENATED PEROVSKITE NICKELATE SYNAPTIC NETWORKS

[EFRC – Q-MEEN-C]

Ravindra S. Bisht[1], Jaeseoung Park[2], Haoming Yu[3], Chen Wu[4], Nikhil Tilak[1], Sylvie Rangan[1], Tae J. Park[3], Yifan Yuan[1], Sarmistha Das[4], Uday Goteti[4], Hee Taek Yi[1], Hussein Hijazi[1], Abdullah Al-Mahboob[5], Jerzy T. Sadowski[5], Hua Zhou[6], Seongshik Oh[1], Eva Y. Andrei[1], Monica T. Allen[4], Duygu Kuzum[2], Alex Frañó[4], Robert C. Dynes[4], and Shriram Ramanathan[1]

[1]Rutgers University; [2]Purdue University; [4]University of California San Diego; [5]Brookhaven National Laboratory; [6]Argonne National Laboratory

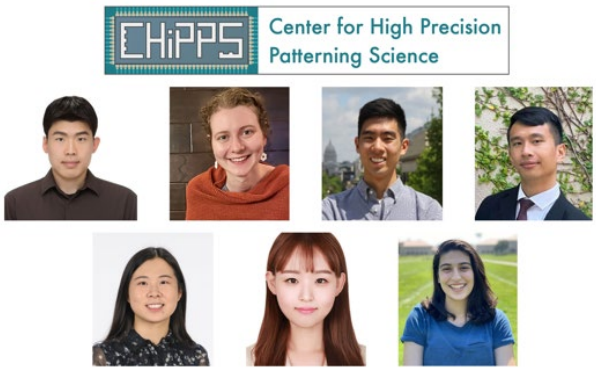
Presenter: Ravindra S. Bisht

Emulating features of biological intelligence in physical substrates is a central goal of neuromorphic computing. Chemical gradients at synaptic junctions influence signal transmission in spatially-distributed biological neural circuits through extracellular fields. Thus, one key aspect of how the brain learns and enables decision-making processes is via non-local synaptic interactions. Emulating such non-local behavior in synthetic networks can be of potential use for neuromorphic learning and hardware implementation of artificial intelligence. In this talk, we present a design concept for an artificial neural network where a stimulus across one synaptic junction can propagate non-locally onto other adjacent junctions. We made a network of hydrogen-doped perovskite nickelate devices, such that an electric bias across a single junction can tune the coupling strength between the neighboring cells in a non-local manner. Multi-modal spectroscopic studies on devices utilized for electrical measurements suggests that spatially graded hydrogen doping of the nickelate film enables the creation of an heterogenous electronic medium that can serve efficiently as a neuromorphic computing primitive. We further demonstrate a weighted sum operation with the nickelate platform, representing an essential function in artificial neural networks but in a much simpler way. This work demonstrates that the heterogeneity in the electronic properties of strongly correlated materials can be tailored and tuned to create a medium in which signals are transferred, which could lead to highly efficient design theme for hardware neural networks with scalable advantages.

Affiliated poster: [III-S2-12] Neuromorphic Networks with Quantum Materials.

III-T2-6: PUSHING THE PRECISION LIMITS IN EUV LITHOGRAPHY: OVERCOMING STOCHASTICS WITH DIRECTED SELF-ASSEMBLY AND AREA-SELECTIVE ATOMIC LAYER DEPOSITION

[EFRC – CHiPPS]
Kyunghyeon Lee[1,2], Emma Vargo[3], Christopher J. Eom[1,2], Areza Sumitro[3], Beihang Yu[3], Yujin Lee[4], Maggy Harake[4], Rachel Segalman[5], Stacey Bent[4], Ricardo Ruiz[3], Paul F. Nealey[1,2]
[1]Argonne National Laboratory; [2]University of Chicago; [3]Lawrence Berkeley National Laboratory; [4]Stanford University; [5]University of California, Santa Barbara



Presenter: Kyunghyeon Lee

Caption: (from upper left) Kyunghyeon Lee, Emma Vargo, Christopher J. Eom, Areza Sumitro (from lower left) Beihang Yu, Yujin Lee, Maggy Harake

The introduction of EUV lithography has provided a pathway for continued scaling of semiconductor manufacturing by enabling smaller features thanks to the much shorter wavelength of EUV photons. However, the use of this high energy radiation has also led to stochastic variations due to both low photon counts and random variations within the patterning materials that limit the quality of the lithographic patterns at high resolution and throughput. To mitigate stochastic effects, we've turned to two bottom-up approaches: First, we demonstrate directed self-assembly (DSA) of block copolymers to rectify imperfections in EUV patterns that leverages smooth interface between two immiscible blocks. Our approach starts with a new family of A-b-(B-r-C) copolymers where the surface energy and the interaction parameter χ between the polymer blocks can be tuned separately, enabling self-assembling structures that are compatible with lithographic processes at EUV-relevant dimensions. This material provides improved roughness control within the high χ region as well as insights into the impact of χ on pattern quality. Second, recognizing the challenges in pattern transfer from thinner resist films at smaller dimensions, we introduce the use of sequence-define polypeptoid brushes as preferential nucleation sites for a new type of area-selective deposition by vapor phase infiltration. By grafting these brushes in targeted areas alongside blocking agents, we successfully create an inorganic hardmask after a minimal number of atomic layer deposition cycles, facilitating a fast and precise pattern transfer. Through these comprehensive strategies, we address the stochastic challenges in EUV lithography, enabling high-precision patterning for next-generation lithography.

Affiliated poster: [III-S2-36] Overcoming Stochastics in EUV Lithography by Directed Self-Assembly and Area-Selective Atomic Layer Deposition.

III-T2-7: CIRCULAR DICHROISM OF CRYSTALS FROM FIRST PRINCIPLES

[CCS – ADEPTS]

Christian Multunas[1], Andrew Grieder[2], Junqing Xu[2], Yuan Ping[2,3], and Ravishankar Sundararaman[1]
[1]Rensselaer Polytechnic Institute; [2]University of Wisconsin-Madison; [3]University of California, Santa Cruz

Presenter: Rafi Ullah

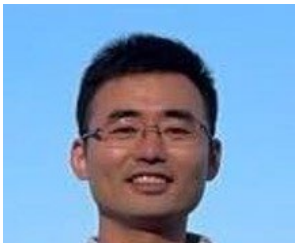
Caption: Christian Multunas

Chiral crystals show promise for spintronic technologies on account of their high spin selectivity, which has led to significant recent interest in quantitative characterization and first-principles prediction of their spin-optoelectronics properties. Here, we develop a computational framework for efficient ab-initio calculations of circular dichroism (CD) in crystalline materials. We leverage direct calculations of orbital angular momentum and quadrupole matrix elements in density-functional theory (DFT) and Wannier interpolation to calculate CD in complex materials, removing the need for band convergence and accelerating Brillouin-zone convergence compared to prior approaches. We find strong agreement with measured CD in molecules and crystals, ranging in complexity from small bulk unit cells to 2D hybrid perovskites, and show the importance of the quadrupole contribution to the anisotropic CD in crystals. We showcase the capability to predict CD for complex structures on a 2D hybrid perovskite, finding strong orientation dependence and identifying the eigen-directions of the unit cell with the strongest CD. We additionally decompose CD into separate contributions from inorganic, organic, and mixed organic-inorganic transitions, and find that the chiral molecules dominate the CD, with the inorganic lattice contributing at higher frequencies in specific directions. This unprecedented level of detail in CD predictions in crystals will facilitate experimental development of complex chiral crystals for spin selectivity, and lays the groundwork for first-principles simulation of spin transport and dynamics in these materials within our CCS collaboration targeting spin-selective chemistry.

Affiliated poster: [III-S2-35] Spin Dynamics and Transport using Ab initio Density-Matrix Dynamics.

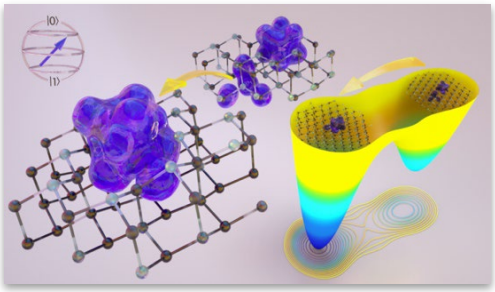
III-T2-8: ENGINEERING THE FORMATION OF SPIN-DEFECTS FROM FIRST PRINCIPLES

[CMS – MICCoM]
Cunzhi Zhang[1], Francois Gygi [2], Giulia Galli [3, 1]
[1]University of Chicago; [4]University of California, Davis; [3]Argonne National Laboratory



Presenter: Cunzhi Zhang

The full realization of spin qubits for quantum technologies relies on the ability to control and design the formation processes of spin defects in semiconductors and insulators. We present a computational protocol to investigate the synthesis of point-defects at the atomistic level, and we apply it to the study of a promising spin-qubit in silicon carbide, the divacancy (VV). The strategy combines electronic structure calculations based on density functional theory and enhanced sampling techniques coupled with first principles molecular dynamics. We predict the optimal annealing temperatures for the formation of VVs at high temperature and show how to engineer the Fermi level of the material to optimize the defect's yield for several polytypes of silicon carbide.



Caption: Pictorial representation of the free energy of formation of a double vacancy in SiC.

Affiliated poster: [III-S2-05] MICCoM: Recent progress and new directions.

III-T2-9: A NEW GENERATION OF RARE-EARTH PSEUDOPOTENTIALS AND APPLICATIONS TO QUANTUM MATERIALS

[CMS – CPSFM]

Gani Annaberdiyev[1], Haihan Zhou[2], Benjamin Kincaid[2], Guangming Wang[2], Subhasish Mandal[3], Jaron T. Krogel[1], Lubos Mitas[2], Panchapakesan Ganesh[1]
[1]*Oak Ridge National Laboratory;* [2]*North Carolina State University;* [3]*West Virginia University*

Presenter: Paul Kent

In this poster we highlight recent progress in many-body quantum mechanical calculations for correlated and quantum materials including for $TbMn_6Sn_6$, a proposed quantum limit Chern magnet, the antiferromagnetic topological insulator, $MnBi_2Te_4$, and the 2D magnetic monolayer CrI_3. The electronic correlations, magnetism, van der Waals, and spin-orbit interactions in these materials challenge first principles methods. We therefore have developed and utilize new first-principles Quantum Monte Carlo (QMC) techniques including for obtaining fully relaxed geometries in QMC, for including spin-orbital effects, and make use of our newly developed correlation-consistent effective core potentials (ccECPs), including for the rare-earths. These developments are released for wider application in the open-source QMCPACK code (https://qmcpack.org, https://github.com/QMCPACK/qmcpack) and website https://pseudopotentiallibrary.org. These activities are part of the Center for Predictive Simulation of Functional Materials (https://cpsfm.ornl.gov) which is focused on the development, validation, and distribution of external-parameter-free methods and open-source codes to predict and understand the properties of functional materials, emphasizing those with strong electronic correlations, van der Waals, and spin-orbit interactions.

Affiliated poster: [III-S2-22] Center for Predictive Simulation of Functional Materials.

III-T2-10: CHEMOMECHANICAL MODIFICATION OF QUANTUM EMISSION IN MONOLAYER WSe_2

[EFRC – CMQT]

M. Iqbal Bakti Utama[1], Hongfei Zeng[1], Tumpa Sadhukhan[1], Anushka Dasgupta[1], S. Carin Gavin[1], Riddhi Ananth[1], Dmitry Lebedev[1], Wei Wang[2], Jia-Shiang Chen[2], Kenji Watanabe[3], Takashi Taniguchi[3], Tobin J. Marks[1], Xuedan Ma[2], Emily A. Weiss[1], George C. Schatz[1], Nathaniel P. Stern[1], Mark C. Hersam[1]
[1]Northwestern University; [2]Argonne National Laboratory; [3]National Institute for Materials Science, Japan

M. Iqbal Bakti Utama

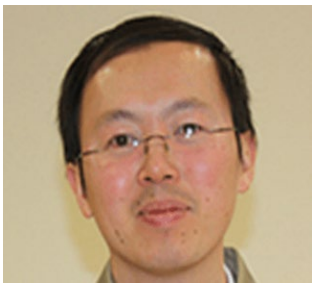
Presenter: M. Iqbal Bakti Utama

Two-dimensional (2D) materials have attracted attention for quantum information science due to their ability to host single-photon emitters (SPEs). Although the properties of atomically thin materials are highly sensitive to surface modification, chemical functionalization remains unexplored in the design and control of 2D material SPEs. Here, we report a chemomechanical approach to modify SPEs in monolayer WSe_2 through the synergistic combination of localized mechanical strain and noncovalent surface functionalization with aryl diazonium chemistry. Following the deposition of an aryl oligomer adlayer, the spectrally complex defect-related emission of strained monolayer WSe_2 is simplified into spectrally isolated SPEs with high single-photon purity. Density functional theory calculations reveal energetic alignment between WSe_2 defect states and adsorbed aryl oligomer energy levels, thus providing insight into the observed chemomechanically modified quantum emission. By revealing conditions under which chemical functionalization tunes SPEs, this work broadens the parameter space for controlling quantum emission in 2D materials.

Affiliated poster: **[III-S2-09]** Chemomechanical modification of quantum emission in monolayer WSe_2.

III-T2-11: IMPACTS OF SHORT-RANGE ORDER ON PROPERTIES OF GROUP IV ALLOYS

[EFRC – μ-ATOMS]
Shunda Chen[1], Shang Liu[2], Xiaochen Jin[1], Yunfan Liang[3], J. Zach Lentz[4], Lilian Vogl[5], Damien West[3], Dragica Vasileska[6], Shui-Qing Yu[7], Paul McIntyre[4], Andrew Minor[5], Shengbai Zhang[3], Jifeng Liu[2] and Tianshu Li[1]
[1]George Washington University; [2]Dartmouth College; [3]Rensselaer Polytechnic Institute; [4]Stanford University; [5]University of California, Berkeley; [6]Arizona State University; [7]University of Arkansas



Presenter: Dr. Shunda Chen

Group IV alloys hold great promise as silicon-compatible materials, enabling complementary metal-oxide-semiconductor (CMOS) monolithic integration for electronic, photonic, and topological quantum applications. A precise control of their structure and properties requires a deep understanding of the structure-property relationship in these alloys. Our recent theoretical studies have revealed a significant short-range order (SRO) behavior in Group IV alloys and further showed SRO leads to substantial changes in electronic band structures, vibrational properties, thermal transport, and topological properties. These findings suggest that the traditional composition-property paradigm is insufficient in group IV alloys, and more importantly, atomic ordering can constitute a new tuning dimension for enabling novel applications. To gain a deep understanding of the alloy structures obtained by different growth methods, we utilized a combined theory-characterization approach. This involves a multi-modal characterization using atom-probe tomography, 4D-STEM, and EXAFS, confirming the presence of SRO in (Si)GeSn. Additionally, we developed a highly accurate and efficient machine-learning interatomic potential based on an evolutionary neural network framework, trained from DFT calculations. This new development enables a side-by-side comparison with experimental techniques such as atom probe tomography and 4D-STEM at the same spatial scale while uncovering new and intriguing SRO structural properties. Our collaborative research sheds light on the importance of SRO in Group IV alloys and its potential implications for novel applications. By providing fundamental insights into the structure-property relationship, it may open new pathways for materials design and engineering, advancing technological applications.

Affiliated poster: [III-S2-23] Nature of short-range order in group IV alloys.

III-T2-12: CONTROLLING LIGHT EMISSION FROM MONOLAYER MoS_2 WITH DIELECTRIC METASURFACES

[EFRC – PTL]
S. C. Lau[1], Y. Liu[1], W. S. Cheng[2], A. Johnson[1], Q. Li[1], E. Simmerman[1], O. Karni[1,3], J. Hu[1], F. Liu[1], M. Brongersma[1], T. F. Heinz[1,3], and J. A. Dionne[1]
[1]Stanford University. [2]National Cheng Kung University, Taiwan. [3]SLAC National Accelerator Laboratory

Presenter: Sze Cheung Lau

We investigate the modulation of excitonic properties in monolayer molybdenum disulfide (MoS_2), a semiconducting transition metal dichalcogenide (TMDC), through the use of dielectric metasurfaces comprised of silicon nano-disks. MoS_2 monolayers possess robust excitons with a valley degree of freedom, which is accessible through circularly polarized light. By strategically coupling MoS_2 with metasurfaces, we achieve precise manipulation of valley excitonic emission, impacting intensity, wavelength, and polarization.

By tailoring the dimensions of silicon nano-disks, we tune the disks' Mie scattering modes to match the frequency of MoS_2 exciton emission. The design yields an enhancement of MoS_2 photoluminescence (PL) intensity exceeding 30 times that of monolayers on flat substrates. The enhancement results from both excitation and emission amplification by metasurface modes.

We also observe notable modifications in MoS_2 emission spectral distribution due to interactions between neutral excitons, trions, and defect-bound excitonic states with metasurface resonances. The correlation between circular polarization of PL emission and metasurface modes is attributed to the Purcell effect, which is supported by photoluminescence lifetime measurements.

Beyond the experimental findings, our study employs comprehensive electromagnetic simulations to elucidate the metasurface response, advancing our comprehension of nanoscale light-matter interactions. The research highlights the potential of dielectric metasurfaces for shaping and exploiting excitonic behavior in semiconducting monolayers like MoS_2, which support tailored nanophotonic applications of such material systems.

Affiliated poster: [III-S2-41] Controlling Light Emission from Monolayer MoS_2 with Dielectric Metasurfaces.

POSTER PRESENTATION ABSTRACTS

Day 1 – September 19, 2023

Poster Session 1

I-S1-01: DIRECT INSERTION POLYMERIZATION OF IONIC MONOMERS: RAPID PRODUCTION OF ANION EXCHANGE MEMBRANES

[EFRC – CABES] Jesse H. Hsu,[1] Cheyenne R. Peltier,[1] Megan Treichel,[2] Jamie C. Gaitor,[2] Qihao Li,[1] Renee Girbau,[1] Alexandra J. Macbeth,[1] Héctor D. Abruña,[1] Kevin Noonan,[2] Brett Fors,[1] Geoff Coates,[1]
[1]Cornell University; [2]Carnegie Mellon University

The limited number of methods to directly polymerize ionic monomers currently hinders rapid diversification and production of ionic polymeric materials, namely anion exchange membranes (AEMs) which are essential components in emerging alkaline fuel cell and electrolyzer technologies. Herein, we report a direct polymerization of cationic monomers, providing the first direct synthesis of aliphatic polymers with high ion incorporations and allowing facile access to a broad range of materials.

I-S1-02: STABLE SOLID MOLECULAR HYDROGEN ABOVE 900K FROM A MACHINE-LEARNED POTENTIAL TRAINED WITH DIFFUSION QUANTUM MONTE CARLO

[CMS – QMC-HAMM] Hongwei Niu,[1] Yubo Yang,[2,3] Scott Jensen,[3] Markus Holzmann,[4] Carlo Pierleoni,[5] and David M. Ceperley[3]
[1]Institute of Technology, China; [2]Flatiron Institute; [3]University of Illinois at Urbana-Champaign; [4]University Grenoble Alpes, France; [5]University of L'Aquila, Italy

AFFILIATED TALK – I-T1-8: Stable solid molecular hydrogen above 900K from a machine-learned potential trained with diffusion Monte Carlo

We survey the phase diagram of high-pressure molecular hydrogen with path integral molecular dynamics using a machine-learned interatomic potential trained with Quantum Monte Carlo forces and energies. Besides the HCP and C2/c-24 phases, we find two new stable phases both with molecular centers in the Fmmm-4 structure, separated by a molecular orientation transition with temperature. The high temperature isotropic Fmmm-4 phase has a reentrant melting line with a maximum at higher temperature (1450K at 150GPa) than previously estimated and crosses the liquid-liquid transition line around 1200K and 200GPa.

I-S1-03: ADVANCING IN SITU CHARACTERIZATION TO PROBE DYNAMIC CATALYTIC STATES AND FUNCTIONALIZATION

[ERFC – CD4DC] Simon M. Vornholt[1], Haomiao Xie[2], Qining Wang[2], Andrew Ritchhart[3], Špela Kunstelj[3], Zhihengyu Chen[1], Zoha Syed[2], Seryeong Lee[2], Julian Schmidt[4], Luke M. Tufaro[1], Nancy M. Washton[4], Johannes Lercher[4], Anna Wuttig[3], Massimiliano Delferro[5], John S. Anderson[3], Justin Notestein[2], Omar K. Farha[2], Joseph T. Hupp[2], Karena W. Chapman[1]

[1]Stony Brook University, [2]Northwestern University, [3]University of Chicago, [4]Pacific Northwest National Laboratory, [5]Argonne National Laboratory

The dynamic structure and chemistry of metal-organic frameworks (MOFs) that make them excellent platforms for catalysis design, also make it both challenging and important to understanding their structure and how they transform during reactions. Advanced spectroscopic and scattering approaches are needed to resolve MOF defects and dynamics at multiple spatial and temporal scales, to identify the active catalytic state as feedback for complementary computation and catalysis development. Within CD4DC, we combine advanced probes such as pair distribution function (PDF) analysis, single crystal and powder diffraction, X-ray absorption spectroscopy and solid-state nuclear magnetic resonance (NMR) spectroscopy.

For sulfur-based MOFs, which have promising electrochemical properties, we have harnessed multivariate data analytics to resolve preferential ordering in directly synthesized S-based MOFs and to interpret *in situ* PDF studies to sulfidize conventional non-S containing MOFs by substituting bonded oxygen or halides with S atoms. These first-of-a-kind measurements and analysis significantly push the frontier of MOF characterization.

For Zr_6O_8 based MOFs, we have identified how the catalytic activity is enhanced by chemical functionalization the MOF surface. We have documented rich cooperativity and hysteresis in the Zr_6O_8 node distortions dynamics—with the distorted node being linked to higher catalytic activity, this has important implications for understanding the catalysis.

I-S1-04: TARGETED CARGO LOADING AND CHARACTERIZATION OF REACTION MICROENVIRONMENTS INSIDE BACTERIAL MICROCOMPARTMENTS

[EFRC – CCBC] Alexander Jussupow,[1] Michael Feig,[1] Yali Wang[1], Robert P. Hausinger,[1] Nicholas M. Tefft,[1] Michaela A. TerAvest,[1] Joel Landa,[1] Eric L. Hegg,[1] Samuel Snyder,[2] Lisa M. Utschig,[2] Nina Ponomarenko,[2] Oleg Poluektov,[2] Karen L. Mulfort,[2] Markus Sutter[3] and David M. Tiede[2]
[1]Michigan State University, [2]Argonne National Laboratory and [3]Lawrence Berkeley National Laboratory

An integrated program of computational modeling benchmarked to experimental measurements is being developed within the CCBC to resolve mechanisms by which Nature spatially organizes catalysis across scales using compartmentalization and tuned microenvironments within selectively permeable protein shell wall-based bacterial microcompartments (BMCs). This program includes the development of a molecular modelling approach to address the fundamental mechanisms for BMC assembly and targeted enzyme cargo loading. Ongoing computational work compares the energetics of BMC shell protein oligomer interactions with cargo protein condensation as key determinants of spontaneous assembly of enzyme-loaded microcompartments. Experimental approaches for testing the effects of confinement on catalytic pathways are being developed using several enzyme based and abiotic catalyst systems. Enzyme systems include pathways for aromatic metabolism, nitrate reduction, and glycolysis. Abiotic catalyst systems include photocatalysts and biohybrids for hydrogen production. Finally, site-specific optical and electron paramagnetic resonance (EPR) nitroxide spin molecular probes are

being used to interrogate microenvironments within cargo-loaded BMCs, including assessing pO_2, pH, viscosity, and enzyme dynamics at local interior sites. For example, using EPR spin labeling of site-directed cysteine mutations in a multiheme PpcA as a model cargo protein, we have implemented multiscale modeling protocols for analysis of site-specific protein dynamics from EPR spin probe line broadening measurements. These labeling approaches will enable effects of protein crowding and viscosity within BMC shells to be characterized, including quantitative benchmarking to dynamics modelling, and will be extended to probe local sites on a suite of HO-BMC shell proteins and targeted enzyme cargo.

I-S1-05: STIMULATED ABSORPTION AND EMISSION FROM DIVERSE TiO_2 CRYSTAL FACETS DURING THE OXYGEN EVOLUTION REACTION

[EFRC – CEDARS] Michael Paolino[1], Casey Boyd[1], Jennifer Sormberger[1], Luka Mitrovic[1], Shaylee McBride[2], Sheilah Cherono[3], David Jonas[1], Darrell Schlom[4], Jin Suntivich[4], Shyam, Aravamudhan[3], Geoffroy Hautier[2], Dhananjay Kumar[3], Tanja Cuk[1]
[1]University of Colorado at Boulder; [2]Dartmouth College; [3]North Carolina Agricultural and Technical State University; [4]Cornell University

AFFILIATED TALK – I-T1-9: Electrocatalytic Properties of Pulsed Laser-Deposited Titanium Dioxide and Titanium Oxynitride Thin Films Grown on Photo-adsorbing Single Crystal Substrates with Different Orientations

Optical spectroscopy of the photo-electrochemistry of TiO2 for the oxygen evolution reaction (OER) from water serves as the model system for disentangling non-equilibrium intermediates of the driven catalytic cycle. Here, ultrafast optical spectroscopy is carried out on single crystal surfaces with controlled electron doping by Nb upon the trigger of the spontaneous, downhill reaction. The current focus is on the absorptive and emissive transitions and their assignment to surface intermediates across diverse crystal facets of TiO2. There are three fronts to the assignment. The first is the time-resolved broadband, visible probe of the surface hole kinetics. Certain optical transitions may be meta-stable, identifying intermediate populations of the reaction. These intermediate populations should further be sensitive to varying conditions of the interface, including electron-hole recombination (by circuit conditions) and the protonation of the hydration layer (by the crystal facet and the electrolyte). The second is a theoretical effort to determine the energetics of optical transitions between electrons at the band edges and surface hole traps, or hole polarons, which are largely associated with the visible regime but can vary within it. The goal is to correlate with experiment where the absorptive and emissive transitions lie spectrally across the diverse surfaces. The last front is to utilize the optical transitions themselves to identify thermodynamics of excited states at the solid-liquid interface. This will be advanced using a recent extension of Einstein's stimulated emission, stimulated absorption, and spontaneous emission coefficients to a broadband probe of thermal quasi-equilibrium in the excited state.

I-S1-06: CONTROL OVER PHOTOCHEMICAL CHARGE ACCUMULATION VIA LONG-LIVED EXCITED STATES IN ENSEMBLES OF PHOTOSYNTHETIC NANOREACTORS

[EFRC – EPN] Lauren Pellows[1], Faith Flinkingshelt[2], Zejie Chen[2], Olivia Bird[1], Bradley W. Layne[2], Honghao Liu[2], Evan Gowdy[3], Kenneth Drbohlav[3], Sophia Click[1], Hiroaki Maekawa[2], Shane Ardo[2], Jenny Yang[2], Gordana Dukovic[1], Kenneth A. Miller[3], Nien-Hui Ge[2]
[1]University of Colorado Boulder; [2]University of California Irvine; [3]Fort Lewis College

Photocatalytic charge separation and charge accumulation are poorly understood processes at the nanoscale, motivating our approach to incorporate well-defined reaction centers on nanoparticle surfaces and study their influence on photogenerated carrier lifetimes and the efficiency of solar water splitting. Toward this, we take a multifaceted approach that involves nanomaterial and molecular synthesis, steady-state and time-resolved spectroscopy, and photocatalytic performance. Semiconductor materials such as CdS nanocrystals were chosen as they are strong light absorbers and have tunable band structures and surface chemistries for coupling to precise molecular sites for charge accumulation. We have identified strong bonding of phosphonate-modified viologens and phenothiazines as target electron and hole acceptors, respectively, and shown that long-lived singly reduced viologens can be formed upon photoexcitation. Motivated by this results, we synthesized phosphonate-modified $[Ni(PR_2NR_2)_2]^{2+}$, a state-of-the-art molecular electrocatalyst for the H_2 evolution reaction, and bound it to nanocrystals to study the dependence of driving force on charge accumulation required for effective light-driven multiple electron/proton photochemistry. Experimental investigations are supported by numerical Monte Carlo simulations of the kinetics of the steps involved in the photochemical reactions to understand how to balance catalytic rates, catalyst coverage, and inhibiting back reactions. Modeling efforts are being expanded to include the effects of optical properties and spatial light intensities within a three-dimensional reactor to inform us of performance expected from ensembles of photosynthetic nanoreactors under solar illumination.

I-S1-07: CHARGE TRANSPORT AND DURABILITY IN N-TYPE CONDUCTING POLYMERS: COMBINING THEORY, COMPUTATION, AND PRACTICAL APPLICATION

[EFRC – SPECS] Joseph A. Romo[5], Jean-Luc Bredas (KI)[3], Dean Deanlongchamp[6], Marlow M. Durbin[4], Aalok Gaitonde[5], Lucas Q. Flagg[6], Seth Marder(KI)[2], Jianguo Mei (KI)[5], Adam Printz (KI)[1] Erin Ratcliff (PI)[1], Chad Risko (KI)[4], Andrew Setley[4], Chad R. Snyder[6], Natalie Stingelin (KI)[4]
[1]University of Arizona [2]University of Colorado Boulder Department; [3]University of Kentucky; [4]Georgia Institute of Technology; [5]Purdue University; [6]National Institute of Standards and Technology (NIST)

The SPECS vision is to use low-cost, highly scalable, durable electroactive polymers for energy conversion and storage technologies. Ubiquitous across multiple energy platforms is the use of electrochemical doping of conductive polymers to promote large changes in material conductivity and carrier density. For aqueous electrolytes, the emerging strategy has been the use of glyoclated side chains, an approach that rarely yields stable materials, especially for n-type materials. Here we show that using a set of different side chains, active swelling under conditions of applied bias is dominated by side-chain free volume. We then compare these insights with a major surprise has been observed in the development of a highly conductive n-type polymer with no side chains,

based on n-type poly(benzodifurandione) (n-PBDF) - a breakthrough in the field of conducting polymers. In comparison with the existing electroactive polymers, n-PBDF is scalable and durable, and has high electrical conductivity. Theoretical investigations using long oligomers and one-dimensional (1D) periodic chains as model systems have predicted near-metallic conductivity in the quasi one dimensional chains arising from a singlet bipolaron (energetically most favorable species) that is achieved when protons bind to two adjacent carbonyl groups in nearest-neighbor benzodifuran moieties. Preliminary investigations using time-dependent density function theory (TDDFT) have predicted changes of optical signatures with degradation. Experimentally, investigations include understanding strain and delamination effects and structural characterizations of n-PBDF thin films and correlated morphological information with their electrochemical properties. Collectively these results are informing next-generation materials design with advances in both transport and materials durability.

I-S1-08: NOVEL DIGITAL LIFECYCLE APPROACH TO MODELING THERMOFORMED POLYMER COMPOSITES: FROM PROCESS PARAMETERS TO MACROSCALE PROPERTIES

[AIM for Composites] Sai Aditya Pradeep[1], Tatiana Stepanova, Madhura Limaye[1], Madhura Athale[2], Taejoon Park[2], Farhang Pourboghrat[2], Gang Li[1], Srikanth Pilla[1]
[1]Clemson University; [2]The Ohio State University

The thermoforming process fabricates polymer composites via a complex interplay between material, process, microstructure, and performance (MP2). Aspects such as pre-heating temperature, cooling rate, mold design, sheet thickness, and clamping force significantly affect fiber orientation, void distribution, and residual stress. These variables introduce anisotropy within thermoformed polymer composites, creating challenges in characterization and modeling. Further complexities stem from strain-rate and temperature-dependent properties of polymers and fibers, and the localized crystallinity induced by the cooling rate. This leads to location and time-specific properties, as well as a tension-compression asymmetry due to uneven distributions of fibers and voids.

A key focus of our study is to address the above challenges by constructing a computational model that incorporates process-induced factors, predicting the properties of the composite part and thereby forming the foundation of our innovative Digital Lifecycle (DLC). Our DLC employs high-fidelity Finite Element Analysis models of the thermoforming process to accurately capture thermo-mechanical behavior and the effects of fiber reinforcements. This approach aims to elucidate the influence of process parameters on the final properties of composites and provide insights for developing an inverse design model.

I-S1-09: QMC-HAMM: HIGHLY ACCURATE MULTISCALE MODELS FROM QUANTUM MONTE CARLO SIMULATIONS

[CMS – QMC-HAMM] Tawfiqur Rakib,[1] Kittithat Krongchon,[1] Daniel Palmer,[1] Sonali Joshi,[1] Scott Jensen,[1] Elif Ertekin,[1] Harley T. Johnson,[1] David M. Ceperley,[1] Lucas K. Wagner[1]
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Large length scale effective models form a cornerstone of our understanding of physics in materials. These models include atomic-scale force fields, lattice models of electrons, and continuum/field models. With the development of practical neural networks and other machine learning tools, these models now have the capability to come close to the accuracy of first principles calculations. Thus to move to more accurate models, the accuracy of the first principles data is the limiting factor. Quantum Monte Carlo (QMC) simulations allow us to improve accuracy significantly over density functional theory, albeit at a higher computational cost.

In QMC-HAMM, we develop tools and techniques that allow us to base effective models on QMC calculations. We have focused on two main application areas: hydrogen at high pressure and bilayer graphene. Because of the high cost of the QMC calculations, part of the tool development is in the development of multilevel models and smart generation of data. In both of these systems, we have produced high accuracy models that can be used to compute phase diagrams, electronic behavior, and quantitative atomic motion.

I-S1-10: SYNTHESIS AND ASSEMBLY PATHWAY MANIPULATION VIA DYNAMIC INTERVENTION

Huat Chiang[1], Kacper Lachowski[1], Kiran Vaddi[1], Nada Naser[1], Kaylyn Torkelson[1], Will Wixson[1], Yifeng Cai[1], Zhiyin Zhang[2], Abdul Moeez[1], Muammer Yaman[1], Hao Shen[1], Eric Lynch[1], Susrut Akkineni[1], Maxim Ziatdinov[6], Justin Kollman[1], David Baker[1], James De Yoreo[1,3], Oleg Gang[4], Francois Baneyx[1], James Pfaendtner[1,3], Akif Tezcan[2], Andy Ferguson[5], Sergei Kalinin[7], David Ginger[1], Lilo Pozzo[1]
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Pathway manipulation in the synthesis and assembly of organic and inorganic nanomaterials opens opportunities to achieve complex ordered structures that are metastable, transient or that can switch between multiple states through their inherent out-of-equilibrium nature. However, achieving control over the assembly, disassembly, and/or reversible state 'switching' of nanomaterials requires the application of detailed molecular design principles, tools for rapid structure/property characterization, informed manipulation, and effective exploration of very large multi-dimensional design spaces. Here, we showcase examples of (1) integrated experimental and modeling frameworks to enable the design of metastable nanomaterials and (2) the effective exploration and optimization of target nanostructures using dynamic intervention, which is the temporal manipulation of pathways to alter the assembly of nanoscale structures. We demonstrate dynamic intervention for the synthesis of metallic 2D nanomaterials using peptide-directed growth, where the influence of the sequence of the peptide, the relative concentration or reagents and the delivery 'schedule' is systematically explored using robotic tools and artificial intelligence (AI). We also demonstrate the molecular design and dynamic manipulation of switchable protein assemblies, based on optical and chemical stimulation. Finally, we outline how the center integrates automation, machine learning (e.g. variational autoencoders), AI-based exploration of large molecular design spaces, intentional molecular design of metastable states, and powerful tools (i.e. SAXS, hyperspectral imaging) for in-situ structural assessment that can

enable access to new sophisticated approaches for dynamic pathway manipulation in diverse material systems.

I-S1-11: SELECTIVE CONVERSION OF CAPTURED CO_2 VIA IONIC LIQUIDS ON METALLIC LEAD INTERFACES IN NON-AQUEOUS ELECTROLYTES

[EFRC – 4C] Rowan Brower[1], Saudagar Dongare[2], Libo Yao[4], Charles McCrory[4], Burcu Gurkan[2], Jesús Velázquez[1]
[1]University of California, Davis; [2]Case Western Reserve University; [3]University of Michigan, Ann Harbor

The successful reactive capture and conversion (RCC) of CO_2 into valuable chemicals are pivotal in advancing renewable energy and mitigating greenhouse gas emissions. Despite significant progress in reactor and catalyst design, achieving optimal CO_2 conversion efficiency, stability, and selectivity remains a challenge. Exploring catalytic systems with tunable surface-active sites under relevant RCC conditions is crucial. A promising strategy for gaining better control over product selectivity and activity involves enhancing the microenvironment of metallic catalysts through polymer overlayers.

This research collaboration within 4C capitalizes on the expertise of the Gurkan Lab in synthesizing ionic liquids and the McCrory Lab's ability to tailor microenvironments in molecular catalysis. Preliminary results show that when polarized, Pb electrodes are used in nonaqueous electrolytes containing ionic liquid EMIM [2-Cynpr] product selectivity shifts from oxalate to more efficient CO production. Moreover, in nonaqueous electrolytes, we have successfully created an enhanced microenvironment on trace metallic Pb for selective CO_2 conversion to oxalate on carbon supports. Notably, trace metallic Pb on the ppb scale demonstrates comparable faradaic efficiencies (FE), FE_{ZnC2O4} ~ 84%, to bulk metallic Pb, FE_{ZnC2O4} 90%, from -2.1 to -1.8 V vs. Fc/Fc+ for the reductive coupling of CO_2, and polymer encapsulation of trace Pb fosters an enhanced microenvironment promoting oxalate selectivity over CO. Trace metallic Pb was quantified using Inductively Coupled Mass Spectrometry (ICP-MS), and CO_2 conversion to oxalate was determined via isotopic labeling using MALDI mass spectrometry (MALDI-MS) with $^{13}CO_2$.

I-S1-12: A TANDEM PHOTOELECTROCHEMICAL/PHOTOTHERMAL SYSTEM FOR CO_2 REDUCTION TO LIQUID FUELS

[Hub – LiSA] Aisulu Aitbekova,[1,2] Kyra Yap,[1,3] Matthew Salazar,[1,2] Magel Su,[1,2] Tobias A. Kistler,[1,4] Peter Agbo,[1,4] Theodor Agapie,[1,2] Jonas C. Peters,[1,2] Thomas F. Jaramillo,[1,3] Alexis T. Bell,[1,4] Harry A. Atwater[1,2]
[1]Liquid Sunlight Alliance, [2]California Institute of Technology, [3]SLAC National Accelerator Laboratory, [4]Lawrence Berkeley National Laboratory

AFFILIATED TALK – I-T1-3: A Tandem Photoelectrochemical/Photothermal System for CO2 Reduction to Liquid Fuels

Tandem processes are a promising approach to generating solar fuels and chemicals. However, only a few studies report the successful operation of such integrated systems due to a requirement for simultaneous optimization of each step. We have developed a two-step photoelectrochemical-photothermal system to convert CO_2 into multicarbon (C4-C6 hydrocarbons) products**.** In the first

step of the process, CO_2 reduces to ethylene in a photovoltaic-electrochemical cell. Here we focus on a catalyst design and show how functionalizing a copper electrode with molecular additives enhances ethylene formation and suppresses hydrogen generation via water splitting. The working hypothesis for this selectivity change is the inhibited proton transfer through hydrophobic molecular additive films, which results in diminished hydrogen evolution reaction rates. In the second step, ethylene oligomerizes into butenes inside a photothermal reactor with a selective solar absorber. Operating such a reactor under sunlight requires maximizing the light-to-heat conversion and minimizing heat losses. We accomplish this goal by simultaneously optimizing the absorber's optical properties, the reactor's geometry, and insulation. The heat required to run this reaction is provided by sunlight. The optimized reactor reaches a temperature of 100 °C (under 3-sun intensity), sufficient to drive an industrially relevant ethylene oligomerization reaction to convert ethylene into C4-C6 hydrocarbon solar fuels. Moreover, we demonstrate that this process works using a diluted ethylene stream gas directly produced by a CO_2 electrolysis cell that produces ethylene. Overall, we successfully perform solar-driven conversion of CO_2 into valuable products through combined catalyst design and reactor engineering.

I-S1-13: DEVELOPMENT OF A PURIFIED AND WHOLE CELL REDUCTIVE ENZYME CASCADE FOR THE VALORIZATION OF POLYETHYLENE TEREPHTHALATE DECONSTRUCTION PRODUCTS

[EFRC – CPI] Roman M. Dickey, Madan R. Gopal, Neil D. Butler, Michael R. Talley, Michaela A. Jones, Daniel T. Nakamura, Ashlesha Mohapatra, Mary P. Watson, Wilfred Chen, and Aditya M. Kunjapur
University of Delaware

To better incentivize the recycling of plastics waste, chemical transformations must be developed that add value to plastic deconstruction products. Here, we demonstrate the production of useful monoamine and diamine building blocks from known PET deconstruction products. We first achieved this by designing one-pot biocatalytic transformations in vitro through use of an ω-transaminase and carboxylic acid reductases (CAR). We first establish that an ω-transaminase from Chromobacterium violaceum can efficiently catalyze amine transfer to potential PET-derived aldehydes to form monoamine para-(aminomethyl) benzoic acid (pAMBA) or diamine para-xylylenediamine (pXYL). After characterizing 17 CARs in vitro, we then showed that the CAR from Segniliparus rotundus had the highest observed activity on terephthalic acid (TPA) to terephthalaldehyde (TPAL). In one pot, we achieve a 69 ± 1% yield of pXYL from TPA. We then aimed to utilize this cascade in live cells to provide a more cost effective and efficient biosynthetic process compared to the use of purified enzymes. Here, we showed that the addition of the dialdehyde intermediate TPAL to growing cultures of Escherichia coli wild-type strain MG1655 and an engineered strain for reduced aromatic aldehyde reduction (RARE) strain resulted in substantial reduction. Encouragingly, we created a newly engineered strain with 10 additional knockouts in RARE that enabled a 2.5-fold higher retention of TPAL and observed a 6.8-fold increase in pXYL titer over RARE at 24h. This work expands the breadth of products derived from PET deconstruction and lays the groundwork for eventual valorization of waste PET to higher-value chemicals and materials.

I-S1-14: CHEMICAL RECYCLING OF THIOL-EPOXY THERMOSETS VIA LIGHT-DRIVEN C—C BOND CLEAVAGE REACTIONS

[EFRC – BioLEC] Suong Nguyen[1], James Cox[1], Lydia Fries[1], Yuting Ma[2], Brett Fors[2], Robert Knowles[1]
[1]Princeton University; [2]Cornell University

Thermosets are a class of polymers characterized by the presence of covalent crosslinks between polymer chains. Their high strength and resistance to heat and chemicals impart significant value to their products but also present a considerable challenge for their recycling at their end of life. Here, we demonstrate the first example of a catalytic method for the closed-loop recycling of thiol epoxy thermosets *via* C–C bond cleavage. This depolymerization process is enabled by the homolytic activation of in-network hydroxyl groups as alkoxy radicals through proton-coupled electron transfer (PCET). These light-driven reactions are efficient, operate near ambient temperature, and enable the depolymerization of a range of thiol epoxies with diverse material properties. The products of the depolymerization are a set of well-defined small molecules that can all be converted to bisphenol A (BPA) in one synthetic step. Notably, this method exhibits excellent selectivity for depolymerizing epoxy thermosets in the presence of various common additives, such as commodity thermoplastics, carbon fiber, and mica dyes.

I-S1-15: CLOSING THE LOOP: STRUCTURE-PROPERTY RELATIONSHIPS IN CIRCULAR POLYOLEFINS

[EFRC – CPI] Sam Marsden[1], María Ley-Flores[1], Riccardo Alessandri[1], Isabella Vettese[1], Zubin Kumar[1], Archit Chabbi[2], Juan J. de Pablo[1], Stuart J. Rowan[1]
[1]University of Chicago; [2]Rice University

AFFILIATED TALK – I-T1-4: Circular Polyolefins: Design Principles for Sustainable Plastics

Polyolefins represent the largest fraction of global plastic waste generation. Most current recycling efforts focus on mechanical recycling of plastics, often leading to performance losses and short usage cycles. In recent years, chemical recycling technologies have emerged as promising solutions to deconstruct polymers into small molecules for a wide range of applications, including as feedstocks for new polymers. However, due to the high energetic cost of breaking down the carbon-carbon σ bond, progress in polyolefin chemical recycling has been particularly challenging. To address this issue, our study explores a series of circular polyolefins featuring cleavable moieties based on ester, anhydride, and carbonate functionalities to incorporate controllable degradation through glycolysis or hydrolysis. The main objective of this work is to develop structure-property relationships that facilitate the prediction of properties for these candidate polymers. By integrating experimental studies and molecular simulations, we have identified trends in the thermophysical properties of these candidate polymers in the melt, which are relevant for processing applications, and compared them to the performance of commercial polyethylene. Furthermore, our findings have provided valuable insights into how these cleavable bonds impact the crystallinity of the polymers. This research contributes to advancing our understanding of circular polyolefins and their potential as sustainable alternatives to polyethylene, paving the way for more efficient and sustainable recycling practices.

I-S1-16: DEGRADATION PATHWAYS FOR AMINE-BASED DIRECT AIR CAPTURE (DAC) ADSORBENTS

[EFRC – UNCAGE-ME] Botagoz Kuspangaliyeva[1], Shubham Jamdade[1], Nickolas Joyner[2], David A. Dixon[2], David S. Sholl[1], Christopher W. Jones[1], and Ryan P. Lively[1]
[1] Georgia Institute of Technology; [2] University of Alabama

Direct Air Capture (DAC) via adsorption is a promising technology for mitigating CO_2 emissions from the atmosphere. However, most prior research studies on DAC adsorbents have been conducted under ideal conditions with clean feed streams, neglecting the influence of impurities present in real-world applications. Emerging contaminants in the atmosphere may strongly interact with the surface functional materials of adsorbents, affecting their performance and structural integrity. This study aims to explore the role of trace biogenic and anthropogenic species on the long-term degradation of amine-based DAC adsorbents.

Metal ion species are of particular importance as potential contaminants, as even trace concentrations are expected to catalyze amine oxidation. This work presents ongoing research investigating the effect of metal contaminants (Cu^{2+}, Fe^{2+}, Ni^{2+}) on the degradation and performance of a polyethyleneimine (PEI)/SBA-15 composite. The research methodology involves varying metal ion loadings in the adsorbents, evaluating their CO_2 capture capacity, and examining their oxidative stability.

We are also exploring the effect of ozone-induced degradation as another largely unstudied "contaminant". We are specifically focusing on quantifying ozonolysis of amine-functionalized metal-organic frameworks (MOFs). We estimate ozone reaction rates with amine groups and carbon-carbon double bonds in the MOF using Density Functional Theory (DFT) calculations. In the preliminary work, we benchmarked the accuracy of the DFT method by reproducing literature results on ozone reactions with small alkyl amines and olefins in the gas phase. Additionally, the accuracy of several DFT functionals was compared with the gold standard CCSD (T) level in capturing the biradical character of ozone.

I-S1-17: STUDY AND DEVELOPMENT OF MOF-COATED ELECTRODES FOR ELECTROCATALYSIS

[ERFC – CD4DC] Joseph Hupp,[1] Chibueze V Amanchukwu,[2] Anna Wuttig,[2] Ksenija D Glusac[3], Laura Gagliardi[2], Gautam Stroscio,[2] Arturo Sauza de la Vega,[2] Hannah Fejzic,[2] Reginaldo J. Gomes,[2] Špela Kunstelj,[2] Biki Behera[3]
[1]Northwestern University; *[2]The University of Chicago; [3]Unviersity of Illinois at Chicago*
AFFILIATED TALK – I-T1-11: Mechanistic Insights of RuO_2-Mediated Butene Electrosynthesis

Electricity-driven reaction paradigms enable the practical use of renewable electricity (i.e., electrons or holes) and water (i.e., proton donors/acceptors) to drive hydrogen atom addition or removal and hydrogenation/dehydrogenation chemistries. The use of MOFs to control the efficiency and selectivity of electricity-driven reactions enables us to capitalize on the intrinsic structural periodicity and synthetic tunability of these structures as design handles. We show spectroscopic, reactivity, and computational results that establish the underlying selectivity of electrocatalytic target decarbonization chemistries of CD4DC, including the selective reduction of

CO, hydrogenation of model LOHCs, and oxidative transformation of biogenic carboxylates (pollutants) to desirable chemical and materials building blocks. These results establish a mechanistic baseline to leverage MOFs to manipulate reaction selectivity where electrons are sourced electrochemically and hydrogen is sourced from water.

I-S1-18: AB INITIO CALCULATIONS AND EXPERIMENTAL MEASUREMENTS OF QUANTUM BEATS AND SPIN RELAXATION IN HALIDE PEROVSKITES

[EFRC – CHOISE] Rikard J. Bodin,[1] Uyen Huynh,[1] Junqing Xu,[2] Kejun Li,[2] Paul Bailey,[1] Yuan Ping,[2,3] Pete C. Sercel,[4] Jinsong Huang,[5] Z. Valy Vardeny[1]
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Spin lifetime is a key parameter for determining a material's applicability for spintronics and spin-based quantum information applications. Here we use picosecond time-resolved Quantum Beatings (QBs) in circularly polarized photo induced reflection of $CsPbBr_3$ single crystal in the Voight configuration to measure these spin dynamics. We measure the QB dynamics versus magnetic field and temperature to determine the mechanisms behind spin relaxation rates and the Landé g-factors for electrons and holes from linear relationships between QB oscillation frequency vs Magnetic field. The g-factors are measured to be $|g^e_{[001]}| = 1.95\pm0.04$ and $|g^e_{[010]}|=1.82\pm0.04$, whereas for holes $|g^h_{[001]}| = 0.69\pm0.02$ and $|g^h_{[010]}| = 0.76\pm0.02$. Fitting the measured g-factors using an 8 band **k•p** model for Hybrid Organic-Inorganic Perovskites (HOIPs), we extract various material parameters. In addition the experimental spin dynamics are compared with ab initio density matrix dynamics calculations to determine the dominant and relevant spin dephasing mechanisms. The computational results use quantum dynamics with self-consistent spin-orbit coupling (SOC), quantum descriptions of electron scattering processes, and the Landé g-factor to describe the spin dephasing dynamics at external magnetic fields. We predict intrinsic lifetimes as upper bounds for experiments and determine the spin dephasing's dependence on temperature, external fields, carrier density, and impurities. We find that the persistent spin helix enhances spin lifetimes, but Rashba SOC doesn't enhance spin lifetime. The Overhauser effect is experimentally observed in $MAPbBr_3$ through DNSP generated via fixed circularly polarized light in QB measurements. This is observed as shifts in oscillation frequency and zero field oscillations.

I-S1-19: KINETIC PARAMETERS AND ATOMISTIC REACTION PATHWAYS FOR ION-TRANSFER REACTIONS IN CORROSION FROM EXPERIMENTS AND FIRST-PRINCIPLES CALCULATIONS

[Hub – LiSA] Richard Kang,[1,2] Diptarka Hait,[1,2] Yang Zhao,[1,3] Joseph A. Gauthier,[4] Paul A. Kempler,[1,3] Shannon W. Boettcher,[1,3] and Martin Head-Gordon[1,2]
[1]Liquid Sunlight Alliance; [2]Lawrence Berkeley National Laboratory; [3]University of Oregon; [4]Texas Tech University

The electrified aqueous/metal interface is of central importance in controlling performance and durability across energy-conversion and storage devices that are central to the EarthShot goals,

but the local surface and solvent structures controlling the relevant kinetic pathways and mechanisms are not only difficult to model/compute, but they are also challenging to understand using experiments. Here we report a rigorous, coupled, experiment / first-principles-computational study of model ion-transfer reactions involved in corrosion. The work focuses on understanding the molecular-level details of Ag metal (reversibly) corroding to from a solvated Ag^+ ion – with a ~5 eV change in solvation energy – and how the rate of the process is controlled by both interactions of the nascent ion with electrons in the solid and local solvent. The computations are performed using a Constant Electrode Potential (CEP) model with Density Functional Theory (DFT), the linearized Poisson-Boltzmann (LPB) implicit solvation model, and, essentially, a minimal-explicit-solvation model which balances computational cost and accurate solvation energy. The calculated free-energy barriers, and their asymmetries, generally agree with activation energies and transfer coefficients from temperature-dependent transient voltage-step experiments. The experiments are performed on a model system consisting of Ag nanocluster supported on polycrystalline Au substrates that eliminates convolution of the kinetics of ion generation and transfer with those nucleation or etch-pit formation. Together, these experiments and calculations provide the first validated, accurate, molecular model of the central steps that govern the rates of important corrosion/deposition reactions of broad relevance across the energy sciences.

I-S1-20: INTERACTIVE DYNAMIC ENERGY ANALYSIS (IDEA): A NEW TOOL FOR PREDICTING CATALYTIC REACTION PATHWAYS THROUGH JOINT DENSITY-FUNCTIONAL THEORY

[EFRC – CABES] Colin R. Bundschu, Mahdi Ahmadi, Juan Felipe Méndez-Valderrama, Héctor D. Abruña, Tomás A. Arias
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AFFILIATED TALK – III-T1-13: Interactive Dynamic Energy Analysis (IDEA): A New Tool for Predicting Catalytic Reaction Pathways through Joint Density-Functional Theory

We introduce a new tool for the ab initio study of reaction pathways called Interactive Dynamic Energy Analysis (IDEA), and we apply this novel approach to the study of the alkaline oxygen reduction reaction (ORR) on spinel materials. This reaction holds significant promise for reducing or even eliminating the need for costly platinum group metals (PGMs) in alkaline fuel cells, a development that could be pivotal in advancing this technology. Understanding the underlying mechanism is key to making further progress. Through our first-principles IDEA analysis, we have been able to challenge the traditionally assumed pathway for the reaction. We provide convincing evidence that the previously accepted pathway is incorrect and reveal the true reaction pathway on Co_3O_4. Finally, the IDEA tool enables us to rapidly comprehend how to optimize the resulting reaction by introducing epitaxial strain.

I-S1-21: SYNTHESIS OF (PHOTO)ELECTROCATALYTICALLY ACTIVE THIN-FILMS AT THE CENTER FOR ELECTROCHEMICAL DYNAMIC AND REACTIONS ON SURFACES (CEDARS)

[EFRC – CEDARS] Sheilah Cherono[1], Ikenna Chris-Okoro[1], Swapnil Shankar Nalawade[1], Neha Wadehra[2], Myles Steiner[3], Darrell Schlom[2], Y.Yun[1], Shyam Aravamudhan[1], Tanja Cuk[4], Jin Suntivich[2], Dhananjay Kumar[1]
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AFFILIATED TALK – I-T1-9: Electrocatalytic Properties of Pulsed Laser-Deposited Titanium Dioxide and Titanium Oxynitride Thin Films Grown on Photo-adsorbing Single Crystal Substrates with Different Orientations

We report the growth of (photo)electrocatalytic ruthenium oxide, cobalt oxide, titanium oxide, and titanium oxynitride epitaxial thin films on single crystal substrates with different orientations. These films were grown using state-of-the-art thin growth techniques available in the Center, such as molecular beam epitaxy (MBE), pulsed laser deposition (PLD), atomic layer deposition (ALD), magnetron sputtering, and chemical vapor deposition (CVD). We take advantage of the controlled by the thin film growth to prepare (photo)electrocatalytic active surfaces of the aforesaid materials with well-defined strain, vacancies, step edges, and dislocations by judiciously selecting the substrates and synthesis parameters. The atomically precise growth has allowed us to tailor the electronic structure, for example, band edges of semiconductors, to reveal how band positions with respect to water-splitting potentials facilitate the water-splitting reaction. The goal is to create model (photo)electrocatalyst films for spectroscopic studies of reaction intermediates as a function of potential and/or photo-triggers. We plan to use this capability examine the multi-electron electrochemical reactions during water splitting, *e.g.,* the hydrogen evolution reaction (HER) oxygen evolution reaction (OER).

I-S1-22: INFRARED SPECTROSCOPIC CHARACTERIZATION OF CO_2 REDUCTION CATALYSTS INTEGRATED ON SILICON SURFACES

[Solar Hub – CHASE] Samuel R. Bottum,[1] James F. Cahoon,[1] Chiara Cappuccino,[2] Javier J. Concepcion,[2] Jillian L. Dempsey,[1] Carrie L. Donley,[1] David C. Grills,[2] Nilay Hazari,[3] Brittany L. Huffman,[1] Xiaofan Jia,[3] Aldo M. Jordan,[1] Matthew R. Lockett,[1] James M. Mayer,[3] Thomas E. Mallouk,[4] Hannah S. Nedzbala,[3] André D. Orr,[1] Jin-Sung Park,[1] Adam J. Pearce,[3] Dmitry E. Polyansky,[2] Rebecca Powers,[1] Conor L. Rooney,[3] Renato N. Sampaio,[1] Colton Sheehan,[4] Eleanor Stewart-Jones,[3] Taylor S. Teitsworth,[1] Hailiang Wang[3]
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The mission of the Center for Hybrid Approaches in Solar Energy to Liquid Fuels (CHASE) is to develop molecule/material hybrid photoelectrodes for the cooperative sunlight-driven generation of liquid fuels from CO_2, N_2, and H_2O. Specifically, we are pairing light-absorbing semiconductor materials with surface-attached, fuel-producing molecular catalysts that will operate in tailored microenvironments using a multi-catalyst cascade approach to access liquid fuels. Since CHASE uses visible light-absorbing semiconductor substrates, e.g., silicon, (Si), mid-IR spectroscopy is an important technique for characterizing the functionalized surfaces, determining catalytic

mechanisms, and monitoring the progress of catalysis by detecting intermediates/products. The goal of this sub-project has been to develop highly sensitive IR spectroelectrochemical (IR-SEC) methodologies to probe (photo)electrochemical reaction mechanisms of monolayers of catalysts on Si electrode surfaces. To accomplish this, we fabricated a custom attenuated total reflection (ATR) cell for ATR-IR-SEC that uses a surface-doped Si ATR crystal as the working electrode. Surface-doping eliminates attenuation of the IR beam by free carriers whilst maintaining excellent conductivity for electrochemistry. In parallel, we are also developing transmission-IR-SEC of catalysts immobilized on high surface area porous Si substrates. Here, we present recent work in CHASE on the IR characterization of CO_2 reduction catalysts immobilized on Si by various means. We then show examples of how ATR-IR-SEC is being used to probe mechanisms of catalysis, and to characterize changes that occur in the electrochemical double layer under applied potential. Future directions, including the use of Si wafers instead of expensive ATR crystals, will also be discussed.

I-S1-23: ALL-POLYMER PHOTOCATHODE FOR SOLAR FUEL PRODUCTION

[EFRC – SPECS] Spencer Yeager[1], Neal Armstrong (KI)[1], Brian Breeman[3], Zhiting Chen[1], Andrew Ferguson (KI)[5], Ann Greenaway (KI)[5], Tim Lian (KI)[3], Seth Marder (KI)[2], Aiswarya Abhisek Mohapatra[2], Erin Ratcliff (PI)[1], Obadiah Reid (KI)[2,4], Garry Rumbles (KI)[4], Eui Hyun Suh[1], Fengyi Zhao[4]
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Conjugated (semiconducting) polymers (CPs) show promise as materials for photocathodes as the chemical and physical properties can be tailored to selectively drive fuel-forming reactions such as H_2 evolution. The nanometer-scale chemio-physical behavior of donor-acceptor heterojunctions in contact with an electrolyte is still a significant knowledge gap that must be addressed in order to carry out efficient photoelectrochemical processes that lead to fuels. In this work we investigate a proof-of-concept all-polymer photocathode with a platinum co-catalyst electrodeposited to facilitate proton reduction. We investigate the catalytic function, durability, and transient dynamics of this material system in contact with aqueous electrolytes of varying pH to establish a fundamental understanding of how electrolyte penetration into the junction forms "interphase" regions, impacts charge generation, transport, recombination, and catalytic activity. Operando Raman scattering experiments provided much needed chemical insights via peak shifts whilst transient absorption spectroscopy and time-resolved microwave conductivity provide insight into associated changes in optoelectronic function. We find that this blend of polymers is suitable for photo-induced generation of H_2 from H_2O, with no added energy source, other than AM1.5 solar illumination, with current densities and quantified rates of H_2 formation that suggest that optimized versions of these platforms could eventually compete with some well-established inorganic (hard) material platforms. Future work will include efforts to understand the molecular scale issues that limit both efficiency and durability, and quantification of yields of H_2 and introduction of non-platinum cocatalysts (selectively) to lower activation energies in water splitting reaction and reduce rates of competitive side reactions.

I-S1-24: PREDICTING TRANSIENT RESPONSE OF COMPOSITES SUBJECT TO DYNAMIC LOADING USING DEEP NEURAL OPERATOR LEARNING

[AIM for Composites] Minglei Lu[1], Elham Kiyani[2], Gang Li[1], Zhen Li[1], George Karniadakis[2].
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AFFILIATED TALK – I-T1-10: Predicting Transient Response Of Composites Subject To Dynamic Loading Using Deep Neural Operator Learning

Additive manufacturing allows fabrication of composites with complex 3D structures directly from computer-aided designs. The mechanical properties of these composites, especially response to dynamic loading, highly depend on their 3D structures. In general, for each specified 3D structural design, it could take hours or days to perform either finite element analysis (FEA) or experiments to test the mechanical response of composites to a given dynamic load. To accelerate the physics-based prediction of composite properties for various structural designs, we employ a deep neural operator (DNO) to learn the transient response of composites under dynamic loading as surrogate of physics-based FEA models. Results demonstrate that the trained DNO can act as surrogate of physics-based FEA to predict transient mechanical response in terms of reaction force and stress distribution of the composites to various strain loads, which can reduce the computational cost from hours of FEA to a fraction of a second at an accuracy of 98%. The learned neural operator is able to provide extended prediction of the composites subject to new strain loading patterns at a reasonably well accuracy. Such superfast and accurate prediction of mechanical properties of composites could significantly accelerate the material design processes for desired mechanical properties. Furthermore, we will showcase a physics-informed machine learning framework augmented with symbolic regression for discovery of new governing equations of composites from data, where the equations have explicit mathematical forms that can be easily understood and interpreted by humans.

I-S1-25: A REDOX NEUTRAL BIOCATALYTIC CROSS-COUPLING

[EFRC – BioLEC] Yi Liu[1], Todd K. Hyster[1]
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Enzymes represent unparalleled catalysts for organic synthesis because of their exceptional reactivity and selectivity. Through directed evolution, these catalysts can be optimized to exhibit desired selectivity patterns and reaction outcomes. An innovative fusion of photochemistry and enzymatic catalysis has opened the door to novel enzyme functions via radical mechanisms. We have developed a redox-neutral photoenzymatic catalysis for cross-coupling reactions using a flavin-dependent enzyme as the catalyst and the readily accessible carboxylic acids and alkyl halides as the substrates. Such a biocatalytic C-C bond approach offers exciting prospects in addressing challenges associated with Csp^3-Csp^3 cross-couplings. To gain deeper insights into this unusual mechanism, transient absorption spectroscopy was used in our studies.

I-S1-26: Ni(II) to Ni(I) Photolysis Initiates and Perpetuates Catalysis in Light-Driven Aryl-alkyl Cross Electrophile Coupling Reactions

[EFRC – BioLEC] Max Kudisch[1], Justin D. Earley[1,2], Stephen DiLuzio[3], Lakshmy K. Valloli,[4] Amy Cordones-Hahn[5], Matthew J. Bird[4], Hannah J. Sayre[3], Obadiah G. Reid[1,2], Garry Rumbles[1,2]
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Carbon-carbon bond forming reactions between aryl and alkyl halides constitute an essential tool in organic synthesis. Dual-catalyzed, light-driven methods have recently emerged as alternatives that may be more sustainable than the Pd-catalyzed, heat-driven approaches currently used on an industrial scale. In particular, blue light-driven methods catalyzed by Ni(II) and Ir(III) complexes feature broad substrate scopes and mild reaction conditions, but further development suffers from a lack of mechanistic understanding regarding the initiation of catalysis. Using time-resolved X-ray and optical spectroscopic methods, we have found that a previously unknown 6-coordinate Ni(II) species forms via reaction between the photo-excited Ir catalyst and the Ni(II) precatalyst. Building off this work, we have obtained additional results which are consistent with energy transfer from the excited state Ir complex to a mixture of Ni(II) complexes resulting from glyme solvation of the pre-catalyst. Electron paramagnetic resonance and UV-visible data (both time-resolved and steady state) is consistent with photolysis of a Ni-centered excited state to form Ni(I) and Cl radical, which after hydrogen atom abstraction and radical capture results in the 6-coordinate Ni(II) complex. Further experiments suggest that this 6-coordinate Ni(II) functions as an intermediate towards both the production of Ni(I) which is active towards oxidative addition of aryl halides and the buildup of Ni(II) aryl halide complexes previously identified as on-cycle intermediates. Broadly speaking, we observe two new pathways to form the active Ni(I) catalyst from the Ni(II) pre-catalyst. Knowledge of these pathways can ultimately facilitate the development of improved reaction conditions.

I-S1-27: Simultaneous and Correlated Widefield and Confocal Photoluminescence Micro-Spectroscopy of Photon Recycling between Nanowires in Photosynthetic Arrays

[EFRC – EPN] Danielle R. Lustig[1], Wentao Zhang[2], Olivia Bird[3], Juliane Koch[4], Chengxing He[2], Gordana Dukovic[3], Thomas Hannappel[4], Shu Hu[2], Justin B. Sambur[1]
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Radiative charge recombination is a source of energy loss in photocatalytic systems. Photon recycling offers a means to reduce the impact of this loss pathway, and thus increase solar power conversion efficiency. Photon recycling is the process in which photons emitted via radiative recombination are reabsorbed by the semiconductor itself. While this effect has been demonstrated in photovoltaic systems, it has not been studied in solar-fuel-generating systems, where detailed-balance efficiency analyses suggest that benefits will be significant for ensembles of photosynthetic nanoreactors. To experimentally investigate this, we developed a model system by fabricating GaAs nanowire array photoabsorbers passivated with a GaN coating, resulting in highly emissive, high-quality III-V materials. These arrays were synthesized using reactive ion

etching, electron-beam pattern geometry, and atomic layer deposition. We developed a simultaneous widefield/confocal photoluminescence micro-spectroscopy approach to study the effects of photon recycling between adjacent nanowires. This technique uniquely allows us to excite a single nanowire with a focused laser beam, and detect photons scattered from and/or emitted by nanowires via band-edge recombination using widefield imaging. To facilitate data interpretation, we are developing kinetic Monte Carlo models to simulate the photon recycling processes among these highly emissive nanowires, and to predict key outputs of photon recycling such as photoluminescence quantum yields and excited-state lifetimes.

I-S1-28: MORPHOGENIC MANUFACTURING BY FAST, LOW ENERGY GROWTH PRINTING

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Organisms are created by growth according to a genomic developmental plan where gradients and symmetry breaking steps guide the cell divisions to reach a target morphology. This construction approach is fundamentally different than industrial manufacturing where the final product, with all its geometric and compositional complexities, is first designed, then a fabrication process flow is outlined. Inspired by nature's approach, we present a new growth printing process where a program of instructions describes the thermal and speed gradients of a propagating curing front to rapidly produce a complex polymeric part. This new process is enabled by the frontal polymerization of dicyclopentadiene (DCPD) which follows a self-propagating and self-energized curing front transforming the liquid monomer to a solid polymer.

Growth printing relies on diffusion-reaction-solidification numerical modeling, physical understanding of the complex rheology of the resin, and the development of novel manufacturing equipment. Growth printing is triggered when a heated initiator contacts the uncured liquid resin in an open container. The initiator nucleates the frontal polymerization reaction, and the growth front propagates without additional energy away from the initiator into the liquid resin, curing a solid polymer. Numerical modeling captures the shape of the front and the produced part according to the thermal and speed map. The initiator moves in a linear direction away from the container, and the growing part's morphology results from the interplay between the front and the initiator velocities. Because of this chemistry-directed parts growth, this method is called growth printing.

I-S1-29: INVESTIGATING MOLECULAR ARCHITECTURE AND CARBOHYDRATE-AROMATIC INTERFACE OF PLANT CELL WALLS USING SOLID-STATE NMR

[EFRC – CLSF] Wancheng Zhao[1], Sarah A. Pfaff[2], Frederic Mentink-Vigier[3], Daniel J. Cosgrove[2], Tuo Wang[1]
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Plant cell walls, which make up a significant portion of renewable lignocellulosic biomass, hold great promise as a source of biomaterials and biofuels. The intricate biopolymer networks within

cell walls consist of cellulose microfibrils, hemicellulose, and lignin, forming rigid structures in the secondary cell walls. Traditional techniques like solution NMR and chromatography necessitate isolation, chemical modification, and solubilization procedures which can compromise the physical properties and chemical structures of biomacromolecules. Initially, this method was used to explore the nanoscale arrangement of lignocellulosic components in various plant stems, such as grass (maize), hardwood (eucalyptus and poplar), and softwood (spruce). Through the use of intact plant cells, valuable insights were gained regarding the polymorphic structure, dynamics, hydration profiles, and physical packing of polysaccharides and lignin. Notably, it was observed that lignin has a preference for binding to the non-flat domains of xylan in most plants, but it also binds to cellulose and the flat-ribbon domain of xylan in woody stems. Furthermore, our ongoing research utilizes ssNMR to investigate the lignification process in Arabidopsis. The findings have revealed a correlation between the lignification process, stem height, and the position of stem cuts (basal, middle, and apical). These studies aim to provide guidance for the development of crops that are more easily digestible and to enable cost-effective conversion technologies for biofuel production, as well as the advancement of plant-based biomaterials.

I-S1-30: EFFECT OF METALLIC IMPURITIES ON ELECTROCATALYTIC FUEL-PRODUCING REACTIONS

[EFRC – UNCAGE-ME] Sonakshi Saini[1], Priyadarshini Seshasayee[1], Sankar Nair[1], Jonas Baltrusaitis[2], Juliane Weber[3], and Matthew T. McDowell[1]
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Electrochemical water splitting is a promising method to produce green hydrogen. To design efficient and long-lasting electrolyzers, it is critical to understand the effects of impurities that are present naturally in seawater or other water sources on the structural and chemical evolution of electrocatalyst materials. Here, we present our efforts on investigating the effects of copper ions as an impurity on the hydrogen evolution reaction (HER). Since the deposition of copper depends on the operating potential and the underlying crystal structure of the electrocatalyst, we investigate both platinum and MoS_2 as electrocatalysts in acidic environments. We show that copper electrodeposition occurs in tandem with H_2 evolution on platinum surfaces, which influences the catalytic behavior as a function of time. Future collaborative experiments include probing the real-time growth behavior of copper during H_2 evolution using atomic force microscopy and characterization of impurity deposition under different pH environments. Additionally, we also explore the role of various catalysts and impurities on CO_2 reduction reaction using ionic liquid solvents.

I-S1-31: BACTERIAL MICROCOMPARTMENT SHELL IMMOBILIZATION FOR FLUORESCENCE IMAGING AND ELECTROCHEMISTRY

[EFRC – CCBC] Nicholas M. Tefft[1], Joshua MacCready[1], Paul D. Ashby[3], Daniel Ducat[1], Michaela A. TerAvest[1]
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The CCBC is developing a nanoreactor platform to enhance catalysis based on protein-based bacterial organelles, Bacterial Microcompartments (BMCs). The nanoreactor boundary is a protein shell. An essential characteristic of BMC shells is their selective permeability, which allows generation and maintenance of an interior environment that differs from the exterior. A major goal is to characterize the permeability of BMC shells to develop an engineering framework for developing shells with user-defined permeability. To measure permeability and electron transfer across the shell, it is necessary to measure concentrations within the BMC shells. The internal volumes, however, are too small to be accessed by standard analytical techniques. Therefore, we are loading cargo molecules into the BMC shells that convert information about internal concentrations into light and other electromagnetic signals that can be measured from outside the shell. We have developed specialized devices to immobilize the BMC shells and enable fluorescence and electrochemical measurements with the simultaneous capability to exchange the bulk solution. In addition, we are developing methods to assess ionic and electronic conductivity of the shells by immobilizing sheets of the shell material on specialized devices for scanning electrochemical microscopy (SECM) and scanning ion conductance microscopy (SICM) with integrated conductivity measurements. We are testing a variety of methods for specific and non-specific immobilization of shells, including modification of surfaces to promote nonspecific adsorption and modification of surfaces to adsorb shells with specific protein tags.

I-S1-32: STRUCTURE AND 'TRIMER-TRIMER' INTERACTIONS OF SOY PRIMARY CELL WALL CESA1,3 AND 6

[EFRC – CLSF] Purushotham Palliniti[1], Ruoya Ho[1] and Jochen Zimmer[1,2]
[1]University of Virginia; [2]Howard Hughes Medical Institute

Plants express different isoforms of cellulose synthase (CesA) with specific subsets necessary for primary and secondary cell wall formation. CesAs are membrane integrated processive glycosyltransferases that polymerize UDP-activated glucose and secrete the resulting linear polysaccharide across the plasma membrane. Structural analyses of secondary cell wall CesAs revealed their organization into catalytically active homotrimeric complexes that synthesize and secrete three glucan chains. Here, we present cryo-electron microscopy structures of all essential primary cell wall CesAs, also revealing homo-oligomerization into trimeric complexes. The enzymes share a conserved catalytic core with their secondary cell wall counterparts, while displaying a different organization of their transmembrane region. Further, enzymatic analyses identify subtle functional differences between the isoforms, primarily with regard to substrate binding and turnover. In vitro interaction studies using individually purified homotrimeric CesA complexes demonstrate robust interactions between CesA isoforms. Our structural and biochemical analyses suggest the functional importance of higher-order assemblies of homo-oligomeric CesA complexes, perhaps for the formation of fibrillar cellulosic wall materials.

I-S1-33: EFFECTIVE MULTI-REFERENCE METHODS FOR HETEROGENEOUS TRANSITION-METAL CATALYSTS

[CCS – Exascale] Valay Agarawal[1], Laura Gagliardi[1], Matthew Hermes[1], Cong Liu[2], Christopher Knight[2], Rishu Khurana[2]

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AFFILIATED TALK – I-T1-6: Automating model space selection in fragment-based multireference methods

We aim to predictively design heterogeneous transition-metal catalysts using computationally inexpensive electronic structure methods that accurately model non-dynamic and dynamic electron correlation. To achieve this, we collaboratively focus on several aspects, striving to develop an exascale-capable production implementation of multiconfigurational self-consistent field quantum chemistry methodologies based on the localized active space (LAS) concept. LAS involves partitioning the strongly-correlated part of the electronic Hilbert space into small orthogonal subspaces, assuming weak electronic correlation or entanglement between them.

Our methodological advancements include theoretical extensions of LASSCF and post-SCF methods, enhancing their robustness and reducing user ambiguity. Computationally, we undertake a redesign and refactoring of the implementation. We work from both the bottom up, optimizing performance-critical kernels for GPU acceleration, and from the top down, implementing high-level abstractions for rapid testing and scalable algorithm development.

Chemically, we assemble various polynuclear catalytic systems for oligomerization and polymerization reactions. We conduct preliminary density functional theory calculations to identify spin ladders and transition state geometries, serving as references and input for scientifically meaningful and production-scale test calculations.

Through this multi-pronged approach, we aim to develop a portable and scalable implementation, targeting exascale capabilities. Our goal is to gain fundamental insight into these challenging systems and meet the computational requirements for effective catalyst design.

I-S1-34: MULTISCALE STRUCTURAL CHARACTERIZATION OF EPIDERMAL CELL WALLS DURING MECHANICAL STRETCH

[EFRC – CLSF] Jingyi Yu[1], Joshua T. Del Mundo[1], Esther W. Gomez[1], Enrique D. Gomez[1], and Daniel J. Cosgrove[1]
[1]*The Pennsylvania State University*

Highly extensible epidermal cell walls limit cell growth and enable plants to comply with external loads such as wind and accumulated snow. Seeking to uncover the molecular mechanisms of the walls' high extensibility and strength, we stretched onion epidermal walls uniaxially to various strains and characterized their structures from mesoscale to atomic scale. The rearranged wall structures were fixed by dehydration under tension and the reversibility of molecular rearrangement was examined by drying after relaxation following stretching. Upon deformation at high strain, epidermal walls extended longitudinally and shrank transversely. Atomic force microscopy revealed that cellulose microfibril movements at high strain depend on microfibril orientation. Longitudinally aligned microfibrils straightened out and became highly ordered, while transversely aligned microfibrils became curved and kinked. Small-angle X-ray scattering of walls at high strain revealed a 7.4 nm spacing aligned along the stretch direction, which we attribute to ~4 nm spacing between individual cellulose microfibrils. Furthermore, wide-angle X-ray scattering at high strain revealed widening of (004) lattice spacing and contraction of (200) lattice spacing in

longitudinally aligned cellulose microfibrils, which implies longitudinal stretching of the cellulose crystal. These findings provide molecular insights into the walls' ability to bear more load beyond the yield point: aggregation of longitudinal microfibrils impedes microfibril sliding and enables further stretching of cellulose microfibrils to bear increased loads.

I-S1-35: X-RAY ABSORPTION SPECTROSCOPY OF OXYGEN EVOLUTION CATALYST RuO_2

[EFRC – CEDARS] R. Soyoung Kim[1], Kuntal Chatterjee[1], Brady Bruno[2], Jacob Som[2], Sheilah Cherono[3], Haldrian Iriawan[4], Botao Huang[4], James Stewart[5], Bishnu Bastakoti[3], Jin Suntivich[2], Tanja Cuk[5], Dhananjay Kumar[3], Yang Shao-Horn[4], Junko Yano[1]
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AFFILIATED TALK – I-T1-9: Electrocatalytic Properties of Pulsed Laser-Deposited Titanium Dioxide and Titanium Oxynitride Thin Films Grown on Photo-adsorbing Single Crystal Substrates with Different Orientations

Water oxidation, or oxygen evolution, continues to be a limiting factor in water electrolysis for generating renewable hydrogen or carbon dioxide reduction to liquid fuels. RuO_2 is one of the few oxygen evolution reaction (OER) catalysts that can operate in acidic electrolytes. Its activity and stability vary significantly depending on the synthesis methods, which affect the morphology, crystallinity, strain, exposed facets, and other properties. RuO2 also undergoes varying degrees of restructuring and corrosion during the OER catalysis. Taking advantage of the synthesis expertise in our EFRC, we employed soft X-ray absorption spectroscopy at the O K-edge to understand the electronic structure of RuO_2 prepared by different methods. We are also planning in operando experiments with high-energy resolution fluorescence-detected (HERFD) X-ray absorption spectroscopy at the Ru K-edge to sensitively detect changes in the d-orbital manifold at different applied potentials.

I-S1-36: ENTROPIC VS. ENTHALPIC CONTROLS ON PROTEIN SELF-ASSEMBLY IN BULK AND ON SURFACES

[EFRC – CSSAS] Zhiyin Zhang[1], Ying Xia[2], Huat Chiang[2], Sakshi Schmid[3], Benjamin Helfrecht[3], Amy Stegmann[2], Harley Pyles[2], Robert Alberstein[1], Jesse Prelesnik[2], David Baker[2], James De Yoreo[2,3], Christopher Mundy[2,3], Elias Nakouzi[3], James Pfaendtner[2,3], Lilo Pozzo[2], Akif Tezcan[1], Shuai Zhang[2,3]
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Design of proteins that self-assemble into higher-order structures is a powerful synthetic strategy for creating new materials with complex functions, provided the competing entropic and enthalpic forces can be controlled. Using both site-modified natural proteins and *de novo* designed artificial ones, we investigated the controls on assembly in bulk solution and on inorganic surfaces through molecular simulations and electron and atomic force microscopy. On one front, a C4 -symmetric protein (RhuA) was functionalized alternatively with complementary host (β-cyclodextrin) and guest (azobenzene) molecules, which promoted its self-assembly into 1D nanotubes of variable diameters or crystalline 2D arrays in a metal-ion-dependent fashion. When these RhuA variants are allowed to self-assemble on mica, they separate into new 2D phases whose structures are

tuned by regulating surface charge through electrolyte adsorption and by varying the strength and flexibility of the protein-protein bonds to modulate the entropic forces associated with shape complementarity. On a second front, we computationally designed proteins that display arrays of carboxylic groups matched to the mica lattice. When these artificial proteins assemble in electrolyte solutions, 2D phases arise that are not expected based on the mica lattice symmetry. Yet, atomistic simulations show that electrolytes produce dramatic effects on protein-mica interactions, which are mediated through water's response to the surface, yielding a transition from 3-fold to 2-fold symmetry in the near-surface solvent structure and thus reconciling the observed 2D phases. Informed by these atomistic studies, we are now establishing coarse grained models to predict the collective outcomes of proteins at interfaces.

I-S1-37: PROXIMITY-EFFECT-INDUCED REMOTE CHIRALITY TRANSFER IN HALIDE PEROVSKITES

[EFRC – CHOISE] Md Azimul Haque,[1] Roman Brunecky,[1] Steven P. Harvey,[1] Bennett Addison,[1] Andrew Grieder,[2] Yi Xie,[3] Junxiang Zhang,[4] Yifan Dong,[1] Matthew P. Hautzinger,[1] Heshan Hewa Walpitage,[5] Zeev Valy Vardeny,[5] Seth R. Marder,[4] David B. Mitzi,[3] Yuan Ping,[2] Matthew C. Beard,[1] Joseph M. Luther[1]
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Hybrid organic/inorganic halide perovskites are intriguing chiral material systems owing to their excellent optoelectronic properties and potential to impart chirality with the organic A-site cation. Typically, chiroptical properties arise due to structural symmetry breaking from chiral A-site organic cation to the inorganic framework. In the present work, we demonstrate a proximity effect of remote chirality transfer to induce chirality in otherwise *achiral* 2D halide perovskites. A chiral organic ligand is introduced in the perovskite lattice without altering the structure, thus introducing chirality into existing 2D perovskites. Furthermore, we construct a chirality-composition library with varying the A, B, X-sites, along with the dimensionality, revealing the essential role of each atomic component in the perovskite structure. This approach of remote chirality transfer in halide perovskites could lead to new prospects in terms of composition, spin transport properties, and devices without extensive chemical modifications.

I-S1-38: ORIGINS OF ENHANCED OXYGEN REDUCTION ACTIVITY OF TRANSITION METAL NITRIDES

[EFRC – CABES] Rui Zeng[1], Huiqi Li[1], Zixiao Shi[1], Lang Xu[2], Jinhui Meng[3], Weixuan Xu[1], Hongsen Wang[1], Qihao Li[1], Christopher J. Pollock[4], Tianquan Lian[3], Manos Mavrikakis[2], David A. Muller [1,5], Héctor D. Abruña[1]
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Hydrogen fuel cell technologies, especially in acid, have been challenged by the need to use costly platinum (and other precious metals) to accelerate the sluggish oxygen reduction reaction (ORR). Transition metal nitride (TMN) electrocatalysts have recently emerged as promising non-precious alternatives in alkaline media, but the lack of well-defined surfaces has limited the fundamental understanding of the structure-activity relationships. Here we demonstrate how a well-defined

TMN can dictate the as-formed oxide surface and the ORR electrocatalytic activity. Structural characterization of carbon-loaded MnN nanocuboids established that a ~1.5-nm thick Mn_3O_4 shell grew around the MnN core. The catalysts enabled the 4-electron ORR pathway with an intrinsic activity over 300 % higher than that of spinel oxides, achieved a record-high peak power density of ~900 mW cm^{-2} in alkaline media, and maintained their crystal structure during normal operating potentials. A combined microscopic and theoretical investigation showed that such impressive performance likely originates from a more hydroxylated oxide surface since the expansively strained surface spinel oxide strengthened OH binding. Our work reveals the origins of enhanced ORR activity in TMNs and establishes a catalyst platform that can be extended to other applications.

I-S1-39: SYNTHESIS OF PLATINUM NANOPARTICLES ON METAL OXIDE SUPPORTS VIA SURFACE ORGANOMETALLIC GRAFTING FOR THE CATALYTIC HYDROGENOLYSIS OF PLASTIC WASTE

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$Pt/SrTiO_3$ (Pt/STO), prepared on small scale by atomic layer deposition (ALD), is a capable heterogeneous catalyst for the selective hydrogenolysis of waste plastics to high-quality liquids, providing a promising approach for upcycling plastic waste. However, because deposition by ALD is costly and resource-intensive, a new synthesis of Pt/STO was needed. To that effect, this work details a scalable deposition method for Pt/STO made by surface organometallic chemistry (SOMC) techniques using Pt(II) acetylacetonate or trimethyl(methylcyclopentadienyl)platinum. Following pre-treatment, a clean STO surface populated with only hydroxyl groups was obtained. The Pt precursors were dissolved in toluene and deposited onto STO, decorating the support with 1.0–1.5 nm Pt nanoparticles after reduction. The size and loading of these nanoparticles were varied by employing a multi-cycle deposition and oxidation and/or reduction process. These Pt/STO catalysts hydrogenolyzed isotactic polypropylene into liquid products (>95% yield) with average molecular weights of 200–300 Da (~25 carbon atoms) and narrow size distributions at 300 °C and 180 psi H_2. The data suggests that smaller Pt nanoparticles are more active for polyolefin hydrogenolysis. Pt deposited onto other metal oxide supports (M_xO_y = STO, SiO_2, γ-Al_2O_3, SiO_2-Al_2O_3, CeO_2, and TiO_2) via SOMC were studied for polyethylene hydrogenolysis to evaluate support effects on catalysis. Pt/SiO_2-Al_2O_3 and Pt/STO showed the highest conversion to liquid products with product properties (saturation, branching etc.) dependent on catalyst acidity. Overall, the results suggest that SOMC-derived Pt/M_xO_y catalysts meet several proof-of-concept criteria and have the potential to be commercially viable upcycling catalysts.

I-S1-40: TASK SPECIFIC IONIC LIQUIDS FOR DIRECT AIR CAPTURE AND ELECTROCHEMICAL CONVERSION OF CO_2

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This collaborative project is focused on the fundamental study of ionic liquids (ILs) for Direct Air Capture of CO_2 and its electrochemical conversion to chemicals. In particular, we are addressing the design, synthesis, CO_2 absorption mechanisms, and electrolytic mechanisms of ILs. To develop an initial understanding of these issues, we have synthesized several ILs with high potential for CO_2 capture from dilute sources (such as DAC), and we are characterizing their properties for both DAC and CO_2 electrochemical reduction reaction (CO_2ERR) to value added C_1 and C_2 chemicals. Absorption isotherms at bulk conditions (1 atm of CO_2) and at DAC conditions (~400 ppm of CO_2) are measured to determine the absorption uptake and relate this information to the chemistry of the IL. Through detailed molecular modeling, the interactions of these ILs with CO_2 are being quantified by means of absorption energy calculations. This approach is beginning to allow the design of Task-Specific ILs (TSILs) with anion-cation pairs that have selective properties for DAC. On the other hand, cyclic voltammetry (CV), chronoamperometry (CA), and electrochemical atomic force microscopy (EC-AFM) measurements are being designed for understanding the electrochemical stability, redox behavior, kinetics of CO_2ERR in CO_2-TSIL systems, and surface interactions between TSIL and electrocatalyst.

I-S1-41: POLYETHYLENE UPCYCLING TO LONG-CHAIN ALKYLAROMATICS

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The catalytic conversion of waste polyethylene (PE) into valuable long-chain alkylaromatics, which are used as precursors to anionic surfactants, could contribute to a more circular carbon economy and mitigate the environmental impact of plastic waste. Pt/γ-Al_2O_3 converts PE to alkylaromatics with average $C_{\sim 30}$ at ca. 280 °C in the absence of external H_2. Coupling endothermic dehydroaromatization with exothermic C-C bond hydrogenolysis makes the tandem reaction possible. However, depolymerization proceeds slowly, and the alkyl side-chains are longer than desired for direct use in anionic surfactants ($C_{16\text{-}22}$).

Halogenated aluminas are widely used as supports for Pt in industrial catalytic reforming of small molecule hydrocarbons to aromatics. Reformulating the catalyst as Pt/F-Al_2O_3 resulted in five-fold enhancement in the rate of C-C bond scission and a change in selectivity to surfactant-range alkylaromatics (ca. C_{20}). Since physical mixtures of weakly acidic Pt/γ-Al_2O_3 or non-acidic Pt/SiO_2 with strongly Brønsted acidic F-Al_2O_3 or Cl-Al_2O_3 are also effective, the tandem reaction does not require nano-scale intimacy between the metal and the acid sites. Kinetic studies with triacontane as a model for PE show that Pt-catalyzed dehydrogenation/hydrogenation reactions are quasi-

equilibrated, while acid-catalyzed C-C bond scission and skeletal transformations (isomerization and cyclization) determine the overall rates of depolymerization and aromatic formation.

Catalyst acidity also promotes the formation of undesired polyaromatics. Moderate hydrogen pressure further accelerates depolymerization and directs the selectivity of Pt/SiO_2-Al_2O_3 towards alkylbenzenes.

I-S1-42: BACTERIAL MICROCOMPARTMENT SHELL ORTHOGONALITY IN CELLS AND *IN VITRO*

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AFFILIATED TALK – I-T1-5: Characterization of bacterial microcompartment shell formation through denaturant-induced sheet dismantling and subsequent shell self-assembly

Over 60 different classes/sub-types of bacterial microcompartments (BMC) are broadly distributed across 45 phyla of prokaryotes, presenting a correspondingly broad diversity of the structural shell proteins that self-assemble to define BMC boundaries. All identified BMC shells appear to be composed of elements that are evolutionarily related across different BMC classes: hexameric (BMC-H), trimeric (BMC-T), and pentameric (BMC-P) shell proteins. This evolutionary conservation across BMCs implies a degree of interchangeability of these structural components between different BMC classes while raising questions of how microcompartment identity is preserved in bacterial species encoding two or more BMC classes. One CCBC research goal is the identification of features of BMC shell proteins contributing to their specificity of self-assembly with selected protein partners, to the exclusion of other closely related shell proteins. Here, we summarize parallel, cross-Center research activities for identifying features determining orthogonality of shell protein assembly using *in vivo*, *in vitro*, and *in silico* approaches. In living cyanobacteria, we present evidence that two microcompartment classes can be maintained independently, even while individual shell proteins may exhibit latent capacity to integrate across either BMC class. We further describe a pipeline for purifying shell proteins and interrogating their temporal assembly dynamics *in vitro* – laying the groundwork for a combinatorial approach to analyze the assembly properties of defined mixtures of different shell proteins. Ultimately, understanding shell protein features that determine compatibility/orthogonality will enable rational design of higher-order arrays of BMCs containing multiple compartment classes.

I-S1-43: SPEEDING UP MATERIALS SYNTHESIS BY MANIPULATING TRANSPORT ON DIFFERENT LENGTH SCALES

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AFFILIATED TALK – I-T1-1: Speeding Up Materials Synthesis by Manipulating Transport

The discovery of new materials is a bottleneck in the development of next generation technologies. While we can predict hypothetical materials (and their properties!), at present, we cannot predict how to synthesize them. GENESIS is exploring how materials synthesis is governed by the flow of energy and atoms across multiple length scales to enable predictive synthesis of next generation materials.

For solid state synthesis of inorganic materials, reactions evolve from the interfaces between reactive precursors, as atoms move within and between particles, on the nanometer- and micron-scales. Using in situ synchrotron scattering we interrogate these non-equilibrium synthesis pathways experimentally to resolve how the composition, structure, and heterogeneity of multi-component reactions evolve over multiple length scales, following a free-energy pathway.

For model reactions that produce $LiFeO_2$, anode material Li_4Ti5O_{12}, and $Fe_2[MoO_4]_3$, we explore how changing the reaction architecture and reactive interface density on the particle-scale impacts the relative reaction kinetics – this allows us to distinguish the how different transport pathways limit the reaction. We use in situ X-ray scattering and phase-field simulations to identify how reaction microstructure on different length scales can control reactivity in the solid state. Our results challenge the view that solid-state reactions are necessarily slow and represent a key step towards predicting and controlling these reactions. Optimizing architecture to decouple reaction temperature, time, and yield may allow reactions to be tailored to control phenomena such as transition-metal migration and inter-site mixing seen in layered transition metal oxides.

I-S1-44: QUANTIFYING POLARON-COUNTERION INTERACTIONS IN ELECTROCHEMICALLY DOPED Π-CONJUGATED POLYMERS

[EFRC – SPECS] Joel Bombile[3], Jean-Luc Bredas (KI)[1], Megan Brown[3], Zhiting Chen[1], Veaceslav Coropceanu[1], Casey Davis[2], Andrew Ferguson (KI)[5], Melissa Gish[5], Chamikara Karunasena[1], Erin Ratcliff (PI)[1], Obadiah Reid (KI)[5], Andrew Setley[4], Natalie Stingelin (KI)[4], Michael Toney (KI)[2], Chad Risko (KI)[3] Mark Weber[4]
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Electrochemically doped π-conjugated polymers (CP) are central to several emerging energy applications such as batteries, capacitors, and photoelectrochemical solar fuel generation. During the doping process, charge carriers are introduced into the polymer to form polarons, and counterions from an electrolyte source are drawn into the polymer to balance these charges. The counterions can deeply impact the optical and electronic properties of doped CP's. It is thus crucial to understand how counterions interact with doped polymers to identify suitable ion-polymer systems with improved performance. Predicting how a given counterion will influence charge-carrier transport in doped CP's remains a challenge. An accurate description of charge transport in these materials necessitates a good understanding of how polaron characteristics are affected by counterions. Here, with a focus on electron-transport (n-type) polymers, and specifically N2200, we use first-principles calculations based on density functional theory (DFT) and time-dependent density functional theory (TD-DFT) to determine various polaron characteristics in CP's

with and without counterion present. Steady-state and transient spectroelectrochemical methods, thermal analysis (including fast calorimetry), and density measurements based on the Archimedes method, are used to complement the calculations. We find that the Coulomb interactions between the polaron and the counterion lead to smaller polarons that are more strongly bound, as reflected by changes in the NIR/vis polaron absorption spectrum. Both polaron (de)localization and binding play an important role in charge transport. The DFT results also serve as important input for future molecular dynamics (MD) simulations combined with characterization techniques across SPECS to examine the polymer:electrolyte interphase.

I-S1-45: INFLUENCE OF POLYMER ARCHITECTURE ON CATALYTIC DECONSTRUCTION OF POLYOLEFINS

[EFRC – CPI] Alex H. Balzer, Zachary R. Hinton, LaShanda T.J. Korley, Thomas H. Epps, III
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Plastics are indispensable materials found in countless consumer products. Yet, their growing use combined with limited recycling strategies has led to a rapid accumulation of plastics waste and produced many negative environmental impacts. Thus, efforts to improve end-of-life strategies to address plastics pollution are expanding. Polyolefins, which comprise over half of new plastics production, can be chemically recycled into valuable carbon feedstocks, such as oils and lubricants. This deconstruction process is non-trivial and requires fundamental understanding of the polymer physical properties (*e.g.*, viscosity, crystallinity) that are affected by molecular weight distributions and architectures across polyolefin feedstocks. Herein, we report the use of thermal fractionation, via self-seeding and annealing, to separate polymer crystals by their methylene sequence lengths and determine the branching architecture of polyethylenes after chemical deconstruction. By combining this thermal analysis with gel permeation chromatography, several reaction pathways, such as isomerization and chain scission, commonly found in hydrocracking, hydrogenolysis, and pyrolysis can be simultaneously tracked and quantified. Deconstructed solid products have an increased branching density compared to the neat polymer, however changes in methylene sequence length distributions after deconstruction are not consistent for all branching architectures. By identifying trends in molecular weight distributions and branching architecture, our combined technique allows for further insight into other polymer physical processes that affect deconstruction, including adsorption and transport.

I-S1-46: CO_2 REDUCTION TO METHANOL ON SILICON PHOTOELECTRODES VIA MOLECULAR CATALYSIS

[Solar Hub – CHASE] Bo Shang[1], Conor Rooney[1], Fengyi Zhao[2], Sungho Jeon[3], David Gallagher[1], Oliver Leitner[1], Langqiu Xiao[3], Colton Sheehan[3], Samuel Bottum[4], James Cahoon[4], Gerald Meyer[4], Thomas Mallouk[3], Eric Stach[3], Tianquan Lian[2], Hailiang Wang[1]
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AFFILIATED TALK – I-T1-12: Enhanced Methanol Production from Photoelectrochemical CO2 Reduction via Interface and Microenvironment Tailoring

We present precious-metal-free molecular catalyst-based photocathodes that are active for aqueous CO_2 reduction to CO and methanol. The first generation photoelectrode is composed of cobalt phthalocyanine (CoPc) molecules anchored on graphene oxide and integrated via a (3-aminopropyl)triethoxysilane linker to p-type silicon protected by a thin film of TiO_2. The photocathode reduces CO_2 to CO with high selectivity at potentials as mild as 0 V versus the reversible hydrogen electrode (vs RHE). Methanol production is observed at an onset potential of -0.36 V vs RHE, and reaches a peak Faradaic efficiency (FE) of 8% and a peak turnover frequency of 0.18 s^{-1}. This was the first molecular catalyst-based photoelectrode that is active for the six-electron reduction of CO_2 to methanol. In the second generation, we fabricate the p-type silicon substrate surface into an array of micropillars, which enables effective integration of an amine-substituted CoPc/carbon nanotube catalyst without sacrificing light absorption as well as improves retention of the key CO intermediate. We further implement a superhydrophobic carbon fluoride coating on the substrate to enhance the conversion of the gaseous reactant and intermediate. The design of the semiconductor/catalyst interface and the electrode microenvironment plays a critical role in optimizing the cascade CO_2 reduction to methanol process and improves the performance to over 20% FE, a remarkable partial photocurrent density of 3.4 mA cm^{-2}, and a high turnover frequency of 1.5 s^{-1}.

I-S1-47: CIRCULARIZING HIGH-PERFORMANCE FROMP THERMOSETS WITH CHEMISTRY

[EFRC – REMAT] Yasmeen S. AlFaraj[1], Yuyan Wang[1], Jeremiah A. Johnson[1], Avni P. Singhal[1], Rafael Gómez-Bombarelli[1], Francesca Starvaggi[2], Xuyi Luo[2], Yan Xia[2], Benjamin Suslick[3], Anzhi Chen[3], Jeffrey S. Moore[3], Saurabh Bagare[3], Jeffrey W. Baur[3], Samuel C. Leguizamon[4], and Leah N. Appelhans[4]
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AFFILIATED TALK – I-T1-2: Accelerating Energy-Efficient Advanced Materials Discovery: Degradable pDCPD Thermosets

High-performance thermosets derive many of their desirable properties (e.g., chemical and thermal stability, stiffness, and durability) from their permanently crosslinked network structures; however, these same structures come at the cost of circularity. REMAT is taking a multi-pronged, transformational approach to address this problem, leveraging scientific intuition, high-throughput experimentation, and machine learning (ML) to discover novel "cleavable comonomers" that can be added during thermoset manufacturing to produce new thermosets with equivalent properties compared to current thermoset yet capable of undergoing selective chemical deconstruction for subsequent recycling or upcycling. This poster highlights these efforts in the context of polydicyclopentadiene (pDCPD) thermosets produced via energy efficient "frontal" ring-opening metathesis polymerization (FROMP). First, we introduce an ML model that enables the prediction of a key thermoset property—the glass transition temperature— with high fidelity based on the molecular structure and loading of bifunctional silyl ether (BSE)-based cleavable comonomers and crosslinkers. Additionally, we have advanced the chemistry of deconstructable pDCPD thermosets containing a low-cost, commercially available cleavable enol ether comonomer, dihydrofuran. We revealed how our cleavable comonomers control key aspects

of FROMP curing (e.g., resin stability, front propagation rate, and thermoset deconstructability). Moreover, we have successfully employed cleavable comonomers in FROMP-based additive manufacturing of deconstructable pDCPD; the relationships between cleavable comonomer structure and printing behavior are used to update our ML models to improve their prediction capability. Finally, we introduce new strategies for "refunctionalization" of pDCPD deconstruction products, achieving key first steps toward a circular process involving FROMP, deconstruction, refunctionalization, and re-FROMP.

I-S1-48: A SUFFICIENT DIAGRAMMATIC THEORY FOR EXCITONS IN STRONGLY CORRELATED MATERIALS

[CCS – QuestC] Swagata Acharya[1], Dimitar Pashov[2], Alexander I. Lichtenstein[3], Mikhail I. Katsnelson[4], Dmitri N. Basov[5], Konstantin S. Novoselov[6], Maciej Koperski[6], Mark van Schilfgaarde[1]
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AFFILIATED TALK – I-T1-7: Efficient and Scalable, High-Fidelity Green's function theory of Electronic Structure and Response functions

Why certain molecules and compounds have the color they do has been a long-standing problem in chemistry. Ligand field theory, developed by Tanabe and Sugano many decades ago, is the traditional way of characterizing excitonic states in transition metal complexes that are responsible for color. It has been very successful for describing multiples near the atomic limit, including weak perturbations from bonds in a molecular environment. Green's function theory is the traditional method for optical properties of systems in the thermodynamic limit. This work formulates two approaches, Green's function theory and Dynamical Mean Field theory. It can span the traditional atomic limit of Ligand field theory, and at the same time take into account longer range interactions often important, particularly in the one- and two-dimensional systems that have become recently popular. This ab initio, two-particle description can quantitatively describe key features of excitons in both the molecular and thermodynamic limits. Self-consistency in the Green's function theory provides high fidelity, which can be essential for a quantitative description. This work shows the range of validity of both ligand-field theory and perturbative Green's function theory, and the elements necessary for a comprehensive description of color, including what kinds of symmetry-lowering mechanisms govern the brightness of the excitons. As examples we show unique features of NiO, MnF_2, and CrX_3 (X=Cr, Br, I), and the impact of magnetic disorder on excitons in low dimensional magnets.

I-S1-49: DECOUPLED ARCHITECTURES FOR SOLAR LIQUID FUELS: CONVERSION OF CO TO METHANOL USING RENEWABLE ORGANIC HYDRIDES

[Solar Hub – CHASE] Andressa V. Mueller,[1] Jake Sirlin,[2] Chiara Cappuccino,[1] Shahbaz Ahmad,[1] M. Zahid Ertem,[1] Dmitry E. Polyansky,[1] Gerald J. Meyer,[2] David Grills,[1] Jose Rodriguez,[1] Irene Barba Nieto,[1] Allison Smith,[2] Sergio Fernandez,[2] Alexander J. M. Miller,[2] James Mayer,[3] Hannah Nedzbala,[3] Renato N. Sampaio,[2] Javier J. Concepcion[1]
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CO_2 reduction to fuels is anticipated to play an important role in global efforts to reduce the devastating effects of climate change. Among various approaches being explored, strategies that provide access to solar liquid fuels are particularly important to achieve carbon-neutral cycles. But the underlying chemistry to generate liquid fuels from CO_2 efficiently and selectively has yet to be developed. Achieving this goal with a single catalyst is difficult and cascade strategies using a combination of catalysts that can carry out some of the required multistep reactions are being pursued. One of these strategies involves CO_2 reduction to CO by one catalyst and further reduction of CO to a liquid fuel by another catalyst or a combination of catalysts. In this work, a strategy for the generation of methanol from CO is presented, using a transition metal-organic hydride combination. NMR, IR, and mass spectrometry, together with labeling studies, chemical synthesis of authentic samples of intermediates and theoretical calculations, were used to demonstrate the conversion of CO to methanol. The key to the high selectivity achieved is the use of organic hydride donors that are inactive towards direct CO_2 reduction and hydrogen generation. These organic hydride donors are inexpensive and renewable and are a promising platform for solar fuels generation from CO_2. Strategies for the transfer of this chemistry to "decoupled architectures" for the conversion of CO_2 to methanol using solar energy will also be presented and the challenges and progress to date towards that goal will be discussed.

I-S1-50: DISENTANGLING CHEMICAL ORIGINS: IN SITU STUDIES OF SOLUTION-PHASE REACTION MECHANISMS

[EFRC – GENESIS] Michelle L. Beauvais[1], Bryan A. Sanchez Monserrate[1], Peter J. Chupas[1], John B. Parise[1], Karena W. Chapman[1]
[1]*Stony Brook University*

In situ X-ray scattering provides valuable insight into the mechanism and kinetics of materials synthesis reactions. Different tools (e.g. XRD, PDF, SAXS) probe structural changes on different length scales. Solution-phase synthesis are particularly difficult to understand and control owing to the dilute nature of the reacting species, their dynamic structure/chemistry, the potential interference from non-reactive species (e.g. solvent, counterions), and the broad timescales involved.

Within GENESIS, we developed reactors for in situ synchrotron experiments that expand our ability to probe solution-phase reactions on the fast and slow limits of experimentally accessible timescales. This has yielded a new window into solution synthesis, with fast sub-second resolution studies capturing transient intermediates and multiplexing capabilities allowing efficient studies of how the reaction mechanism and kinetics depend on the system chemistry (i.e., different compositions, stoichiometries, chemical precursors). These chemical insights have allowed key causal relationships and inter-dependencies to be disentangled—these are difficult to distinguish from analysis of the X-ray scattering data alone.

For hydrolysis to form TiO2, an important photocatalytic material, we see evolution in the product demonstrating the sensitivity of the synthesis (polymorph selectivity, size distribution) to the concentration of reactive and non-reactive species in the solution as they evolve continuously throughout the reaction.

The critical role of ion interactions seems broadly relevant to solution-phase reactions. For the crystallization of CaCO3, we can correlate the reaction kinetics and phase distribution to the competitive binding of reactive ions and "spectator" ions which are now identified as key parameters for controlling the reaction outcome.

I-S1-51: ACCELERATED SORBENT SCREENING FOR REACTIVE CARBON CAPTURE

[EFRC – 4C] Samuel Greenback[1], Ryan J. Jones[2], Kevin Kan[2], Brandon Van[3], Clarabella Li[3], Jenny Y. Yang[3], John M. Gregoire[2], Anastassia N. Alexandrova[1]
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To reactively capture carbon dioxide, a new class of sorbents must be identified that exhibit capture from dilute streams, capture-conversion durability, and activation of electrochemical transformations. To accelerate sorbent discovery, we have designed an integrated theory-experiment workflow and present herein its initial demonstration. The Alexandrova group has established a computational workflow to understand the scaling relationship between pKa and CO_2 binding energy for a given class of molecules, building towards a map of the chemical descriptors that underlie scaling parameters. Deployment of the computational workflow revealed a strong scaling relationship for N-heterocyclic carbenes (NHCs), while NHCd and cyclic alkyl amino carbenes (CAAC) were found to deviate from the scaling relationships. These results are informing experimental efforts in the Yang group as well as future sorbent design. Given the throughput of candidate identification via the computational workflow, the Gregoire group has created the carbon capture screening instrument (CCSI) to provide quantitative characterization of sorbent capacity, from which binding constant may be inferred. Due to the combinatorial nature of the solvent composition search space, a multi-channel media preparation unit is coupled to a gas recirculation loop to accelerate equilibration of CO_2 in the gaseous and sorbed state. This capability enables the automated preparation and execution of a CO_2 sorption experiment in less than 10 minutes, a more than 10× acceleration over traditional methods. This capability helps match the throughput of experiment and theory, informing the next generation of research workflow and molecular design and realizing a new paradigm in sorbent discovery.

I-S1-52: PULSED PHOTON FLUXES FOR MANIPULATING CATALYSIS

[EFRC – CPEC] Ryan Berry[1], Arik Beck[1], Michael Allan[2], Michael Gordon[1], Eranda Nikolla[2], Phillip Christopher[1]
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Recent research has shown that the illumination of supported metal catalysts with visible light can influence catalytic reactivity and selectivity through non-thermal mechanisms. Photo-excitation induces transient charge transfer to adsorbed species on catalytic surfaces in a chemical specific way, influencing the rates of some elementary steps more than others. These findings suggest that the use of programmed photon pulses on time scales that are "resonant" with the times scales of important elementary steps within catalytic mechanisms may provide a unique handle for

influencing and controlling catalytic reactions. In this poster, we highlight initial work from the center aimed at three primary goals: (1) resolving the time scales of the influence of photons on catalytic function (e.g. after the introduction of photons, when do adsorbate coverages and reaction energetics respond), (2) measuring the influence of continuous wave and pulsed photon illumination on the kinetics of NH_3 decomposition on Ru and Ru alloy surfaces, and (3) synthesizing photo-responsive doped perovskite catalytic materials. These goals are being achieved through a collaborative effort involving the design of new reactors, the development of spectroscopic tools, execution of kinetic and spectroscopic measurements, the correlated synthesis and characterization of new materials, and theoretical analysis of the results.

I-S1-53: STUDYING CHARGING IN PT-BASED CATALYTIC CONDENSERS USING X-RAY SPECTROSCOPIES

[EFRC – CPEC] Susannah Scott[1]
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Catalytic condensers may be able to store enough charge (either as electrons or holes) in their metal nanoparticles (e.g., Pt) to modify the binding energy of adsorbates (e.g., CO), and thereby influence the rate and/or selectivity of reactions. Furthermore, density functional theory calculations predict that charge accumulates at undercoordinated edge and corner sites of metal nanoparticles, which are often highly reactive sites. We aim to investigate where charge accumulates in these devices and the impact of the charge on the structure of the metal nanoparticles. Specifically, we used X-ray photoelectron spectroscopy (XPS) and X-ray absorption spectroscopy (XAS) to probe the electronic and physical structure of metal nanoparticles while charging. An in-situ XPS sample stage was fabricated to charge the catalytic condensers. Preliminary experiments show that the kinetic energy of electrons originating in Pt 4f states shifts by 1 eV per 1 V of condensed charge. Complementary XAS experiments at the Pt L 3 and L 2 edges directly probe the 2p 5d electronic transition, whose intensity depends on the occupancy of the Pt 5d orbitals. Therefore, Pt L-edge XANES can in principle confirm and quantify the extent of charge accumulation in the catalytically relevant valence band as a function of applied voltage. We also plan Pt L-edge EXAFS to elucidate structural changes that occur during charging, in order to inform modeling of structure-sensitive catalytic reactions.

I-S1-54: REACTOR DESIGN FOR CONTINUOUS CATALYTIC CONDENSER KINETICS

[EFRC – CPEC] Omar A. Abdelrahman[1]
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An experimental reactor was designed, fabricated, and validated for continuous flow catalytic reaction of a catalytic condenser at industrially-relevant conditions to assess the kinetics of dynamic surface chemistry. Reactor configuration accounts for <3 deg C temperature variation across the catalytic condenser while also allowing for voltage feedthroughs and device contacting to deliver +/- 10V across the condenser stack. In addition, reactor design permitted continuous flow operation in variable temperature conditions at low conversion (<0.1%) with accompanying

analytical methods measuring conversion of hundreds of ppm. This methodology permitted the first measurement of continuous flow catalytic condenser kinetics under different applied voltage, indicating significant variation in surface turnover frequency with applied voltage.

I-S1-55: AUTONOMOUS PHOTOTAXIS OF HYDROGEL SWIMMERS

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The design of robotic soft matter has recently expanded greatly through strategies inspired by living organisms, such as using external sources of energy to generate shape transformations, locomotion, self-regulation, and autonomy. Encoding soft matter with life-like functionalities could enable new soft robotics or control over chemical reactions. Functionalized hydrogels are excellent candidates for such materials since they can operate in water and are highly responsive to their environment, but their response times can be slow. We report here on the design of photo-responsive hybrid hydrogel polymers that integrate supramolecular nanofibers and ferromagnetic nanowires that couple to magnetic fields. Compared to our previous work at CBES,* these hydrogels have much faster response times enabled by the supramolecular skeleton, creating materials capable of swimming underwater. Interestingly, we also discovered that these robotic hydrogels spontaneously swim toward an external light source, a phenomenon similar to phototactic processes observed in nature. To analyze the complex behavior of these robots, we developed a continuum model that incorporates the coupling between the physics of polymer hydrogels, photoactive chemical reactions, and magnetism. The model is solved using finite element methods, and the theoretical results agree with experimental data. This model will facilitate the design of future robotic soft matter with even more complex functionalities.

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Poster Session 2

I-S2-01: FUNCTIONALIZED IONIC LIQUID ELECTROLYTE CONTROLS CO_2 ELECTROREDUCTION PRODUCT SELECTIVITIES AND OVERPOTENTIALS OVER TRANSITION METALS

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AFFILIATED TALK – I-T2-3: Functionalized Ionic Liquid Electrolyte Controls CO2 Electroreduction Product Selectivities and Overpotentials Over Transition Metals

Electrochemical CO_2 reduction (ECO_2R) is an attractive technology platform to convert CO_2, a greenhouse gas, to fuels and other commodity chemicals considering its modularity and mild operational conditions. Despite the wide research efforts in the development of selective and stable catalysts in aqueous electrolytes, ECO_2R remains challenging due to competition from the hydrogen evolution reaction and high overpotentials needed to drive the conversion reaction. Novel electrolytes such as those based on ionic liquids (ILs) have the potential to synergize reactive carbon capture and conversion due to their tunability in CO_2 solubility, selectivity, and reduction potentials. However, the electrolyte effects on ECO_2R, specifically in the presence of functionalized ILs, is not well understood. In particular, the role of the common imidazolium cation has been a matter of debate. Here, we present the interfacial liquid behavior and the specific surface species as examined by in-situ surface enhanced Raman spectroscopy (SERS), electron paramagnetic resonance (EPR), static and dynamic electrochemical impedance spectroscopy (dEIS), differential electrochemical mass spectrometry (DEMS), and Density Functional Theory (DFT) calculations on Ag, with ongoing working including Cu electrode. A systematic study of structures was synthesized to probe the role of the cation, anion, and the generated carbamate and carboxylate species from absorption of CO_2 by the ILs on ECO_2R. A superior selectivity for CO_2-to-CO reaction on Ag at lowered overpotentials was achieved compared to non-aqueous electrolytes and unfunctionalized ILs. C_{2+} products including C_4 were possible with Cu. Not only imidazolium but also the pyrrole anion were found to co-catalyze ECO_2R by enabling high concentrations of CO_2 at the interface and stabilizing reaction intermediates, thus enabling a mechanism for tuning selectivity and overpotentials.

I-S2-02: RAPID MANUFACTURING OF ARCHITECTED MATERIALS

[EFRC - REMAT] Anna Cramblitt[1], Natalie Larson[2], Justine Paul[1], Jackson Wilt[2], Luis Rodriguez Koett[1], Philippe Geubelle[1], Jeffrey Moore[1], Jennifer Lewis[2], and Nancy Sottos[1]
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Natural material systems autonomously generate intricate hierarchical architectures that combine soft and hard material domains with coalesced interfaces. Such architected structures often possess superior material properties compared to their homogeneous counterparts. The efficient manufacture of geometrically complex, free-form objects with tailored microstructure and properties at submicron length scales remains a significant challenge. In the current work, we

explore two promising pathways to achieve hierarchical architectures in synthetic materials. In the first additive manufacturing approach, we exploit direct ink writing with multi-material rotational printheads to produce pre-programmed helically oriented features composed of pure and filled thermoset resins. Rotational printheads enable seamless switching of individual input channels on and off, varying both the feature composition and internal geometry on demand. In a second complementary approach, we harness frontal polymerization dynamics to spontaneously fabricate molecularly architected polymers with multiscale organization. This dissipative fabrication method leads to the formation of amorphous and semi-crystalline domains emerging from the internal interfaces generated between the solid polymer and the propagating cure front. The size, spacing, and arrangement of the domains are controlled by the interplay between the reaction kinetics, thermodynamics, and boundary conditions. Small perturbations in the fabrication conditions lead to remarkable changes in the strength, elastic modulus, and toughness of the resulting materials. This ability to control mechanical properties and performance solely through initial and boundary conditions represents a significant advancement in the design and manufacturing of advanced multiscale materials.

I-S2-03: FIRST PRINCIPLES STUDY OF TRANSITION METAL OXIDE SURFACES IN ELECTROCHEMICAL CONDITIONS

[EFRC – CEDARS] Shaylee McBride[1], Geoffroy Hautier1, Maria Maalouf[2], Simon Gelin[2], Ismaila Dabo[2], Joan Ejeta[3], Kristen Rhinehardt[3]
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Identifying intermediates involved in important electrochemical reactions such as the oxygen evolution reaction (OER) require the combination of advanced experimental techniques with first principles modeling. We will report here on recent advances in our theoretical efforts within the CEDARS EFRC focusing on the identification of surface coverage, polarons and their optical response as well as modeling of hydrogen transfer rates on important transition metal oxides used in (photo-)catalysis.

First, we will show how first principles computations can identify the hydrogen coverage as a function of the voltage applied and pH providing simulated cyclic voltammetry curves that can be directly compared to experimental data on single-crystal metal oxides such as RuO_2 and IrO_2. The combined theory and experiment approach identifies surface phase transitions during cyclic voltammetry in metallic rutile oxides. Challenges in extending this approach to semiconducting catalysts such as $SrTiO_3$ or TiO2 will be discussed. Next, we will report on our results on the modeling of surface polarons on $SrTiO_3$ and TiO_2 surfaces. These polarons are important spectroscopic signatures observed during ultra-fast spectroscopy experiments. We report on the stabilization energy and nature of the polarons as well as their optical response. Finally, while ultra-fast spectroscopy can identify rate constants for potential processes such as hydrogen transfer, the theoretical description of these rates remains challenging, and we will report on recent developments in that front.

I-S2-04: ADVANCES IN CATALYTIC HYDROCONVERSION OF PLASTICS WASTE TO VALUABLE CHEMICALS

[EFRC – CPI] Christine M. Oberhausen[1], Jessie A. Sun[1], María Ley-Flores[2], Zachary R. Hinton[1], Pavel A. Kots[1], Darien K. Nguyen[1], Sibao Liu[1], Brandon C. Vance[1], Panagiotis Dimitrakellis[1], Robert M. O'Dea[1], Mya Soukaseum[1], Michael R. Talley[1], Mary P. Watson[1], Thomas H. Epps, III[1], LaShanda T.J. Korley[1], Raul F. Lobo[1], Juan J. de Pablo[2], Dionisios G. Vlachos[1]
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Plastics are ubiquitous in the modern world, yet current methods for managing plastic waste are unsustainable. Thus, hydroconversion has emerged as an attractive route to chemically convert polyolefins (POs) to valuable fuels, lubricants, and waxes. Our previous work has demonstrated $Pt/WO_3/ZrO_2$ as an active and selective hydrocracking catalyst for deconstructing various POs into branched, liquid fuels and platform chemicals. Investigations via molecular dynamic simulations and statistical associating fluid theory equations of state have elucidated composition-property relationships in binary mixtures containing polyethylene (PE) and higher n-alkanes. Such insights permit the advancement of more efficient reaction systems. However, real-world plastics also contain complex formulations of small-molecule additives to improve performance and processability. Thus, the impact of a common class of additives, antioxidants, on catalyst performance was also investigated. The presence of such additives in high density polyethylene (HDPE) caused a two-fold decrease in gas and liquid product yields compared to additive-stripped HDPE. Infrared spectroscopy determined that antioxidants altered the catalyst metal acid site balance, causing reduced activity. This work outlines a framework for future investigations on additional classes of additives to understand, and ultimately mitigate, their effects. Finally, the oxidation of alkanes, like those produced via hydroconversion, was achieved via thermal, atmospheric plasma. Power output and reaction time were tuned to produce optimal molar yields of 29.2% alcohols and ketones, demonstrating the potential to upgrade hydroconversion alkane products into value-added oxygenated chemicals. Ultimately, by combining computational and experimental approaches, significant progress toward the development of plastics waste upcycling was achieved.

I-S2-05: REALIZATION OF A PHOTOELECTROCHEMICAL CASCADE FOR THE GENERATION OF METHANOL, A LIQUID SOLAR FUEL

[Hub – LiSA] Thomas Chan,[1,2] Calton J. Kong,[1,3] Grace Rome,[1,4] Darci Collins,[1,4] Alex King,[1,3] Rajiv R, Prabhakar,[1,3] Sarah Collins,[1,4] Michelle Young,[1,4] Mickey Wilson,[1,4] Myles Steiner,[1,4] Adele C. Tamboli,[1,4] Emily L. Warren,[1,4] Clifford P. Kubiak,[1,4] Ann L. Greenaway,[1,4] Joel W. Ager[1,3]
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Natural and synthetic biochemical networks use reaction cascades to achieve selectivity, suggesting a route for improving the selectivity of photoelectrochemical (PEC) production of liquid fuels. The LiSA team has utilized cross-institutional, cross-field expertise to co-design and implement a two-step cascade PEC scheme for the reduction of CO_2 to CO (CO_2R) and subsequently of CO to a liquid product (COR). The co-design process established design principles, synthesized and integrated components, and has evaluated the performance of

photoelectrochemical architectures for this scheme. To provide the two, large potentials required for efficient CO_2R by this approach, we modified the design of III-V-based 3 terminal tandem (3TT) solar cells for PEC compatibility. Cobalt phthalocyanine (CoPc) immobilized on carbon nanotubes (CNTs) is known to produce CO with high selectivity but has recently been shown to produce methanol at more reducing potentials, and thus is employed here as the catalyst for both CO_2R and COR. Factors influencing the behavior of the complete device, such as illumination, Faradaic efficiency, and electrolyte flow, are addressed computationally and provide inputs to the experimental co-design process. The light-driven performance of the integrated 3TT/CNT/CoPc devices will be presented. Prospects for using the co-design process to target other liquid fuels or chemical products will also be discussed.

I-S2-06: COMBINING X-RAY SCATTERING AND OPTICAL SPECTROSCOPY TO CHARACTERIZE ION AND SOLVENT INTERCALATION IN Π-CONJUGATED POLYMERS AND THEIR IMPACT ON OPTOELECTRONIC FUNCTION

[EFRC – SPECS] Casey Davis[2], Stephen Barlow (KI)[2], Joel Bombile[3], Megan Brown[3], Zhiting Chen[1], Andrew Ferguson (KI)[4], Ann Greenaway (KI)[4], Elisa Miller (KI)[4], Obadiah Reid (KI)[2,4], Erin Ratcliff (PI)[3], Chad Risko (KI)[3], Alberto Salleo (KI)[5], Jonathan Thurston[2], Michael Toney (KI)[2]
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Conjugated polymers are promising materials for energy applications ranging from batteries to photoelectrochemical cells due to advantages of low cost, high flexibility and scalability, and facile tuning of redox properties. A conjugated polymer in contact an electrolyte can be doped through multiple processes, resulting in both ions and solvent intercalation into the polymer. The physical structure dynamically changes across length scales, thereby impacting their charge transport characteristics and photo-physics. SPECS is employing a number of in-situ and ex-situ X-Ray scattering techniques to investigate structural changes in the polymer and optical, electronic, and chemical spectroscopy methods to correlate these changes with optoelectronic function and transport phenomena. Results to be presented include grazing-incident X-ray scattering to discern changes in pi-pi packing (angstroms) and swelling in side chain regions (nanometers) that arise from doping and ion intercalation and structural shifts on the order of 10 to 100 nm. Pair distribution function and x-ray absorption spectroscopy are used to examine the ion coordination environment, supported with *in situ* x-ray photoelectron spectroscopy and conventional spectroelectrochemical approaches from the visible to the mid-IR. Critical results from density functional theory (DFT) calculations identify the nature of the polaron states and changes with proximity to counterions. These changes will be correlated with alterations in transient absorption dynamics and photoinduced charge generation that take place with degrees of swelling/intercalation. Within the context of social impact, it is crucial to assess the social and environmental justice landscapes in which this technology will be developed.

I-S2-07: XYLAN PLAYS A CRITICAL ROLE IN PATTERNED SECONDARY CELL WALL FORMATION

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AFFILIATED TALK – I-T2-8: Xylan Plays a Critical Role in Patterned Secondary Wall Formation

Numerous cellular processes act in a coordinated manner to deposit patterned secondary cell walls (SCWs). Arabidopsis protoplasts, transiently transformed with *VND7* overexpression, were used to investigate the role of xylan in patterned SCW formation. Cellulose and xylan patterns were examined with fluorescence labeling and confocal microscopy. Protoplasts with shortened xylan backbones (*irx9-2*, *irx14*, and *endo*-1,4-β-xylanase-treated) produced distorted SCWs bands with coincident cellulose and xylan patterning. Protoplasts isolated from the mutant *esk1*, where cellulose-xylan interactions are limited[1], also produced distorted SCWs but, uniquely, the cellulose and xylan patterns did not coincide.

Our research shows that SCW patterning in the regenerated wall is disrupted by altered xylan structure. We propose that a cellulose-xylan network is established during early wall synthesis which acts as a scaffold to direct subsequent microtubule-independent cellulose deposition[2]. Short-chain xylans do not properly tether cellulose microfibrils[3], which results in polymer drift, yielding an indistinct scaffold that is reinforced in later synthesis. When cellulose and xylan do not interact, their patterns remain misaligned during SCW formation. We are continuing to investigate whether the SCW influences cytoskeletal remodeling, which would affect the sites of cellulose synthase and xylan delivery later in wall development. Finally, we present SCW-regenerating protoplasts as a novel platform to research the deposition of xylem vessel-type SCWs.

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I-S2-08: HIGH-FIDELITY, HIGH-THROUGHPUT ELECTROCHEMISTRY WITH Δ-LEARNING AND SOLVATED BEYOND-DFT METHODS

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Accurate modeling of electrochemical reactions requires electronic structure methods beyond semi-local density-functional theory (DFT), including hybrid DFT and many-body perturbation theory using *GW* and the random-phase approximation (RPA). Since these methods are computationally expensive for high-throughput calculations and for explicit treatment of solvation by the electrochemical environment, the BEAST CCS collaboration is developing machine-learning (ML) methods for beyond-DFT-quality predictions from DFT calculations and accurate implicit solvation approaches for *GW* and RPA calculations.

Here, we first show an ML model that can quickly and accurately predict electronic structure at the hybrid DFT level using atomic band character features and eigenvalues from semi-local DFT

calculations. The ML-predicted eigenvalues result in remarkably accurate band structure, projected density of states, and band gaps, even though the model was not explicitly trained on these properties. Further, the ML model retains its accuracy for materials well outside the initial training set indicating its potential to predict higher-level electronic structures for more complex materials, shown here with hybrid DFT and extensible to *GW*/RPA in ongoing work.

Second, we develop a framework for implicit solvation of *GW* calculations that introduces the frequency-dependent liquid polarizability from implicit solvation models into the screened Coulomb interaction of *GW* calculations with a solvated-DFT starting point. We show that the liquid screening contributions substantially reduce the HOMO-LUMO gap of molecules, in agreement with beyond-DFT predictions of solvated electronic structures. Together, these studies lay the groundwork for the unification of high-throughput and high-fidelity first-principles electrochemistry.

I-S2-09: UNDERSTANDING AND MANIPULATING INORGANIC NANOPARTICLE ORGANIZATION AND ASSEMBLY USING PEPTIDES, PEPTOIDS, AND PROTEINS

[EFRC – CSSAS] Yifeng Cai[1], Xin Qi[1], Nada Naser[1], Kacper Lachowski[1], Madison Monahan[1], Helen Larson[1], Chris Lowe,[1] Jim Pfaendtner[1], Jaehun Chun[2], Chun-Long Chen[1,2], Lilo Pozzo[1], Chris Mundy[1,2], Brandi Cossairt[1], François Baneyx[1]
[1]University of Washington; [2]Pacific Northwest National Laboratory

With richness in chemistry, structure and function, high information content building blocks have considerable potential for orchestrating inorganic assembly and reconfiguration. Realizing this promise requires an (ideally predictive) understanding of how interfacial molecular interactions including sidechains and solvent responses underpin assembly outcomes. Here, we report on recent CSSAS advances using three types of biomacromolecules and inorganic nanoparticles. In an effort involving pH-controlled assembly of SiO_2 nanoparticles with bifunctional solid-binding proteins, we show how an energetically benchmarked multiscale framework that characterizes the aggregation ensemble by integrating long-range colloidal forces from DLVO theory and short-range protein-silica interactions from atomistic MD simulations, captures the system's reversible association-dissociation behavior over one pH unit. The model forecasts how small changes in pH modulate cluster size and accurately predicts chemical fatigue associated with Na^+ accumulation over repeated cycles of base addition. In a study focused on reversible thermal assembly of AuNP by a Cys-terminated elastin-like peptide (ELP), we uncover a crucial role for free ELPs in determining cluster size and plasmonic responses, and exploit this knowledge to entrap precise amounts of cargo within coacervates. Finally, we show how changes in solubility and size of peptoid-terminated QDs enables access to distinct assembly regimes. We navigate from QD-linked multilayered peptoid sheets in aqueous solvents, to QD-facilitated or inhibited assembly in organic solvents depending on the relative hydrophobicity of surface ligands, to large hybrid and binary sheets by manipulating QD size. This progress in fundamental understanding has led to design rules that will usher in next generation advanced materials.

I-S2-10: STRUCTURAL ORGANIZATION OF APO-STATE AND UDP-GLUCOSE AND Mn^{2+}-BOUND PHYSCOMITRIUM PATENS CELLULOSE SYNTHASE 5 HOMOTRIMERIC ASSEMBLIES

[EFRC – CLSF] Lynnicia Massenburg[1], Alexis Williams[2], Joseph Cho[1], Carol Bator[1], Hugh O'Neill[2], B. Tracy Nixon[1]
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Plant membrane proteins called cellulose synthases (CesAs) make cellulose, the most abundant biopolymer in the world. The recent structure of poplar CesA8 trimer provided the first structural insights into this important protein complex, but an evolutionary context of CesA structure in other plant species is needed. Our overall aim is to investigate the mechanism of plant CesA oligomerization in cellulose synthesis. To achieve this, we characterized the structure of an evolutionary precursor to vascular plants, *Physcomitrium patens* (Pp) CesA5, in the apo-state and uridine diphosphate (UDP) glucose and Mn^{2+} bound state using cryo-Electron Microscopy (cryo-EM). This structural analysis provided residue-level details about oligomer interactions and the global conformation of PpCesA5 trimers. PpCesA5 was successfully expressed in insect cell cultures and a protein purification approach was developed to optimize the isolation of PpCesA5 trimers. The apo-state PpCesA5 cryo-EM structure was determined at 3 Å resolution. Interestingly, PpCesA5 shows dynamic transmembrane helix packing with a likely flexible transmembrane helix 7 that was not reported previously. Moreover, density for a glucan chain is visible in the translocation tunnel of the enzyme. Cryo-EM analysis of the PpCesA5 UDP-glucose and Mn^{2+}-bound state are underway. These data will be used for an evolutionary structure comparison with poplar CesA8 and cotton CesA7 for insights on domains involved in oligomerization and function. In future work, it will be possible to utilize the knowledge gained by solving the structures of CesA proteins to rationally guide protein design for biofuels and new biomaterials.

I-S2-11: EXPLORING SYMMETRY BREAKING AND STRUCTURAL DIMENSIONALITY ENGINEERING IN HOIPS: UNRAVELING EMERGENT SPIN, ELECTRONIC, AND OPTICAL PROPERTIES

[EFRC – CHOISE] Yi Xie,[1] Jack Morgenstein,[1] Gabrielle Koknat,[1] Nicholas J. Weadock,[2] Junxiang Zhang,[2] Heshan Samuditha Weerasinghe Hewa Walpitage,[3] Peter C. Sercel,[4] Alan Phillips,[5] Naidel A. M. S. Caturello,[6] John Colton,[7] Xiaoping Wang,[8] Ruyi Song,[1] Benjamin G. Bobay,[1] Jeffrey Blackburn,[5] Matthew C. Beard,[5] Zeev Valy Vardeny,[3] Seth Marder,[2] Michael F Toney,[2] Volker Blum,[1] and David B. Mitzi[1]
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AFFILIATED TALK – I-T2-10: Exploring Symmetry Breaking and Structural Dimensionality Engineering in HOIPs: Unraveling Emergent Spin, Electronic, and Optical Properties

Hybrid organic-inorganic perovskite (HOIP) semiconductors enable remarkable compositional, structural, and dimensional versatility owing to the broad flexibility in selecting single or mixed organic cations within the HOIP framework. Consequently, novel structural dimensionality, varying degrees of distortions and symmetry breaking, and associated impacts on optoelectronic properties can be targeted. One of our current works demonstrates a chiral-chiral mixed-cation system wherein a controlled small amount (<10 %) of dopant chiral cation can be doped into a

chiral 2D HOIP system to modulate the structural symmetry from a higher symmetry (*C*2) to the lowest symmetry state (*P*1) and impact the spin-related, chiroptical, and thermal properties. However, an understanding of the microscopic mechanisms behind the structural distortions and symmetry breaking has remained elusive. Temperature-dependent neutron diffraction was therefore performed for a new PbI_4^{2-}-based 2D HOIP, wherein a thermally-induced structural transition leads to inversion symmetry breaking and a substantial spin splitting (~33 meV). A precise estimation of H atom positions unveiled the templating effect of organic cations by investigating how organic-inorganic hydrogen-bonding tailors the perovskite structure and modulates spin-related properties. Moreover, we developed novel HOIPs exhibiting an intermediate structural dimensionality (between 1D and 2D) with varying widths of the inorganic ribbons, suggesting the potential to tune quantum confinement and modulate exciton properties. The tunable perovskite structures and their associated structure-sensitive properties underlie a deeper comprehension of the structure-property relationship and therefore benefit future semiconductor design and prospective application in energy harvesting, light-emission, spin-control, and ferroelectricity.

I-S2-12: PHOTOCATALYSIS IN A NEW LIGHT: A BIOHYBRID APPROACH FOR IMPROVED REACTIVITY WITH TUNABLE LOW-ENERGY LIGHT EXCITATION

[EFRC – BioLEC] Paul T. Cesana[1], Beryl X. Li[2], Claire G. Page[2,3], Samuel G. Shepard[4], Stephen I. Ting[2,5], Dvir Harris[1], Stephanie M. Hart[1], Courtney M. Olson[1], Megan A. Emmanuel[2], Jesus I. Martinez Alvarado[2], Minjung Son[1], Talia J. Steiman[2], Felix N. Castellano[4], Abigail G. Doyle[2,5], Todd K. Hyster[2,3], David W. C. MacMillan[2], Gabriela S. Schlau-Cohen[1]
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AFFILIATED TALK – II-T2-6: Photocatalysis in a New Light: A Biohybrid Approach for Improved Reactivity with Tunable Low-Energy Light Excitation

Photocatalysts convert light into chemical reactivity, yet are light-limited and often require blue-to-UV excitation. In photosynthesis, light capture and reactivity have been optimized by separation into distinct sites. Inspired by this molecular architecture, we synthesized biohybrid photocatalysts by covalent attachment of a light-havesting component to a reactive component. Spectroscopic investigation using pump—probe spectroscopy and fluorescence lifetime measurements found that absorbed energy was efficiently transferred to the reactive component, and the utility of the biohybrids was demonstrated via an increase in product yields using test reactions. This generalizable biohybrid strategy has been broadly demonstrated with photosynthetic proteins or dyes as the light-harvesting component and transition metal photocatalysts or photoenzymes as the reactive component, and it can be readily implemented in future applications.

I-S2-13: CATALYST DESIGN FOR DECARBONIZATION CENTER

[ERFC – CD4DC] Laura Gagliardi[1], Joseph Hupp[2], Nancy Washton[3], Chibueze Amanchukwu[1], John Anderson[1], Karena Chapman[4], Juan de Pablo[1], Massimiliano Delferro[5], Omar Farha[2], Andrew Ferguson[1],

Ian Foster[1], Rachel Getman[6], Ksenija Glusac[7], Johannes Lercher[3], Matthew Neurock[8], Justin Notestein[2], Donald Truhlar[8], Anna Wuttig[1]
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The central goal of CD4DC is to discover, design, and synthetically realize novel metal-organic framework (MOF) catalysts for the decarbonization of the chemical and energy industries as well as to optimize the key catalytic reactions involved. Three types of highly active and selective catalysts are targeted: (1) MOFs with components that provide a high degree of polarizability and softness especially suited for superior hydrogen transfer; (2) MOF-based systems that use external electric potential; and (3) MOFs for H_2 storage and sustainable fuels. These catalysts drive two proposed reaction classes: H_2 addition and release from liquid organic hydrogen carriers and the efficient combination of C-C bond formation with H_2 management. To advance the discoveries CD4DC follows two cross-cutting research approaches, one based on theory, computation, and active learning and one on advanced characterization.

I-S2-14: MEASURING AND MODELING PERMEATION AND TRANSPORT PROCESSES WITHIN BACTERIAL MICROCOMPARTMENTS

[EFRC-CCBC] Saad Raza[1], Neetu Yadav[1], Nicholas M. Tefft[1], Nina Ponomarenko[2], Karen L. Mulfort[2], David M. Tiede[2], Oleg G. Poluektov[2], Samuel Synder[2], Lisa M. Utschig[2], Markus Sutter [1,3], Michaela A. TerAvest[1], Josh V. Vermaas[1]
[1]Michigan State University; [2]Argonne National Laboratory; [3]Lawrence Berkley National Laboratory

Bacterial microcompartments (BMCs), protein-based encapsulating shells are found in multiple prokaryotes and hold exciting potential for encapsulating a diverse range of metabolic pathways. Genomic data infer remarkable tailored functional diversity, including control of metabolite confinement, diffusional control across shell walls, and the creation of unique reaction microenvironments. However, to-date, there is only limited understanding of BMC metabolite permeation and transport processes at the molecular level. Understanding these fundamental mechanisms is essential to harness the full potential of BMCs across multiple applications. A CCBC-wide effort spanning from wet-bench experiments to molecular simulation is working to unravel the structure function relationships that control permeation of molecular metabolites across BMC shell walls. Molecular simulations offer a virtual window into the behavior of small molecules as they traverse BMC shell pores. These atomically detailed simulations provide critical insight on permeability control factors and provide concepts necessary to guide BMC design and engineering. These concepts are being tested with explicit measurements of permeability using BMC encapsulated redox enzymes, biohybrids, and catalysts that provide fluorescent, optical absorption, and EPR detected responses to selective small molecule permeants, including pO_2, pH, and a range of redox metabolites, variable by size, charge, hydrophobicity/hydrophilicity. We are also investigating natural and engineered systems to transfer electrons into and out of the shells. These experiments will validate simulation results and offer new perspectives on the

intricate mechanisms governing permeation. This work will help to unlock the full potential of BMC shells by enabling design of customized permeability.

I-S2-15: PRECISE CONTROL OVER THE FORMATION AND TRANSITION OF PEPTOID SELF-ASSEMBLED NANOMATERIALS

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Among the various sequence-defined polymers developed as functional building blocks for biomimetic material synthesis, peptoids, or poly-N-substituted glycines, have some unique advantages for the controllable formation of hierarchical materials. Peptoids are easy to synthesize and exhibit lower structure complexity than peptides and proteins by having no backbone chirality and hydrogen bond donors. They are highly programmable with various side-chain chemistry enabled for precise control over peptoid-peptoid and peptoid-surface interactions. In CSSAS, peptoids are the primary building block to address several scientific gaps across scales. Starting from the individual peptoid sub-monomers, we have developed a force field library that helps us predict the folding of peptoid molecules into secondary and tertiary structures. Up to the peptoid molecules, we have demonstrated that peptoids self-assemble into various nanostructures, including nanosheets, nanotubes, and nanohelices. Their formation mechanisms were investigated through state-of-art microscopic techniques and molecular dynamic simulations, leading to a better understanding of the peptoid design rule for predictive materials synthesis. Within these peptoid assemblies, we developed different systems employing interconversions between the morphologies controlled by electrostatic interactions, temperature, and light-responsive motifs. The morphological transitions provide information on thermodynamics and dynamics during the self-assembly and open access to the design of stimuli-responsive materials. We further showed the use of metal-ligand coordination to assist the formation of multi-layered hybrid materials. Our results showed that peptoids are good candidates to translate sequence chemistry into self-assembly outcomes and to understand how molecular interactions can control the energy landscapes across which hierarchy develops.

I-S2-16: PHOTOREDOX AND ELECTROCHEMICAL METHODS OF POLY(ACRYLIC ACID) VALORIZATION

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Poly(acrylic acid) (PAA) is a widely used polymer that predominantly finds application as a superabsorbent polymer for diapers and other single-use hygiene products. Although single-use hygiene products improve our quality of life, they generate nearly 3.5 million tons of waste, which presents an ongoing challenge for both current and future generations. As a result of this issue, there has been growing interest in recycling and upcycling this type of polymer waste. Because

superabsorbent polymers are challenging to recycle as they have been designed to withstand degradation, we focused on valorization via chemical modification of PAA. Post-polymerization modification of PAA by photoredox and electrochemical methods has been demonstrated. Photoredox decarboxylative fluorination of PAA using several organic photocatalysts allows for the tunable synthesis of valuable copolymers of poly(acrylic acid) and poly(vinyl fluoride). Conveniently, low and high levels of vinyl fluoride content can be achieved by varying the concentration of the fluorine donor (SelectFluor), the photocatalyst, and the duration of irradiation, allowing the synthesis of copolymers with tunable properties. PAA has also been oxidatively decarboxylated by leveraging electrochemical methods to install alkyl ethers, namely methyl ethers, on the polymer backbone to transform PAA to poly(vinyl methyl ether) (PVME), a tackifier, and plasticizer for adhesives. Additionally, the innate tunability of this electrochemical method delivers novel vinyl ether copolymers that are comparable to polymers that receive use in dental care products.

I-S2-17: CO-DESIGN OF ZINC TITANIUM NITRIDE SEMICONDUCTOR TOWARDS DURABLE PHOTOELECTROCHEMICAL APPLICATIONS

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Development of photoelectrochemical systems requires, among other advances, photoelectrode materials that are photocatalytically active and stable in harsh electrochemical environments. Our Liquid Sunlight Alliance team has intentionally searched for a candidate photo-absorber based on co-design principles, wherein design for photoactivity is based on the ability to integrate the new material with established semiconductors and design for stability is based on the propensity for the photo-absorber to self-passivate during operation. This has led to a tightly integrated experimental and computational investigation of wurtzite $ZnTiN_2$ as a photoabsorber. We first experimentally show that unintentional cation disorder in sputtered $ZnTiN_2$ films can be utilized to reduce the bandgap to make it appropriate to drive solar fuel redox reactions, and leverage the transformation of the $ZnTiN_2$ surface under CO_2R-relevant conditions to protect the semiconductor surface. We then use first-principles calculations to explain the origins of band gap reduction: cation disorder, associated with a large concentration of low formation-energy antisite defects, results in charge-imbalanced environments, driving a broadening of both the conduction and valence bands and reducing the band gap. Finally, experimental integration with established semiconductor systems allows us to rapidly improve the optoelectronic properties of the sputtered $ZnTiN_2$ films, paving the way for high photocatalytic activity for PEC to be demonstrated using this material. Future work will focus on developing PEC device structures based on the improved $ZnTiN_2$ photoelectrode films by optimizing semiconductor properties (e.g. doping) and interfaces with surrounding device layers.

I-S2-18: IDENTIFYING ELECTROCATALYSTS FOR THE REDUCTION OF CAPTURED CO_2

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Reactive carbon capture is an emerging technology for the capture and conversion of dilute waste CO_2 streams into valuable chemicals and fuels. The key distinguishing feature of reactive carbon capture is that after nucleophile sorbents are used to capture CO_2, the resulting Nuc-CO_2 species are directly reduced by electrocatalysts to generate C-containing products and regenerate the nucleophile sorbents:

$$\mathrm{Nuc} + \mathrm{CO_2} \rightleftarrows \mathrm{Nuc} - \mathrm{CO_2}$$

$$\mathrm{Nuc} - \mathrm{CO_2} + \mathrm{ne^-} + \mathrm{nH^+} \rightleftarrows \mathrm{Nuc} + \mathrm{products}$$

However, the reduction of Nuc-CO_2 species is an underexplored field, and there are few known electrocatalysts that facilitate these transformations. Our experimental testing of representative Nuc-CO_2 species with molecular electrocatalysts for captured CO_2 reduction will be outlined. The goals are to: (1) determine activity trends correlating Nuc-CO_2 adsorption energy with electrocatalytic reduction activity and (2) identify promising catalyst/Nuc-CO_2 combinations for more detailed studies for rate and product selectivity optimization at milder potentials. Early successes in promising catalyst/Nuc-CO_2 systems will be highlighted as well as our computational efforts correlating nucleophile sorbent properties with reaction kinetics for model catalyst systems. These initial results point to fundamental differences in reactive capture of CO_2 and pure CO_2 reduction, both in overall activity and primary products. This project addresses the 4C mission to advance both sorbent discovery and efficient production of carbon-based products.

I-S2-19: WHEN AI MEETS REAL EXPERIMENTS IN A TEAM ENVIRONMENT, BOTH BENEFIT

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There is a huge need to use artificial intelligence (AI) and machine learning (ML) to extract meaningful science rapidly from high throughput experiments such as the *in situ* and *operando* measurements of phase and structural evolution during synthesis in the GENESIS center. But real experiments are not ideal, they are messy. Under real experimental conditions the desired target, the structural and phase evolution during the experiment, can be lost in less interesting experimental factors such as thermal expansion under changing temperature. The tight coupling of experimentalists, computational scientists and applied mathematicians within GENESIS allowed us to propose and then implement and test novel unsupervised ML models to accurately extract phase behavior under these challenging conditions. The result, novel stretched and sparse-

stretched non-negative matrix factorization (NMF) ML models, significantly out-performed conventional NMF models and resulted in extraction of meaningful chemical component signals in real-time from real experiments. On the other hand, the new algorithms, inspired by the experiments in GENESIS, have much wider applicability and can be applied to any set of signals where a stretching component is present, enriching the basic canon of ML capabilities more widely. The resulting stretchedNMF and sparse-stretchedNMF algorithms are easy to use and fast and are being implemented in python packages for wide dissemination.

I-S2-20: UNCOVERING SUBTLE RELATIONSHIPS IN FRONTAL RING-OPENING METATHESIS POLYMERIZATION USING DATA-DRIVEN FORMULATIONS

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Frontal ring-opening metathesis polymerization (FROMP) provides an opportunity to fabricate high-performance thermoset polymers, without the need for lengthy high-temperature autoclave batch curing processes, by using the reaction's heat to cure the material quickly. It has been demonstrated in free-form 3D printing, vacuum-assisted resin-transfer molding, and fiber-reinforced polymer composite (FPRC) parts. There exists a delicate balance between pre-activated pot life, activated frontal velocity, and cured surface morphology that arises from the choice of catalyst, inhibitor, comonomer, and monomer materials. The REMAT data-driven formulation team aims to probe that balance by applying high-throughput processes (HTP), convolution neural networks, multivariate linear regressions, and chemical space mappings to identify "goldilocks reactivity zones". Towards this goal, we leverage simple experiments, with minor setup modifications for reproducibility and efficiency, to generate large amounts of convoluted data (Front rate video analysis: front rate and T_{max}; differential scanning calorimetry, DSC cure: T_{onset}, max heat flow, ΔH_r; DSC post-cure: T_m, T_g, max heat flow, residual exotherm ΔH_r). Data-driven formulations allow us to parse through the data to identify and map new promising chemical space areas for further analysis and deeper dives. We have identified promising: FP-compatible (frontal polymerization) materials that mitigate the characteristic smell associated with dicyclopentadiene (DCPD) and enable further reactivations toward recyclability/upcycling, and more stable inhibitors that enable faster incorporation of cleavable comonomers for recyclability.

I-S2-21: SPATIAL REACTION SELECTIVITY OF PLANAR PHOTOCATALYST ANALOG ENABLED BY AREA-SELECTIVE ATOMIC LAYER DEPOSITION AND MOLECULAR DYNAMICS SIMULATIONS

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Photocatalytic water splitting using ensembles of photosynthetic nanoreactors holds great potential in the pursuit of the DOE Hydrogen Shot initiative to bring the cost of H_2 to $1/kg by

2031. The main challenge is to increase overall solar-to-hydrogen conversion efficiency, while maintaining a high-level of stability. We seek to design tunable interphase layers for selective oxidation and reduction reaction sites, which increases both redox selectivities and charge separation, and thus overall efficiency. A critical need is spatial control over deposition of these interphase layers, selectively directing their growth on sites of reduction or oxidation. Toward this, we developed an area-selective atomic layer deposition (ALD) approach for a planar photocatalyst analog composed of interdigitated arrays of Pt and Au, which represent cocatalyst sites for reduction and oxidation, respectively. Selective deposition of nanoscopic oxide overlayers was first demonstrated on monometallic Pt and Au planar thin-film electrodes in which Au was selectively deactivated toward ALD growth through self-assembled thiol monolayers. The selectivity of TiO_x ALD was assessed through ellipsometry, X-ray photoelectron spectroscopy, and cyclic voltammetry. Atomistic simulations were also carried out to elucidate the impact of encapsulated environments on selective oxidation and reduction reactions. Specifically, we show that selective inhibition of iron redox shuttle reactions by the TiO_x overlayer stems from a mixture of size exclusion and the desolvation of ionic species. In addition, interdigitated planar samples were exposed to the selective ALD procedure, and scanning electrochemical microscopy was used to probe the local activity of different regions of the patterned surface.

I-S2-22: IDENTIFYING THE ROLE OF CU CO-CATALYSTS IN HYBRID P-GAN/AU/CU PHOTOCATALYSTS BY OPERANDO X-RAY SPECTROSCOPIES

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Photoelectrodes combining p-GaN semiconductor films with gold and copper nanoparticles were demonstrated to promote unassisted photocatalytic gas-phase CO_2 reduction and water oxidation under visible light illumination. Initial mechanistic studies suggested that plasmonic excitation of Au results in interfacial charge separation, with hole transfer to p-GaN promoting water oxidation, and electrons in Au promoting CO_2 reduction. The addition of Cu particles enhanced the rate of CO_2 reduction, suggesting that further Au-to-Cu electron transfer supports the reduction reaction, however, direct evidence for the mechanistic role of Cu was not obtained. We have applied in situ and operando x-ray spectroscopy techniques, including XAS and XPS, to identify the role of the Cu co-catalyst in the p-GaN/Au/Cu system. The element specificity of the techniques allows us to track charge migration across material interfaces, as well as site-specific chemical changes, under operating conditions. We find that the Cu particles in the as-prepared catalysts are not metallic Cu, but instead consist of a mixture of oxidized Cu(I) and Cu(II) species. We observe chemical changes to Cu(II) upon exposure to CO_2/H_2O vapor, towards the formation of more carbonate and hydroxide species. Finally, we observe further oxidation of Cu(I) to Cu(II) under visible illumination, suggesting Au-to-Cu hole transfer occurs. Our results suggest that the Cu co-catalyst does not participate in the reduction reaction, as initially proposed, but instead promotes oxidative pathways. This work highlights the importance of operando characterization of photocatalyst

components to obtain an accurate mechanistic understanding of the role of co-catalysts in hybrid systems.

I-S2-23: ATOMIC DETAILS OF RUO2-WATER ELECTROCHEMICAL INTERFACES: THIN-FILM MODEL SYSTEMS

[EFRC – CEDARS] Austin J. Reese[1], Haldrian Iriawan[2], Simon Gelin[3], Neha Wadehra[1], Jacob Som[1], Joshua F. Neal[1,4], Maria Maalouf[3,5], Shay McBride[6], Botao Huang[2], Johannes Mahl[7], James Stewart[8], Tanja Cuk[8], Ethan J. Crumlin[7], Yang Shao-Horn[2], Geoffroy T.F. Hautier[6], Ismaila Dabo[3], Dhananjay Kumar[4], Darrell G. Schlom[1], Jin Suntivich[1]
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This poster reports the characterization of well-defined RuO_2-water interfaces for oxygen evolution reaction (OER) studies. RuO_2 is one of the well-known OER electrocatalysts; however, the structure and morphology of the RuO_2 surface during the OER are still elusive. CEDARS aims to address this knowledge gap by using single crystals and thin-film deposition to synthesize model RuO_2-water interfaces. This poster presents the result of this investigation. The first part compares the electrochemistry of the RuO_2 films grown using different growth techniques (e.g., sputtering, molecular beam epitaxy, also traditional single crystals.) We find that the choice of the RuO_2 synthesis significantly affects the electrochemistry on the surface. We analyze this finding by studying the surface structure and morphology of the RuO_2 electrocatalysts using atomic force microscopy. We compare the results to first-principles grand canonical simulations to connect surface details to electrochemistry. In the final part, we discuss possible surface reconstruction in RuO_2 and how cation and anion additives can affect the interfacial environment during the OER, including our plan to disentangle this effect using synchrotron characterization.

I-S2-24: DESCRIPTOR-BASED APPROACH TO UNDERSTANDING TRANSITION METAL CATALYST ACTIVITY AND STABILITY IN REACTIVE CARBON CAPTURE

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The direct upgrading of CO_2 from carbon capture solutions utilizing renewable electrons is an emerging field of research in carbon capture and utilization. Reactive carbon capture (RCC) opens possibilities for fundamental and applied research in the design of capture agent molecules, catalysts, and process integration. However, degradation and poisoning of transition metal catalysts can be promoted by the capture agent and associated species, and little is known about how the mechanisms of these pathways are correlated to those of RCC.

This multi-PI effort at 4C integrates material synthesis and *operando* characterization, advanced electrochemical corrosion, and DFT calculations to systematically extract descriptors of activity and stability for different combinations of catalyst and capture agents for RCC. The *CO, *COOH, *OCHO, and amine binding energies for different metals (e.g. Ag, Au, Cu, Sn, Bi, In, Ga) have been screened using DFT. CO_2 reduction reaction (CO2RR) and capture agent binding are in a linear relationship, with important outliers chiefly having to do with the change of site. The RCC activity and stability of coinage metals (i.e. Cu, Ag, Au) have been studied experimentally to validate/evaluate the initial descriptors. While Ag is selective towards the reduction of dissolved CO_2, Cu corrodes, and Au is poisoned under RCC conditions. Experimental determination of differences in activity and stability as function of potential, combined with characterization of the surface and electrolyte species are used here to inform the development of DFT methods to advance the understanding of transition metals activity and stability under RCC conditions. DFT predicts capture agents and metals/alloys with superior corrosion resistance and RCC reactivity that will be pursued experimentally. In 4C, a feedback loop has been established between theory, experiments and spectroscopy to refine descriptors that we can use for inverse (predictive) design of new catalysts, including potentially bimetallic catalysts that we are already simulating.

I-S2-25: NEXT GENERATION MOLECULAR DYNAMICS: GPU ACCELERATED QM/MM WITH MULTISCALE REACTIVE MOLECULAR DYNAMICS

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We present here systematic advances to *ab initio* and (coupled to) reactive MD methodologies for modeling complex biological energy transduction processes on nanosecond and microsecond timescales. The simulation of energy transduction starts with modeling the electron-nuclear dynamics across the quantum states associated with electrons, energy transfer, and redox chemistry. Traditional QM/MM methods have proven to be a vital tool to investigate reactive problems in atomistic detail, but are typically limited to timescales of tens or hundreds of picoseconds. Recent advances in the power and bandwidth of graphics processing units (GPUs), along with theoretical developments designed to take advantage of the GPU architecture, have yielded significant performance improvements and enabled the consideration of more expensive and accurate hybrid density functionals. A multigrid DFT approach doubled the computational speed of a QM/MM calculation in CP2K when tested on a benchmark microtubule system. The new QM/MM approach is implemented in PySCF interfaced with LAMMPS, allowing a flexible combination of a wide array of quantum chemistry methods with mainstream force fields, and enabling the parametrization of multiscale reactive molecular dynamics (MS-RMD) against highly accurate QM data. The latter approach, which is three order of magnitude faster than traditional QM/MM, presents a robust extension of *reactive* MD methods and makes at least microsecond MD time scales more readily accessible. Furthermore, initial GPU acceleration efforts of the LAMMPS-based MS-RMD software have reported a doubling of the single-node performance by offloading key nonbonded interactions to the GPU.

I-S2-26: DIRECTING POLYMORPH SPECIFIC CALCIUM CARBONATE FORMATION WITH DE NOVO DESIGNED PROTEIN TEMPLATES

[EFRC – CSSAS] Fatima A. Davila-Hernandez[1], Biao Jin[2], Harley Pyles[1], Shuai Zhang[1,2], Zheming Wang[2], Timothy F. Huddy[1], Marlo Zorman[1], Chun-Long Chen[1,2], Jim Pfaendtner[1], James J. De Yoreo[1,2] and David Baker[1]
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AFFILIATED TALK – I-T2-4: Directing Polymorph Specific Calcium Carbonate Formation with De Novo Designed Protein Templates

Organisms generate biominerals with unique physical properties by controlling the nucleation, growth, and assembly of inorganic crystals. An ability to achieve similar outcomes synthetically would enable the construction of complex hybrid materials and provide a potential strategy for carbon dioxide reduction technologies. The sequences of native biomineral-associated proteins and their effects on mineralization are well characterized for some systems, but the three-dimensional structures of the protein-mineral interfaces that enable such exquisite control are largely unknown. We hypothesized that heterogeneous nucleation of calcium carbonate could be achieved by a structured flat molecular template that pre-organizes calcium ions on its surface. To test this hypothesis, we designed helical repeat proteins displaying regularly spaced carboxylate arrays on their surfaces and found that both protein monomers and protein-Ca^{2+} supramolecular assemblies directly nucleate nano-calcite with non-natural (110) or (202) faces. The nanocrystals then assemble by oriented attachment into calcite mesocrystals. In contrast, in the absence of the designed proteins, vaterite forms first and grows uncontrollably to micron size, before dissolving as calcite crystals with the commonly expressed faces subsequently nucleate and grow. We find further that nanocrystal size can be tuned by varying the length of the designed protein templates, while variations in template surface chemistry impact the resulting crystal polymorph. Thus, bio-mineralization can be programmed using *de novo* protein design, providing a route to next-generation hybrid materials.

I-S2-27: TYPE 3 POROUS LIQUID DESIGN BASED ON PORE ACCESSIBILITY AND FRAMEWORK STABILITY

[EFRC – UNCAGE-ME] Matthew J. Hurlock[1], Matthew S. Christian[1], Jessica M. Rimsza[1], and Tina M. Nenoff[1]
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AFFILIATED TALK – I-T2-11: Mechanisms That Govern Long-Term Stability of ZIF-8-Based Porous Liquids

Type 3 Porous liquids (PLs) are attractive sorbent materials for carbon capture by combining the adsorption capabilities of nanoporous solids with the fluidity of solution-based capture systems. The tunability of metal–organic frameworks (MOFs) offer a unique opportunity to develop selective Type 3 PLs with high CO_2 adsorption capacities when used as the nanoporous hosts. However, solvent-MOF interactions within PLs, and the impact on PL stability and CO_2 adsorption are not well understood. A combined experimental and computational approach was used to investigate these interactions within PLs formed using the zeolitic imidazole framework (ZIF) family of MOFs. From experimental density measurements, the solvent size exclusion limits of ZIF-based

PLs were determined. These results identified that expansion of the pore aperture allowed larger than expected solvents to be adsorbed into the frameworks. Additionally, structural comparison of the ZIFs indicated that this phenomenon was not substantially influenced by metal node identity, framework topology, or ligand functionality. Solvent-MOF interactions with CO_2 exposure were examined through a PL composed of ZIF-8 and a water, ethylene glycol, and 2-methylimidazole solvent system. Aging experiments identified that solvent-CO_2 reactions formed carbonates causing ZIF-8 framework degradation. Atomistic simulations identified a multi-step ZIF-8 framework degradation mechanism arising from the high pH of the PL, illustrating that composition effects the reactivity of solvent components. This work develops a fundamental understanding of solvent-MOF interactions within Type 3 PLs allowing improved PL design for targeted gas capture applications. SNL is managed and operated by NTESS under DOE NNSA contract DE-NA0003525.

I-S2-28: DISCOVERY OF NEW REACTION MECHANISMS WITHIN METALLAPHOTOREDOX TRANSFORMATIONS FOR ORGANIC SYNTHESIS

[EFRC – BioLEC] Stephen DiLuzio[1], Lakshmy Kannadi Valloli[2], Obadiah Reid[3], Garry Rumbles[4], Matthew Bird[2], Hannah Sayre[1]
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Photocatalysis centers on harnessing the energy of light to drive valuable chemical reactions, providing a more sustainable route towards chemical production. These reactions center on the use of a photocatalyst, which is a species capable of absorbing and transforming light energy into the chemical energy needed to power these chemical transformations. Merging a photocatalysts reactivity with a second transition metal catalyst affords access to new cross-coupling reaction platforms in organic synthesis. These “metallaphotoredox” reactions are often believed to proceed *via* photo-induced electron transfer pathways. Despite the unprecedented utility of these dual catalytic systems, the use of two catalysts naturally obfuscates determining the reaction mechanism. Time-resolved spectroscopy and pulse radiolysis have consequently been employed to obtain unique insight into these reactions. While metallaphotoredox mechanisms are often assumed to proceed through electron transfer pathways, our analysis suggests that the electron transfer pathways are inherently inefficient and that an energy transfer pathway is the productive pathway for product formation. In light of this, we have uncovered new transition metal catalyst intermediates that are responsible for product formation. The cooperative reactivity that is integral to success in dual catalytic, metallaphotoredox reactions centers on photocatalyst features that ensure successful energy transfer events to these new intermediates, whereas electron transfer capabilities do not correlate to successful catalytic systems. In turn, this discovery presents opportunities to engineer more advanced dual catalytic systems capable of lowering the cost/energy input of these systems and integrating valuable reactions scopes within this catalytic platform.

I-S2-29: NOVEL MEA AND ELECTROLYZER PLATFORMS FOR ALKALINE ELECTROCATALYSIS AND OPERANDO METHODS

[EFRC – CABES] Qihao Li, Andrés Molina, Schuyler Zixiao Shi, Yao Yang, Yu-Tsun Shao, Xinyao Lu, Yan Yang, Hsin-Yu Ko, Robert A. DiStasio Jr., Francis J. DiSalvo, David A. Muller, Héctor D. Abruña
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Developing compact and highly efficient electrochemical devices for energy conversion and chemical synthesis is a crucial aspect of modern electrochemical research. For instance, in fuel cells and water electrolyzers, the use of polymer electrolytes (PEs) has led to the creation of revolutionary compact membrane electrode assemblies (MEAs). This advancement has significantly reduced the thickness of the cell from millimeters (mm) to micrometers (μm) scale, thereby greatly increasing the power density and efficiency of fuel cells and water electrolyzers. Here we present the employment MEA techniques in alkaline based electrochemical systems in CABES, including alkaline exchange membrane fuel cells (AEMFCs) and water electrolyzers (AEMWEs). Our homemade ultrasonic spray system enables fabrication of uniform MEAs with facile loading control. These high quality MEAs enable high performance alkaline based energy devices. With commercial PtRu/C and Pt/C catalysts, we are able to achieve AEMFCs peak power density (PPD) of 2.5 W/cm^2 and maximum current density of 7 A/cm^2. With non-precious Co_3O_4/C oxygen reduction reaction (ORR) catalysts, a PPD of 2 W/cm^2 with current density larger than 5 A/cm^2 was achieved. For AEMWEs, a current density of 3.5 A/cm^2 was achieved at 2 V cell voltage with commercial PtRu/C and Ir catalysts. These state of the art device performances present the high performance electrochemical device fabricating and testing ability in CABES.

The development of novel operando methods is transforming our thinking of electrochemical phenomena and reactivity. As part of CABES, we have developed operando EC-STEM methodologies that have enabled the operando study of a broad range of electrochemical processes including metal deposition and cathodic corrosion.

I-S2-30: PROTON-COUPLED ELECTRON TRANSFER AND THE NUCLEAR-ELECTRONIC ORBITAL APPROACH

[Solar Hub – CHASE] Sharon Hammes-Schiffer[1], Yosuke Kanai[2], Gerald J. Meyer[2], Tao E. Li[1], Kai Cui[1], Alexander Soudackov[1], Jianhang Xu[2], Ruiyi Zhou[2], Matthew Kessinger[2]
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Proton-coupled energy transfer (PCET) is important for many solar energy conversion processes. We used density functional theory (DFT) to study interfacial PCET to a surface-bound water oxidation catalyst. The computed reorganization energies were consistent with experimentally measured values, and the larger reorganization energy for PCET compared to ET was explained in terms of a greater change in the ruthenium-oxygen bond length for PCET. We also developed a general, multi-channel kinetic model to describe the pH dependence of this process. The experimentally observed weak pH dependence of the apparent PCET rate constant was found to arise from differences in the rate constants and pH dependence of competing channels. The theoretical prediction that the apparent maximum rate constant becomes pH independent at high pH was confirmed experimentally. To include nuclear quantum effects in DFT calculations of interfacial PCET reactions, we are developing periodic DFT methods within the nuclear-electronic

orbital (NEO) framework, where specified protons are treated quantum mechanically on the same level as the electrons. Periodic NEO-DFT calculations of a titanium oxide-water interface with quantized protons showed that the zero-point energy of the protons impacts the density of states and band structure. Real-time NEO time-dependent DFT calculations of excited state proton transfer at a silicon semiconductor-molecule interface elucidated the coupled nuclear-electronic quantum dynamics of such systems and the dependence of the mechanism on the manner in which the molecule is chemisorbed on the surface. These NEO-based approaches will enable the investigation of a wide range of interfacial PCET reactions in heterogeneous environments.

I-S2-31: ASSESSING THERMODYNAMIC SELECTIVITY ENABLES THE PREDICTIVE SYNTHESIS OF INORGANIC MATERIALS

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Synthesis is a major challenge in the discovery of new inorganic materials. There is currently limited theoretical rationale for planning optimal solid-state synthesis procedures that selectively yield desired targets with minimal impurities. Using an interface reaction model, we propose two selectivity metrics – primary and secondary competition – to measure the favorability of target and impurity phase formation in solid-state reactions. We first apply these metrics to assess the selectivity of existing solid-state synthesis recipes in the literature and highlight which approaches are optimal or suboptimal for popular targets in battery science. Secondly, as a case study, we test the quality of our selectivity predictions for barium titanate from 82,985 synthesis reactions created with first-principles materials thermodynamic data from the Materials Project. From this chemical reaction network, we present experimental, synchrotron powder X-ray diffraction of the results from 9 different reactions with contrasting selectivity metrics. We identify two favorably predicted reactions with unconventional precursors that outperform conventional approaches, highlighting the importance of precursor selection, particularly those with hyperdimensional chemistries (e.g., coupled ion exchange reactions). Our data-driven synthesis planning workflow, including the selectivity analyses, enable the predictive synthesis of inorganic materials, facilitating the optimization of existing synthesis approaches and the design of new syntheses to novel materials, including those that cannot be easily made from conventional “off-the-shelf” precursors.

I-S2-32: PYNTA - AN AUTOMATED WORKFLOW FOR CALCULATION OF SURFACE AND GAS-SURFACE KINETICS

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Many important industrial processes rely on heterogeneous catalysis. However, given all possible catalysts and conditions of interest it is impractical to optimize most systems experimentally, and often computational approaches are taken. To model these catalytic systems, it is necessary to estimate a vast number of thermochemical and kinetic parameters efficiently and reliably. We present Pynta, an exascale-ready workflow software for automating the calculation of surface and gas-surface reaction parameters. Using a simple graph-based input, Pynta can generate well and saddle point geometries considering all relevant sites and can compute the associated thermochemistry and rate coefficients. Pynta implements a new saddle point guess generation method called harmonically forced saddle point searching (HFSP), which is reaction class agnostic and fast, and allows Pynta to consider all possible adsorbate site placements efficiently. We demonstrate Pynta on a diverse set of reactions involving monodentate, bidentate and gas-phase species, many distinct reaction classes and both a low and a high index facet. We also present our bonding analysis tool to enable automatic identification of binding sites. Finally, we present performance metrics for our code on DOE leadership computing platforms.

I-S2-33: CATALYTIC CHEMICAL RECYCLING OF POST-CONSUMER POLYETHYLENE

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We report a new approach to transform post-consumer polyethylene into a new polymer with chemical recyclability, while retaining its original material properties. The incorporation of cleavable linkages into polyolefin backbones allows the polymer to be depolymerized into telechelic segments capable of repolymerization to achieve chemical recyclability.

In our initial studies, we developed catalysts for the copolymerization of propylene and butadiene to incorporate internal C=C bonds into a polypropylene backbone and subsequently used catalytic metathesis and transesterification to transform the copolymer into a chemically recyclable ester-linked polypropylene. In the case of post-consumer high-density polyethylene (HDPE), catalytic dehydrogenation using an Ir-POCOP catalyst yielded the HDPE with different degrees of backbone unsaturation at varied reaction time. Cross-metathesis converted the partially unsaturated HDPE into telechelic macromonomers. The direct repolymerization of these macromonomers by transesterification resulted in a brittle material due to the low weight-average molecular weight. Partial aminolysis with trifunctional linkers increased the overall functionality, and subsequent transesterification generated a polymer with comparable thermal and mechanical properties to the starting post-consumer HDPE. Depolymerization of the repolymerized material was catalyzed by an organic base to regenerate the telechelic macromonomers. A follow-up study used a “Trojan Horse” approach to induce masked unsaturation into a polyethylene chain by copolymerization of ethylene and a functional oxa-norbornadiene monomer. The partially unsaturated PE was generated by a retro-Diels-Alder reaction at elevated temperature.

I-S2-34: DEVELOPING EFFICIENT NANOSTRUCTURED CATALYSTS FOR ELECTROCHEMICAL REDOX REACTIONS VIA INTERFACE MODULATION WITH ANTHROPOGENIC CONTAMINANTS

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Electrochemical water splitting has emerged as a promising approach for green hydrogen production. However, electrocatalytic water splitting faces limitations, with the oxygen evolution reaction (OER) being a major obstacle due to its sluggish 4e- transfer and high activation energy barrier. Recently, alternative anodic reactions, such as the oxidation of small organic molecules like hydrazine, urea, benzyl alcohol, and furfural, have gained attention. These organic molecules are abundantly available in various wastewater streams and have a lower thermodynamic potential for oxidation. Extensive research has resulted in the establishment of catalyst libraries for hydrogen evolution reaction (HER), OER, and organic molecule oxidation. Although Pt, IrO_2, and RuO_2 exhibited superior performances, due to their scarcity and cost-limited their application, researchers are focusing on developing abundant transition metal-based catalysts with comparable efficiencies to noble metals. Despite successful developments in electrocatalyst design, the long-term stability and activity of catalysts under extended reaction regimes, particularly surface reconstruction under pulsed and constant potential conditions, remain unresolved. Moreover, the impact of trace metal impurities, commonly present in aqueous solutions used for H_2 production, on the catalyst surface and its intrinsic activity is often disregarded. In this study, we have systematically developed a platform of bimetallic NiMo, CuCo, and emerging perovskite materials as electrocatalysts for redox reactions to optimize their electrocatalytic activity, specifically focusing on the structure-property relationships in the presence of trace metal contaminants like Fe^{3+} or Cu^{2+}.

I-S2-35: ADVANCED RECYCLING METHODS AND SUSTAINABLE SYNTHESIS OF NEW POLYMER MATRICES

[AIM for Composites] James Sternberg[1], Kevin Simmons[2], Srikanth Pilla[1], Mik Carbajales-Dale[1], Yong Huang[3], Dale Hitchcock[4]
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Chemical recycling is a technique that simultaneously breaks down plastic waste and converts it to usable precursors for second generation polymer synthesis. Chemical recycling holds the advantage of returning near pristine monomers for virgin-like production of new polymers. In addition to using sustainable end-of-life solutions for polymer waste, it is also important to devise new ways of synthesizing polymers from renewable sources with accompanying green reagents to enable a fully sustainable lifecycle. We have demonstrated two circular platforms encompassing polyurethane foams and high-performance polyamides that utilize biobased feedstocks, green reagents, and chemical recycling. Flexible and rigid polyurethane foams were synthesized using a non-isocyanate route from industrial kraft lignin. Foams demonstrated properties commensurate with commercial materials and were chemically recycled through hydroglycolysis. The lignin

precursor recovered during chemical recycling was used to synthesize new non-isocyanate foams with very similar properties to first generation materials. In a second work, post-consumer PET was chemically recycled using aminolysis to create an aromatic, amine-terminated precursor to high-performance polyamides. Semi-aromatic polyamides, some falling in the category of polyphthalamides, were synthesized directly from the chemically recycled PET, enabling a scalable platform. These studies represent efforts to use the E3 approach (Energy, Economic, Environmental Analysis) to find viable pathways to polymers by matching synthetic techniques with real-world impacts. Further, these studies combined the efforts of scientists from multiple departments at the Pacific Northwest National Lab and Clemson University with continual collaboration from thrust team members at the University of Florida and Savanah River National Lab.

I-S2-36: SYNTHESIS AND CATALYTIC REACTIVITY OF COORDINATION POLYMERS WITH HIGHLY POLARIZABLE COMPONENTS

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Coordination polymers built with thiolate linkers or sulfide clusters are comparatively uncommon due to synthetic challenges. Still, the orthogonal properties of these building motifs, such as their soft and polarizable nature, suggest they should be ideal candidates for a variety of catalytic applications. Here we will present our efforts at streamlining the discovery of new thiolate- or sulfide-based coordination polymers and MOFs, leveraging both theory and high-throughput experimentation. These efforts offer the promise of much more rapid discovery and reaction screening of new materials. In parallel, initial efforts at using some of the few known sulfide-based coordination polymers in catalytic reactivity will be presented. Heterogenization of iron-sulfur clusters enables robust reductive electrocatalysis. Detailed spectroscopic and theoretical characterization of the coordination polymer offers mechanistic insights, as well as first of its kind characterization of reactive protonated clusters. These findings promise a wealth of reductive catalysis with this class of materials.

I-S2-37: MULTIMODAL *OPERANDO* X-RAY MECHANISTIC STUDIES OF A BIMETALLIC OXIDE ELECTROCATALYST IN ALKALINE MEDIA

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Furthering understanding of the catalytic mechanisms in the oxygen reduction reaction (ORR) is critical to advancing and enabling fuel cell technology. In this work, we use multimodal *operando*

synchrotron X-ray diffraction (XRD) and resonant elastic X-ray scattering (REXS) to conduct a comprehensive investigation of the interplay between the structure and oxidation state of a Co-Mn spinel oxide electrocatalyst, which has previously shown ORR activity that rivals Pt in alkaline fuel cells. During cyclic voltammetry, the electrocatalyst exhibited a reversible and rapid increase in tensile strain at low potentials, suggesting robust structural reversibility and stability of Co-Mn oxide electrocatalysts during normal fuel cell operating conditions. At low potential holds, exploring the limit of structural stability, an irreversible tetragonal-to-cubic phase transition was observed, which may be correlated to reduction in both Co and Mn valence states. Meanwhile, joint density-functional theory (JDFT) calculations provide insight into how reactive adsorbates induce strain in spinel oxide nanoparticles. Through this work, strain and oxidation state changes that are possible sources of degradation during the ORR in Co-Mn oxide electrocatalysts are uncovered, and the unique capabilities of combining structural and chemical characterization of electrocatalysts in multimodal *operando* X-ray studies is demonstrated.

I-S2-38: SURFACE COATINGS ON SILICON FOR PASSIVATION AND INTEGRATION OF MOLECULAR CATALYSTS

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Silicon is the primary semiconductor used for solar photovoltaic devices and thus a natural choice for the design of photoelectrodes that generate liquid fuels from the inputs of CO_2, sunlight, and water. Similarly, molecular catalysts are a natural choice to precisely direct electrochemical reactions toward specific liquid fuel products. However, the integration of molecular catalysts with a silicon semiconductor requires the design of hybrid interfaces that meet several potentially contradictory requirements, including facile charge transfer to molecular species, minimal charge carrier recombination at surfaces, and long-term stability against corrosion. Here, we describe recent results within CHASE to successfully design surface coatings that meet these challenging requirements. For instance, rapid thermal oxidation of silicon was used to create ultrathin (2-3 nm) but high quality SiO_2 coatings. Under illumination, these surfaces formed an inversion layer, facilitating electron transfer via tunneling to catalysts that can either be in homogeneous solution or chemisorbed to the surface. Stable photoelectrocatalysis was observed in aqueous solution. Similarly, plasma-deposition of thin (10-200 nm) graphene layers on thermal oxide surfaces created metal-insulator-semiconductor interfaces with an interfacial silicon carbide layer bonding graphene to the semiconductor. These interfaces permit the non-covalent binding of molecular catalysts to the electrode. Finally, atomic and molecular layer deposition processes are being used to fabricate interfacial layers that facilitate the binding and vertical placement of molecular catalysts at silicon interfaces. Taken together, the results represent a diverse set of strategies to simultaneously integrate molecular catalysts while passivating them against charge carrier recombination and corrosion.

I-S2-39: MECHANICAL PROPERTY PREDICTION AND MICROSTRUCTURE GENERATION OF POROUS MATERIALS USING DEEP LEARNING

[AIM for Composites] Yunpeng Wu[1], Fei Ding[2], Feng Luo[2] and Gang Li[1]
[1]Clemson University

In this work, we first develop deep learning methods to efficiently predict mechanical properties of porous materials from their microstructures. Next, for the purpose of inverse material design, we develop conditional variational autoencoder (cVAE) based neural networks to generate the microstructure of porous materials from prescribed elastic modulus or stress-strain curve. In both the property prediction and microstructure generation, the microstructure of the porous materials is represented using binary images. For property prediction, Resnet-18 neural networks are developed and trained by using the data generated from finite element analysis. A suitable range of hyperparameters is obtained and verified. For microstructure generation, a new condition fusion layer is devised and incorporated into the traditional architecture of cVAE. In addition, a pre-trained regression model is introduced to constrain the decoder so that it generates more physically meaningful mcirostructures. The new generative neural network architectures enable a more explicit representation of the relationship between the microstructure image and the material property parameters. It is demonstrated that the new models are more effective in reducing the standard deviation of the generated results. The results obtained show that the deep learning approach is capable of not only ultra-fast prediction of material properties directly based on microstructure images but also inverse design of material microstructures for achieving desirable mechanical behaviors.

I-S2-40: EXPLORING NOVEL MAGNETIC STATES IN HOIS

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2D magnetic Van der Waals (VdW) materials have seen a surge of interest for their low-dimensional magnetic properties and spintronic applications. However, the tunability of their magnetic properties through their chemical compositions is low, hindering critical progress. Through our work, we demonstrate that hybrid organic-inorganic semiconductors (HOIS) offer a unique advantage in this field, where the organic ligands play a critical role in modifying the magnetic exchange and coupling constants. We found that a magnetic interaction known as the Dzyaloshinskii-Moriya Interaction exists in one of these hybrid systems, which enables the coupling between acoustic and optical magnons through broken symmetry, an effect which eluded the inorganic magnetic VdW materials. Furthermore, structural chirality may be introduced into these magnetic systems through chiral organic molecules, which break the inversion symmetry

and enable the stabilization of exotic spin textures. In a different HOIS material, we also find magnons with left-handed and right-handed chirality, which exhibit an ultra-strong coupling and high cooperativity. Our ongoing work aims to shed light on the mechanism for the modulation of the magnetic properties through the organic molecules, and reveal these HOIS materials as a unique platform for the study of the magnon-magnon coupling. Finally, the magnon-photon coupling is studied which may further serve the importance of HOIS for quantum information processing and storage. This work has the potential to benefit the spintronics and photonics communities by quantifying the behavior of these emergent materials and for elucidating the physics of magnons and photons in HOIS.

I-S2-41: AUTOMATED GENERATION OF MICROKINETICS FOR HETEROGENEOUSLY CATALYZED REACTIONS CONSIDERING CORRELATED UNCERTAINTIES

[CCS – ECC] Bjarne Kreitz, C. Franklin Goldsmith
Brown University

AFFILIATED TALK – I-T2-2: Automated Generation of Microkinetics for Heterogeneously Catalyzed Reactions Considering Correlated Uncertainties

Improving the productivity of heterogeneously catalyzed processes on the atomistic scale requires detailed microkinetics. Complex reaction systems, e.g., the conversion of exhaust gas emissions, have many possible pathways and intermediates, making manual mechanism development a daunting task. This task is further complicated by correlated uncertainties in the kinetic and thermophysical parameters obtained from DFT calculations. In this study, we integrate the correlated uncertainties directly in an automated mechanism generation procedure for emission control catalysis and investigate the effect of the discovered mechanism and its predictions.

Mechanisms are automatically constructed using the Reaction Mechanism Generator (RMG), assuming a Pt(111) facet and a representative exhaust gas mixture from stoichiometrically operated engines. RMG relies on DFT-derived energetic parameters and their correlated uncertainties can be directly assessed with BEEF-vdW functional. This functional was used to create a correlated multi-dimensional parameter space, from which samples are drawn to generate 2000 unique microkinetic models.

Multiscale modeling with all generated microkinetics reveals a broad spread in the predicted results. Yet, the results enclose experimentally recorded light-out curves from a Pt/Al2O3 monolith and a single microkinetic model can be identified, which is in remarkable agreement with the data. This agreement indicates that the Pt(111) facet could be the active site for the oxidation of light hydrocarbons. Due to the high degree of correlation, every generated mechanism can be mapped back to a single exchange-correlation functional. Correlated uncertainty quantification is combined with automated mechanism generation to provide a theory-constrained, universally applicable optimization framework.

I-S2-42: EARTH-ABUNDANT METAL OXIDE NANOPARTICLES CATALYZE CARBON-CARBON BOND HYDROGENOLYSIS

[EFRC – iCOUP] Shaojiang Chen[1], Akalanka Tennakoon[1,2], Kyung-Eun You[3], Mubarak Bello[3], Kajol Tonk[1,2], Thomas H. Johnson[1,2], Longji Li[1,2], Alexander L. Paterson[1], Ryan Yappert[4], Selim Alayoglu[5], Lingzhe Fang[6], Xun Wu[1,2], Tommy Yunpu Zhao[7], Michelle P. Lapak[7], Mukunth Saravanan[1], Ryan A. Hackler[8], Yi-Yu Wang[1,2], Long Qi[1], Massimiliano Delferro[8], Tao Li[6,8], Byeongdu Lee[8], Baron Peters[4], Kenneth R. Poeppelmeier[5], Salai C. Ammal[3], Clifford R. Bowers[7], Frédéric A. Perras[1], Andreas Heyden[3], Aaron D. Sadow[1,2], Wenyu Huang[1,2]
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Between 1950 and 2015, over 4.9 billion metric tons of virgin plastics ended up in landfills or the environment. This amount will continue to rise as more than 350 million metric tons of plastic are produced annually, with 79% being quickly discarded. These plastic wastes pose significant environmental and health concerns, yet they contain valuable amounts of energy and carbon that could be used as feedstock in the chemical industry. To address the plastic waste crisis, there have been increasing efforts to chemically upcycle these wastes into high-value chemicals. We discovered that the earth-abundant zirconia and titania nanoparticles catalytically cleave the C-C bond in polyethylene to a narrow distribution of small hydrocarbon molecules. The material is made up of nanoparticles of a metal oxide (Zr/Ti, Si, O). The zirconia nanoparticles are embedded in the walls of mesoporous silica (L-ZrO_2@$mSiO_2$), which helps to stabilize the coordinatively unsaturated surface sites needed for catalysis. The titania nanoparticles are commercially available. DFT calculations show that these oxides mediate C-C bond hydrogenolysis with comparable activity to Pt/C. This is because L-ZrO_2@$mSiO_2$ has a combination of small crystalline ZrO_2 with $mSiO_2$ which we hypothesize to contain a large number of ZrO_x defect sites that exhibit the catalytic activity. A new bifunctional (hydroxy)organozirconium oxide species has been proposed for catalytic chemistry. Similar to ultrasmall ZrO_2, we find that also TiO_x defect sites can form on titania and that these sites are similarly active for the C-C bond hydrogenolysis even in the presence of small amounts of water. The hydrogenolysis with L-ZrO_2@$mSiO_2$ and TiO_2 is a previously unrecognized heterogeneous analog of the SOMC-catalyzed C-C cleavage processes.

I-S2-43: BACTERIAL MICROCOMPARTMENT STRUCTURE, CARGO LOADING, AND ASSEMBLY INVESTIGATED USING SMALL ANGLE X-RAY SCATTERING COMBINED WITH MODEL-BASED ANALYSES

[EFRC – CCBC] Xiaobing Zuo,[1] Nina Ponomarenko,[1] David M. Tiede,[1] Nicholas M. Tefft,[2] Michaela A. TerAvest,[2] Markus Sutter,[2,3] Cheryl Kerfeld,[2,3] Arinita Pramanik,[3] and Corie Ralston[3]
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Bacterial microcompartment (BMC) shell structure, cargo loading, and mechanisms for assembly are being investigated using X-ray scattering at DOE synchrotron light sources (APS, ALS, NSLS-II). The program highlights quantitative comparison of X-ray scattering experiments to computational models of BMC shell structure and assembly. Here, we report on a survey of BMC shells that differ in size, protein shell constituents, and shell wall-attached protein cargo. These measurements identified information content correlated to regions of spatial resolution in the SAXS data that is needed to design experiments for investigating mechanisms for BMC shell and cargo-loaded BMC

assembly. For example, BMC scattering data extrapolated to zero angle provides an X-ray parameter proportional to the total electron density, offering a measure of the overall concentration of BMC-confined cargo, including both shell wall-attached and free-within-the-shell catalysts. Scattering features resolved at progressively higher angles were found to show intense interference patterns that differed characteristically depending upon BMC shell size, shell wall protein constituents, and the extent to which targeted protein cargo is attached at shell wall sites. Further, wide angle scattering features were found to include "fingerprints" that report on the packing of subunit "tiles" in the shell wall and differences between fixed and positional scrambling of BMC-H and T1 proteins. On-going work is extending structure-based modeling and time-resolved X-ray approaches to link to a Center-wide effort on the development of BMC shell systems for *in vitro* assembly and loading of enzymatic and abiotic catalytic cargo.

I-S2-44: RECONSTRUCTION OF MESOSCALE SYNTHETIC MICROSTRUCTURE AND THERMO-MECHANICAL FE ANALYSIS OF AM PROCESS TO PREDICT MICROSTRUCTURE-DEPENDENT MECHANICAL PROPERTIES OF POLYMER COMPOSITES

[EFRC – AIM for Composites] Madhura Athale[1], Taejoon Park[1], Sai Aditya Praadeep[2], Tatiana Stepanova[2], Mostafa Elnaggar[1], Farhang Pourboghrat[1], Gang Li[1,2], Srikanth Pilla[1,2]
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The present work aims to establish the material-process-microstructure-performance (MP2) relationship of polymer composites produced using the additive manufacturing (AM) process technique. Mesoscale synthetic microstructures are generated to predict macroscopic mechanical properties of AM-built polymer composites based on their underlying microstructural features. Advanced material models are applied to the synthetic microstructures to properly consider the strain-rate and time dependent behavior of polymers as well as their local anisotropy due to the alignment of reinforcement fibers. Thermo-mechanical finite element (FE) analysis of the AM process is performed to evaluate the effect of AM process parameters such as printing pattern, nozzle size, extrusion rate, and process temperature. The nonuniform distribution of voids and residual stress predicted by the AM process analysis is integrated into the synthetic microstructures to precisely predict the mechanical properties of the AM-built polymer composite part. The established MP2 relationship through this research will be utilized to develop an AI-enabled inverse design model for optimizing the manufacturing process and microstructure of polymer composites.

I-S2-45: CORRELATING ELECTRONIC DISORDER TO STRUCTURAL DYNAMICS IN CONJUGATED POLYMERS

[EFRC – SPECS] Henry Kantrow[2], Joel Bombile[3], Jean-Luc Brédas (KI)[1], Brian Breeman[7], Megan Brown[3], Veaceslav Coropceanu[1], Elizabeth Gutiérrez-Meza[4], Chamikara Karunasena[1], Garrett LeCroy[4], Tim Lian (KI)[7], Hongmo Li[2], Erin Ratcliff (PI)[1], Chad Risko (KI)[3], Alberto Salleo (KI)[4], Carlos Silva-Acuña[2,6], Natalie Stingelin (KI)[2], Sergei Tretiak[5], Félix Thouin[2,6], Spencer Yeager[1]
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AFFILIATED TALK – I-T2-5: Correlating electronic disorder to structural dynamics in conjugated polymers

Conjugated hairy-rod polymers, which have emerged as promising photocathode materials for solar-fuel production, are comprised of stiff, low-entropy backbones and complex side-chain substitutions, collectively which affect assembly compared to flexible-chain materials. Here, we unravel the relationship between structural and electronic disorder in the model hairy-rod poly(2,5-bis(3-hexadecylthiophene-2-yl)-thieno[3,2-b]thiophene) (PBTTT). Multiscale electrochemistry identifies a narrow electronic density-of-states (DOS) distribution with weak spatial variations in PBTTT while the prototypical flexible-chain poly(3-hexylthiophene) (P3HT) features an energetically broad, spatially variable DOS distribution. We assign this observation to the fact that PBTTT is structurally homogeneous, resulting from its liquid-crystalline (LC) behavior induced by the hairy-rod nature, contrary to structurally heterogeneous P3HT comprised of molecularly highly ordered and disordered domains. Charge-modulation spectroscopy is used to correlate order/disorder to polaron delocalization. Polarons in PBTTT are primarily 1D-delocalized along the backbone; while, in P3HT, they have substantial interchain delocalization. This difference is due to the higher degree of backbone order in PBTTT due to its LC nature, in agreement with oligomer and periodic density functional theory (DFT) that allows a description of the polaron characteristics and strengths of interchain coupling in PBTTT vs. P3HT. This view is further supported by 2-dimensional spectroscopy results that reveal that PBTTT features dynamic electronic disorder due to its structural homogeneity, *vs.* P3HT, which exhibits static electronic disorder resulting from its structural heterogeneity. Collectively, our work provides understanding into the electrochemistry, photophysics and optoelectronics of conjugated hairy-rod polymers, towards accelerated materials discovery for renewable energy technologies with consideration of structural dynamics which influences electronic processes.

I-S2-46: ILLUMINATING OPTICAL FLOATING ZONE SINGLE CRYSTAL GROWTH WITH SYNCHROTRON X-RAY SCATTERING

[EFRC – GENESIS] Peter G. Khalifah[1,2], Yusu Wang[1], Jonathan J. Denney[1], Dario Lewczyk[1], Adam A. Corrao[1], Mehmet Topsakal[2], Eric Dooryhée[2], Lucas A. Pressley[3], W. Adam Phelan[3], Satya K. Kushwaha[3], Mojammel Khan[3], Eymana Maria[4], Guanglong Huang[4], Mojue Zhang[4], Praveen Soundararajan[4], David Montiel[4], Christopher J. Wright[5], Songsheng Tao[5], Katsuyo Thornton[4], Simon J. L. Billinge[5]
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Although the optical floating zone (OFZ) method has had a transformative impact on the availability of large single crystals of emerging materials for DOE research, OFZ crystal growth remains more an art than a science due to challenges in probing the growth environment. To gain quantitative insights into OFZ crystal growth processes, GENESIS designed an integrated experimental, computational, and modeling infrastructure enabling the first-ever synchrotron experiments probing OFZ growth mechanisms. Thermal processes were understood through the combination of precise *in situ* synchrotron measurements of temperature profiles in tip-heated (to 1500 °C) rods using custom-designed furnace environments and the development of physics-based computational models capable of reproducing the measured profiles after parameter optimization using machine learning. Crystal growth processes were investigated by the development of novel methodologies and code for fast collection of *ex situ* synchrotron mapping

data on large crystal growth boules, the forensic reconstruction of the solid-liquid interface shape through microfocused beam mapping, the spatially-resolved collection of high-resolution rocking curves, the reconstruction of grain shapes using new fast indexing and mapping algorithms, and the elucidation of preferred crystal growth directions from orientation comparisons across many grains. These pioneering non-destructive studies of large OFZ crystal boules provide unique insights into how growth parameters influence the crystal growth product and suggest general strategies for enhancing crystal selection and improving crystal perfection. Furthermore, this work spotlights the feasibility of future *in situ* synchrotron studies of OFZ growth process and their expected value in enhancing the quality and availability of large crystals.

I-S2-47: HIGH-THROUGHPUT POTENTIAL-DEPENDENT MODELING OF THE ELECTROCHEMICAL NITROGEN REDUCTION REACTION

[CCS – BEAST] Cooper Tezak,[1] Nicholas Singstock,[1] Abdulaziz Alherz,[1] Derek Vigil-Fowler,[2] Christopher Sutton,[3] Ravishankar Sundararaman,[4] Charles Musgrave[1]
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AFFILIATED TALK – I-T2-1: High-Throughput Potential-Dependent Modeling of the Electrochemical Nitrogen Reduction Reaction

We showcase the capability enabled by the BEAST CCS collaboration for high-throughput first-principles electrochemistry, including accurate solvation and explicit bias dependence, using the nitrogen reduction reaction (NRR), a promising route to carbon-free ammonia synthesis. Current electrocatalysts do not catalyze NRR at practical temperatures. The failure to design effective NRR catalysts is partly due to the limited understanding of the NRR mechanism and poor description of the effects of bias and the solvent on the reaction energies. We modeled 30 transition metal catalyst surfaces using grand-canonical DFT to identify and understand the bias dependence of the NRR rate limiting steps. We use Φ_{max}, a grand canonical analogue to the thermodynamic screening descriptor G_{max}, which approximates the apparent activation barrier of a reaction network, to quantify catalyst activity accounting for applied bias. This approach yields a thermodynamic activity "volcano" diagram that qualitatively differs from those predicted by models that use simplified proton-coupled electron transfer mechanisms to approximate the effect of the applied potential. We find that NH3 desorption limits NRR activity for materials at the top of the volcano and truncates its peak at increasingly reducing potentials. This approach is transferable to other materials and electrocatalysis systems where both electrochemical and chemical steps are modeled under an applied bias. We used this approach to generate a dataset of >500 metal-adsorbate combinations to enable the machine learned prediction of electrocatalyst properties, including with beyond-DFT methods in ongoing work in the BEAST collaboration.

I-S2-48: BULK AND SURFACE DEFECTS DETERMINATION AND PASSIVATION IN BROMIDE PEROVSKITES

[EFRC – CHOISE] Zhifang Shi,[1] Zhenyi Ni,[1] Liang Zhao,[1] Yifan Dong,[2] Xiaoming Wang,[3] Yeming Xian,[3] Obadiah Reid,[2] Matthew C. Beard,[2] Yanfa Yan,[3] and Jinsong Huang[1]
[1]University of North Carolina, Chapel Hill; [2]National Renewable Energy Laboratory; [3]University of Toledo

Many of the attractive physical properties of metal halide perovskites stem from their unusual defect physics. Prior studies have identified the chemical nature and spatial distribution of major point defects in iodide perovskites. However, understanding of defects in bromide perovskites is still absent despite observation of unique behavior only seen with bromide defects, such as reversible passivation of bromide surfaces by physical absorption of oxygen. Herein, we investigated both bulk and surface point defects in bromide perovskites. By tuning the growth conditions, we determine the two main point defects in the bulk of $MAPbBr_3$ crystals to be A-site vacancies and interstitial, which produce deep levels and cause non-radiative charge recombination. A rational design of the crystal growth can dramatically reduce them, enhancing the two-photon PL lifetime and carrier mobility and reduces self-doping. We identify three types of defects on the crystal surface, namely, A-site vacancies, uncoordinated lead, and Pb-Pb dimers caused by bromide loss. These surface defects form deep traps, resulting in non-radiative interfacial charge recombination. We find that ammonium bromide can passivate these three deep traps resulting in a charge collection efficiency close to unity. Density-functional theory finds that $4AMPBr_2$ is superior to other ammonium bromides because of its capability to passivate two bromide vacancies. The surface passivation also reduces the dark current by tenfold and decreases the dark counts by ~60 times. With a thorough understanding of both bulk and surface defects, we improved the energy resolution of $FAPbBr_3$ γ-ray detectors to 1.7% under 662 keV ^{137}Cs.

I-S2-49: A NEW CENTER-SCALE PROGRAM TO STRENGTHEN THE STEM PIPELINE BETWEEN MINORITY-SERVING PRIMARILY UNDERGRADUATE INSTITUTIONS AND R1 INSTITUTIONS

[EFRC – EPN] Lillianne Alyward[1], Kenny Drbohlav[2], Evan Gowdy[2], Jahsun Hurley[3], Barbara Lewis[3], Chloe Qian Yu Yeap[1], Patrick O. Aghadiuno[4], Justin T. Mulvey[5], Daniel V. Esposito[4], Joseph P. Patterson[5], Kenneth A. Miller[2], Oluwaseun Salako[3], Young-Seok Shon[1], Shane Ardo[5]
[1]California State University, Long Beach; [2]Fort Lewis College; [3]CUNY – Medgar Evers College; [4]Columbia University; [5]University of California Irvine

Opportunities provided to students and faculty at R1 institutions largely differ from those provided at primarily undergraduate institutions (PUIs). This opportunity gap is generally vast for people from historically underrepresented groups. To help bridge this opportunity gap, we have developed and implemented a new pipeline model to strengthen interactions between diverse student populations at PUIs and R1 institutions. Our STEM pipeline model has the Microscopy Bridge Program at its core, with aims to demystify academia and train the next generation workforce of scientists and engineers, and includes training in microscopy and collaborative two-way student exchanges between geographically proximal minority-serving PUIs and R1 universities. Lessons learned to date include the need for substantial (i) rapport building among PIs, graduate student mentors, and undergraduate students to build trust and facilitate mentoring; (ii) undergraduate student input in project planning to instill ownership and drive work ethic; (iii)

financial support to build capabilities and sustained partnerships with PUI PI labs; and (iv) undergraduate research at PUI PI labs – with research representation at >50% of EPN Posters – that culminates with a summer-long research opportunity on the same collaborative project in an R1 lab. We think that our innovative program will help bridge gaps in equity and inclusivity that stymie widespread U.S. competitiveness in energy, and all STEM fields. Moreover, our model is wholly applicable to other large center-scale efforts, including other efforts within DOE like Hubs, CMSs, and CCSs, and analogous programs across other federal agencies.

I-S2-50: PHOTOCONTROL – USING LIGHT TO CONTROL FROMP

[EFRC - REMAT] Zhenchuang Xu[1], Andrew Greenlee[1,2], Daniel Darby[2], Sam Knight[1], Qibang Liu[1], Samuel Leguizamon[2], Devin Roach[2], Adam Cook[2], Jeremiah Johnson[3], Philippe Geubelle[1], Jeffrey Moore[1], Leah Appelhans[2], Yasmeen AlFaraj[3], and Yuyan Wang[3]
[1]University of Illinois Urbana-Champaign; [2]Sandia National Laboratories; [3]Massachusetts Institute of Technology

Frontal ring opening polymerization (FROMP) reactions are an attractive low-energy approach to manufacturing polymers because the polymerization front is self-propagating after initiation. However, this also means that it can be challenging to control the speed and direction of front propagation, and polymer composition is restricted to fixed ratios of comonomers with limited ability to vary compositions or create well-controlled multimaterial architectures. We are developing photochemical methods to control initiation, propagation, and termination of FROMP reactions *in situ*, in order to achieve greater spatial, temporal and compositional control in both FROMP additive manufacturing and bulk polymerizations. Catalyst-based photocontrol methods inhibit or activate catalysts selectively to control the speed and direction of front propagation. Monomer-based photocontrol approaches utilize isomerizable monomers with different activities for ROMP to control both front velocities and the local composition of the polymer. Finally, we envision an approach to incorporate both catalyst- and monomer-based photocontrol methods with closed-loop process control in additive manufacturing in order to enable printing of complex architectures with designed heterogeneous compositions.

I-S2-51: DEVELOPMENT OF A DIVERSE CORRELATIVE MICROSCOPY PLATFORM FOR ADVANCED CHARACTERIZATION OF SOLAR WATER SPLITTING NANOREACTORS IN ISOLATION AND AS ENSEMBLES

[EFRC – EPN] Justin T. Mulvey[1], Wonseok Lee[2], Jocienne N. Nelson[3], Jonathan Stoffel[3], Austin Bhandarkar[3], Avishek Banik[4], Wenjie Zang[1], Zejie Chen[1], Hiroaki Maekawa[1], Akihiko Kudo[5], Shane Ardo[1], Young-Seok Shon[6], Nien-Hui Ge[1], Justin B. Sambur[4], Xiaoqing Pan[1], Daniel V. Esposito[7], Joseph P. Patterson[1], Scott K. Cushing[2], A. Alec Talin[3]
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AFFILIATED TALK – I-T2-12: Temporal Evolution of Nanomaterials Structure and Function during Hydrogen Evolution Induction Period for State-Of-The-Art Pt-Loaded Rh-Doped $SrTiO_3$ Nanoparticles

Correlative microscopy techniques are advantageous to understand, predict, and control the activity, selectivity, and stability of solar water splitting nanoreactors in isolation and as ensembles. Toward this, we are (i) identifying nanoreactor subsets in ensembles, (ii) determining nanoscale materials and optical properties of individual nanoreactors, and (iii) assessing transient dynamics of individual nanoreactors via coupled correlative microscopy/spectroscopy techniques and theoretical approaches. Such an approach is unprecedented for photocatalyst nanoparticle reactors. Our major advances include a new means to affix nanoreactors to surfaces, which has enabled use of complementary correlative multimodal microscopies across multiple platforms to quantify underlying properties of single nanoreactors that dictate ensemble behaviors. Specifically, using a combination of liquid-cell transmission electron microscopy, four-dimensional scanning transmission electron microscopy, scanning photocurrent microscopy, electron-beam-induced current, and scattering-type scanning near-field optical microscopy we have elucidated correlated behaviors for state-of-the-art H_2-evolving doped $SrTiO_3$ nanoreactors and O_2-evolving $BiVO_4$ nanoreactors. We have discovered that Pt cocatalyst deposition on Rh-doped $SrTiO_3$ nanoparticles is accompanied by materials structural and electronic changes, and charge separation in Rh-doped $SrTiO_3$ nanoparticles and $BiVO_4$ nanoparticles is not dictated by band bending or facet-dependent energetics. Each of these observations is being supported by multiscale simulations from DFT to kinetic Monte Carlo to the continuum level. With our new correlative microscopy platform, we aim to reveal detailed photophysical and photochemical mechanisms of species transport and reactivity, and dynamic materials evolution and durability, over a range of length and time scales available from variable-sized nanoreactors in liquid environments.

I-S2-52: MECHANISTIC MOTIFS AND PROCESSIVITY IN POLYMER UPCYCLING

[EFRC – iCOUP] Tommy Yunpu Zhao[1], Max Meirow[2], Akalanka Tennakoon[1,3], Xun Wu[1,3], Ryan Yappert[4], Ziqiu Chen[4], Xingyi Lyu[5], Xuchun Wang[5], Tao Li[5,6], Alexander L. Paterson[1], Long Qi[1], Anne M. LaPointe[7], Jessica V. Lamb[6], Takeshi Kobayashi[1], Massimiliano Delferro[6], Byeongdu Lee[6], Aaron D Sadow[1,3], Wenyu Huang[1,3], Baron Peters[4], Erik Luijten[2], Frédéric A. Perras[1]
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AFFILIATED TALK – I-T2-9: Catalytic Chemical Recycling of Post-Consumer Polyethylene

Catalytic polymer upcycling is an unfamiliar realm of chemical dynamics. While chemists are trained to perform selective conversions from one pure molecular species to another, products of polymer deconstruction are typically generated probabilistically. This ultimately leads to the formation of complex mixtures of many molecular products. For polymer upcycling to be successful as a waste remediation strategy, it is imperative that we develop new ways to control reaction outcomes at the length scales of the macromolecule, and in so doing reduce the complexity of upcycling products.

The crux of the issue is that traditional catalysts are designed to work at the Angstrom scale for the purpose of molecularly precise conversions while typical polymers can extend to the micron scale. *But this is a problem that is nearly as old as time*. Evolution has repeatedly determined that

the conversions of macromolecules (proteins, polysaccharides, DNA, RNA, and now PET) are best performed processively.

In light of this, we have studied processivity at length and time scales that are relevant to selective deconstructions of polymers, by developing microkinetic models that describe the overall reaction processes and molecular dynamics models that track reactions at a monomer level. This work is coupled with the use of advanced spectroscopic and scattering techniques that measure the dynamics of polymers as they interact with porous substrates and the design of novel catalysts that perform processive polyolefin hydrogenolysis reactions. We have found that these catalysts both reduce product complexity and enable its tunability.

I-S2-53: HIGH-THROUGHPUT DISCOVERY OF METAL-SULFIDE BASED MOFS AND COORDINATION POLYMERS FOR CATALYTIC PRODUCTION AND STORAGE OF H_2

[ERFC – CD4DC] Max Delferro[1], Karena W. Chapman[2], Justin Notestein[3], Johannes Lercher[4], Laura Gagliardi[5], Omar K. Farha[3], Joseph T. Hupp[3], Anna Wuttig[5], John S. Anderson[5], Yinjie Ji[4], Julian Schmidt[4], Jacob T. Bryant[1], Magali Ferrandon[1], Andrea Daru[5], Haomiao Xie,[5], Seryeong Lee,[5], Dawson Grimes[3] Milad Khoshooei[4], Spela Kunstelj[5], Ningxin Jiang[5], Andrew Ritchhart[5] Patrick Crossland[5]
[1]Argonne National Laboratory; [2]Stonybrook University; [3]Northwestern University; [4]Pacific Northwest National Laboratory; [5]University of Chicago

Metal-organic frameworks (MOFs) have emerged as promising candidates for thermal, photo-, and photo-electro catalytic hydrogen production and hydrogen transfer reactions, offering a high degree of robustness, chemical tunability, and predictability. Using the principles of reticular chemistry, we designed libraries of permanently porous structures with targeted properties. This provides a platform for fundamental understanding and deconvoluting of structure property-relationships. Typically, MOF based catalysts feature metal-oxygen and metal-nitrogen based secondary building units (SBUs), consistent with many naturally occurring catalysts. The use of metal-sulfur based MOFs and coordination polymers is scarce, and permanently porous 3-dimensional MOFs based on metal-sulfide SBUs remain elusive. By utilizing thiophilic metal centers, and linkers containing thiols, dithiocarbamates, thio-, and dithiocarboxylic acids we aim to access new porous MOF structures. We show that the use of thiol containing linkers such as benzene dithiol (BDT), trithiocyanuric acid (TTCA), biphenyl dithiol (BPDT), and 1,3,5-tris-p-thiophenyl benzene (TTPB) in combination with thiophilic metal cations such as Mn, Ca, Fe, and In led to crystalline materials in the form of powder or single crystals. Synthesis conditions including choice of solvent, metal precursors, links, additives, and their ratios are currently being optimized through high-throughput techniques coupled with machine learning. Structural determination, spectroscopic characterization and catalytic investigations are currently progressing. The physicochemical characterization aims to understand the mode of hydrogen binding (adsorption and desorption) and the specific role of the metal- sulfur bond for hydrogen transfer reactions.

I-S2-54: A MULTISCALE COMPUTATIONAL FRAMEWORK FOR BIOMOLECULAR ENERGY TRANSDUCTION: FROM ELECTRONS TO THE MESOSCALE

[CCS – CMSET] [1]Scott Kaiser, [1]Sahithya Sridharan Iyer, [1]Daniel Beckett, [1]Siva K. Dasetty, [3]Tomasz Skora, [2]Garnet K. L. Chan, [3]Tamara Bidone, [1]Andrew Ferguson, [1]Gregory A. Voth
[1]*University of Chicago,* [2]*California Institute of Technology,* [3]*University of Utah*
AFFILIATED TALK – I-T2-7: A Multiscale Computational Framework for Biomolecular Energy Transduction: from Electrons to the Mesoscale

The Center for Multiscale Simulation of Energy Transduction (CMSET) aims at accurately modeling biomolecular energy transduction across multiple scales in complex environments. The center is focused on developing exascale-ready software which harnesses advanced computing capabilities including machine learning (ML) and graphics processing units (GPUs). Our team provides a complementary blend of expertise in electronic structure, machine learning, statistical mechanics, and mesoscopic modeling of complex soft matter and biomolecular systems. The Chan and Voth groups apply their expertise to accelerate density functional molecular dynamics (and QM/MM) in the PySCF and LAMMPS framework to obtain a factor of two speed over the CP2K QM/MM framework. Connecting to the all-atom scale, the Ferguson group develops and implements neural network-based ML algorithms, which allow an all-atom configuration to 'leap forward' in time. This equation free method interpolates between metastable states of large multimolecular microtubule filament systems bridging the MD simulations to longer time and length scales. This method allows for the exploration of converged equilibrium properties of computationally prohibitive rare events. To access even longer length and time scales, the Voth group–in key collaborations with DOE laboratory personnel–have implemented a coarse-graining method with GPU acceleration in LAMMPS, achieving a significant performance increase over a CPU implementation. At mesoscale resolutions, the Bidone group uses the all-atom simulations by the Voth group to design new equations for the mesoscale motion of microtubules. Taken together, CMSET develops cutting-edge multiscale simulation software for the study of biomolecular energy transduction.

I-S2-55: PROGRAMMABLE CATALYSIS FOR STEAM REFORMING OF METHANE ON RU CATALYST

[EFRC – CPEC] Lars Grabow[1]
[1]*University of Houston*

Researchers at the Center for Programmable Energy Catalysis (CPEC) have shown that periodic modulation of binding energies of surface intermediates can be leveraged to enhance the catalyst turnover beyond the Sabatier limit by several orders of magnitude for a relatively simple model reaction. Practically, modulation of binding energies can be achieved using a catalytic condenser, a novel device that changes the electron density at the catalyst surface via applied potentials in a programmable pattern.

To calculate energies of adsorbed intermediates and transition states on charged surfaces several computational approaches for using density functional theory (DFT) simulations were evaluated and benchmarked. Linear scaling relationships between the binding energies at different surface charges on ruthenium catalyst were calculated and charge-based scaling relations were

developed. To simulate the dynamic response of the reaction rate to dynamic changes of binding energies of surface intermediates, we used a transient kinetic model and explored the potential of dynamically enhancing steam reforming activity by modulating the binding energies as a square wave for a broad range of frequencies. Indeed, our simulations suggest that modest dynamic rate enhancements are possible using a square wave program, but only when the endpoints of the oscillation lie in distinct kinetic regimes. Further improvements may be accomplished with more complex catalytic programs.

I-S2-56: DESIGN AND CHARACTERIZATION OF CATALYTIC CONDENSERS

[EFRC – CPEC] Paul J. Dauenhauer[1]
[1]*University of Minnesota*

AFFLIATED TALK – I-T2-13: Center for Programmable Energy Catalysis

Catalytic condensers were fabricated and characterized with modifications for their ability to modulate surface chemistry. Condensers were synthesized by atomic layer deposition of varying composition and thickness with continuous metal active layers to assess their extent of total charge condensation with design parameters and conditions (i.e., temperature). Additionally, deposition of graphene by various methods was conducted to determine the sheet conductance of the entire device. Devices were analyzed by impedance spectroscopy to identify the corner frequency at each operating temperature, which ultimately determined the frequency at which catalytic surfaces could oscillate in electronic state. Finally, the composition and loading of catalyst active site was varied to quantify the relationship between average charge condensation per active site and associated effect on adsorbate binding energy and transition states. These experiments together identified a device design that provides robust charge condensation over catalytically-relevant length scales at speeds in excess of 100 Hz.

Day 2 – September 20, 2023

Poster Session 1

II-S1-01: MINERAL DISSOLUTION OF CARBONATE-RICH ROCKS INVESTIGATED THROUGH MICROFLUIDIC IMAGE ANALYSIS

[EFRC – CMC-UF] Bowen Ling[1], Siquin Yu[1], J. Hwang[1], Mo Sodwatana[1], Arjun Kohli[1], Cynthia M. Ross[1], [2]Adam Jew, Anthony R. Kovscek[1], Ilenia Battiato[1]
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Carbonate dissolution in porous formations is ubiquitous in nature and relevant to many applications spanning from subsurface carbon sequestration to enhanced geothermal extraction. The system dynamics is controlled by the strong coupling between multiphase flow, mass transport, and reaction. Existing experimental methods mainly focus on characterization by core-based techniques. While such methods provide valuable quantification of dissolution at high spatial resolution, they have limited capability for real-time observation of the reaction dynamics. Microfluidic devices embedded with real rocks have been developed to enable the visualization of the reaction progress at both high temporal and spatial resolution through a combination of optical and non-optical imaging. Here, the method of determining effective multiphase reaction rate by image analysis is first demonstrated and validated against single phase dissolution experiments. We then quantify the decrease of effective multiphase reaction rates due to bubble shielding effects and investigate the impact of complex coalescence dynamics on constitutive relationships correlating effective reaction rates and saturation. Our findings suggest that there exists significant difference between the dissolution of pure minerals and heterogeneous rocks, and that constitutive relationships including information about composition as well as different dynamical regimes might be needed to capture correctly effective reaction rates at the Darcy scale.

II-S1-02: $EuCl_3$-MEDIATED CORROSION OF NI AND NI-20CR ALLOY CORROSION IN THE LICL-KCL SALT SYSTEM

[EFRC – MSEE] Ruchi Gakhar, Kaustubh Bawane
[1]*Idaho National Laboratory*

Molten salt chemistry has a complex impact on corrosion of structural alloys, influenced by salt redox potential, fission product buildup, and the presence of impurities and moisture. Understanding material degradation under extreme environments offered by molten salt is therefore critical for demonstration of sustainable energy systems, such as next-generation nuclear reactors and large-scale concentrated solar thermal power plants. MSEE Thrust 3 focuses on structural and mechanistic descriptions of the processes at the molten salt interfaces including mass and charge transfer (corrosion), through coordinated in-situ and ex-situ characterization techniques. A main objective is to underpin the impact of salt additives on salt chemistry and the structural material interface. Several fission products have two salt-soluble oxidation states, e.g., Eu(II/III), Sm(II/III), Yb(II/III), etc. In molten chloride salts, the formal potential of Eu(III)/Eu(II) is considerably more positive than the oxidation potentials of nickel, iron, and chromium, the major components of structural alloys. This implies that the Eu(III) species may act as a strong oxidant to

cause the dissolution of these metals. In this study, $EuCl_3$-driven corrosion of Ni and Ni-20Cr alloy corrosion in LiCl-KCl salt system at 500 °C will be presented. The in-situ time-resolved optical spectroscopy was applied to probe the change in salt chemistry during corrosion. The Ni and Ni-20Cr wires corroded in LiCl-KCl at 500 °C in the presence and absence of $EuCl_3$ were characterized using advanced electron microscopy techniques, to elucidate the mechanism of corrosion attack.

II-S1-03: COMPREHENSIVE STUDIES ON PROTON DYNAMICS IN $BaCo_xFe_{0.8-x}Zr_{0.1}Y_{0.1}O_{3-D}$ (BCFZY, $0.7 \leq x \leq 0.1$)

[EFRC – HEISs] Yewon Shin[1], Kennedy Agyekum[2,3], Bernadette Cladek[2,3], Erica Truong[4], Jue Liu[2], Katharine Page[2,3], Yan-Yan Hu[4], Ryan O'Hayre[1]
[1]Colorado School of Mines; [2]Oak Ridge National Laboratory; [3]University of Tennessee-Knoxville; [4]Florida State University

Triple-conducting oxides (TCOs) conduct three charge carriers ($H^+/O^{2-}/e^-$), enhancing performance/functionality for numerous electrochemical energy conversion technologies. TCOs may also yield new types of devices (e.g., electrochemical diodes/sensors and "uphill diffusion" membranes). Yet, TCO design is still uncertain due to the complex interplay of dopants; thus, a scientific understanding of how doping affects local structures, defect concentrations, reaction kinetics, and transport behavior is essential.

To establish such understanding, we examine the effect of transition metal (TM) doping in $BaCo_xFe_{0.8-x}Zr_{0.1}Y_{0.1}O_{3-\delta}$ (BCFZY, $0.7 \leq x \leq 0.1$), an archetypical TCO system. Co/Fe doping ensures sufficient electronic conductivity and promotes electrocatalytic activity; but holes are generated at the expense of protons, influencing bulk and surface kinetics. A prior study of these tradeoffs by tracer exchange experiments (Y. Shin et al., DOI 10.1039/D2TA03150G) revealed that high Fe-content increases proton kinetics but decreases oxygen vacancy kinetics.

Solid-state nuclear magnetic resonance is utilized here to compare the H/D spectra and T_1 relaxation times between $BaCo_{0.4}Fe_{0.4}Zr_{0.1}Y_{0.1}O_{3-\delta}$ and $BaZr_{0.8}Y_{0.2}O_{3-\delta}$ (an archetypical "pure" proton conductor). These methods permit detection of differences in extent of electron density localization and local structural environments with Co/Fe doping.

In parallel, neutron diffraction and pair distribution function (PDF) studies explicate the long-range and local structure of BCFZY, providing quantification of oxygen and barium defects. Across the solid solution, a high degree of local atomic distortion related to complex oxidation states is observed. These combined experimental approaches allow us to overcome the challenge of probing proton dynamics in complex oxide environments and gain meaningful insights into TCO behavior.

II-S1-04: MECHANO-ELECTROCHEMICAL INTERACTIONS IN SOLID-STATE BATTERY CATHODES

[EFRC – MUSIC] Partha P. Mukherjee[1], Bairav S. Vishnugopi[1], Kaustubh G. Naik[1], Kelsey B. Hatzell[2], Neil P. Dasgupta[3], Matthew T. McDowell[4], David Mitlin[5], Katsuyo Thornton[3], and Jeff Sakamoto[3]
[1]Purdue University; [2]Princeton University, [3]University of Michigan; [4]Georgia Institute of Technology, [5]University of Texas, Austin

Solid-state batteries, utilizing a solid electrolyte and a lithium metal electrode, promise to offer higher energy and power density and improved safety, when compared to current lithium-ion batteries. Despite the significant efforts made toward the advancement of solid-state batteries, various fundamental challenges pertaining to the electrochemical/mechanical stability, transport and morphology evolution still need to be addressed. Importantly, the origin and progression of such mechanistic interactions in the solid-state cathode plays a pivotal role on the rate performance and degradation of solid-state batteries. The electro-chemo-mechanical response of the solid-state cathode is dependent on a wide range of aspects like the spatial distribution of the constituent phases (e.g., solid electrolyte, active material, carbon/binder), their morphological, mechanical and transport characteristics, and operating conditions including external pressure and temperature. In addition, the presence of microstructural heterogeneities affects the ionic/electronic transport, electrochemical dynamics and mechanical stress evolution in the electrode architecture. Herein, we hypothesize that the underlying coupling in such mechanistic processes in the solid-state cathode, induced by factors such as the volumetric changes of the active material, solid-solid contact distribution, heterogeneities and external pressure, critically influences the lithiation dynamics, chemo-mechanical stability and electrode utilization. Through a combination of mechanistic modeling, operando analysis and mechano-electrochemical measurements, the MUSIC team is conducting a comprehensive analysis of the coupled interactions in solid-state battery cathodes.

II-S1-05: EXPERIMENTAL OBSERVATIONS OF CHEMO-MECHANICAL COUPLING DURING CARBON MINERALIZATION IN FRACTURES

[EFRC – GMCS] Chelsea Wren Neil[1], Haylea Nisbet[1], Uwaila Iyare[1], Yun Yang[1], Bill Carey[1], Hari Viswanathan[1], Peter Kang[2]
[1]Los Alamos National Laboratory; [2]University of Minnesota

AFFILIATED TALK – II-T1-4: Experimental observations of chemo-mechanical coupling during carbon mineralization in fractures

To demonstrate the viability of long-term geologic carbon dioxide (CO2) sequestration in mafic and ultramafic rocks, it is crucial to understand the complex interplay between geochemical changes, triggered by reaction between rock and injected CO2, and geomechanical changes, such as fracture formation and propagation, which will expose new reactive mineral surfaces and allow for prolonged CO2 injection. In particular, we must learn how the CO2 mineralization reaction will progress within both flowing and dead-end fractures and how this reaction will impact the rock structure through reaction-driven cracking, dissolution and weakening of the rock matrix, and changes to frictional forces between rock surfaces. In this poster, we present the current and ongoing research, where we are applying advanced experimental tools to fill these knowledge gaps. These tools include Raman spectroscopy to characterize reacted surfaces, high temperature-pressure microfluidics for in situ observation of reaction in flowing fractures, and scanning electron microscopy observation of fracture propagation in single crystal olivine to investigate reaction-driven cracking. Preliminary results show that fracture properties, including surface

roughness and aperture, impact the quantity and characteristics of reaction products including magnesite and iron oxides. Additionally, precipitation of magnesite within preexisting olivine fractures, as well as dissolution pit formation on the olivine crystal surface, was observed.

II-S1-06: CENTER FOR MATERIALS FOR WATER AND ENERGY SYSTEMS (M-WET)

[EFRC – M-WET] Benny Freeman[1], Lynn Katz[1], Rachel Segalman[2], Berkin Dortdivanlioglu[1], Venkat Ganesan[1], Graeme Henkelman[1], Manish Kumar[1], Nathaniel Lynd[1], Zak Page[1], Gabriel Sanoja[1], Christopher Bates[2], Phillip Christopher[2] Raphaële Clément[2], Glenn Fredrickson[2], Craig Hawker[2], M. Scott Shell[2], Todd Squires[2], Ethan Crumlin[3], Greg Su[3], Dylan McReynolds[3]
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Synthetic polymer membranes are widely used to purify water, mainly because they are more energy efficient than competing (e.g., thermally based) technologies. However, water in energy applications is often contaminated with a plethora of diverse organic and inorganic components. Current membranes were not designed for such applications. Basic science knowledge gaps in thermodynamic and kinetic behavior of complex aqueous mixtures at interfaces, and the effect of such mixtures on the interfacial properties, limit our ability to translate fundamental understanding to transformative membrane materials design and manufacturing for energy/water applications. Current methods for synthesis and precision assembly of novel materials far from equilibrium do not allow for the scalable manufacturing of membranes with mesoscopic control over morphology for highly selective decontamination or resource recovery from such complex aqueous mixtures. The *Center for Materials for Water and Energy Systems* (M-WET) seeks to fill these gaps in the understanding of fluids, materials, and non-equilibrium processing to catalyze the design of novel materials, highly selective solute/fluid interactions, mesoscopic structures, and transformative manufacturing strategies to prepare robust, high-performance membranes for energy applications. Our central goal is to discover and design specific interactions with solutes of interest to create highly manufacturable, scalable, robust, selective, permeable membranes. 3 Gap Attack Platforms (GAPs) address fundamental knowledge gaps: (A) Structure and Dynamics of Water and Solutes Near Interfaces, (B) Role of Hydration in Ion Transport and Separations, and (C) Fundamental Science of Membrane Manufacturing. GAPs work with an overarching Integrating Framework (IF) on Bridging Between Systems/Developing the Bridging Toolset.

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FOR WATER AND ENERGY SYSTEMS

II-S1-07: NEW AM CONTAINING SILICATES, PHOSPHATES, BORATES AND FLUORIDES

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The crystal growth of uranium and transuranium containing phases has been accomplished via two different crystal growth routes, mild hydrothermal and high temperature solution flux growth. In both cases we are targeting the preparation of new compositions to evaluate their potential use as nuclear waste forms. The mild hydrothermal route works extremely well for crystallizing complex fluoride phases, such as $Na_3GaU^{IV}_6F_{30}$, $Na_3AlNp^{IV}_6F_{30}$, $Na_3FePu^{IV}_6F_{30}$, and $Cs_2NiNp^{IV}_3F_{16}$, while the high temperature flux route works well for crystallizing oxide phases, such as $Cs_2Pu^{IV}Si_6O_{15}$, $K_3Am(PO_4)_2$, $Na_3Am(PO_4)_2$, $K_3AmSi_2O_7$, $Ba_3Am_2(BO_3)_4$, $Ca_5Am(BO_3)_4Cl$, and $Na_2Pu^{V}O_2(BO_3)$. The synthesis and structures of these phases will be presented, along with our approach of identifying potential compositions that we can pursue synthetically.

II-S1-08: LINKING MATERIALS SYNTHESIS, MEMBRANE FORMATION, AND PERFORMANCE FOR ISOPOROUS MEMBRANES

[EFRC – M-WET] Matthew R. Landsman[1], Benjamin J. Pedretti[2], Noah Wamble[2], Mostafa Nassr[2], Louise Kuehster[2], Cameron McKay,[2] Zachariah A. Page[2], Lynn E. Katz[2], Glenn H. Frederickson[3], Rachel A. Segalman[3], Gregory M. Su[1], Nathaniel A. Lynd[2], Benny D. Freeman[2]
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This project focuses on developing advanced characterization tools for membranes and scaling materials synthesis strategies to provide large amounts of novel materials for systematic basic science studies of membranes. Self-assembly and non-solvent induced phase separation (SNIPS) can yield isoporous membranes, which have excellent permeability and selectivity. The SNIPS process is highly nonequilibrium, and many parameters influence final membrane morphology. Small variations in polymer properties can change membrane morphology. To enable consistent membrane preparation, large batches (e.g., tens to hundreds of grams) of novel polymer materials

are required. Anionic polymerization techniques have been scaled to synthesize a library of 60-100 gram batches of tetrablock copolymers which are mechanically tough, functionalizable, and amenable to isoporous membrane formation. This library permits rational, systematic studies of the influence of polymer properties and casting parameters on SNIPS-based membranes. *In situ* x-ray spectroscopy/scattering techniques are employed to determine the morphology of polymer dispersions in membrane casting solutions as well as *operando* measurements of the transition of polymer dispersions to highly selective membrane materials. A battery of x-ray characterization techniques provides molecular-to-macroscopic information on the mechanisms by which membranes interact with contaminants (e.g., membrane fouling), providing insight required to design and produce membranes with ideal transport and antifouling properties. Leveraging both synthetic and analytical toolsets enable better understanding of the relationships between polymer properties, casting conditions, and membrane characteristics for highly selective isoporous SNIPS membranes and provide data sets to compare with simulation studies.

(from left, top) Matthew Landsman, Benjamin Pedretti, Noah Wamble
(from left, bottom) Louise Kuehster, Mostafa Nassr, and Cameron McKay

II-S1-09: ENGINEERED INTERFACES FOR UNDERSTANDING RADIATION INDUCED DEFECT SEGREGATION AND TRANSPORT

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The presence of defects transport in all materials. Irradiated materials reveal segregation of defects to grain boundaries or interfaces; the abundance of grain boundary surfaces in high burnup structures serves to remove intragranular defects, removing phonon scattering sites, resulting in enhanced thermal conductivity. Recent observations of exceptionally high

radiation tolerance of heterointerfaces in oxide composite systems are attributed to structural disorder, defect annihilation by residual stress, or differences in thermal expansion. However, the fundamental mechanisms responsible for this defect segregation in high burnup structures and their influence on thermal transport are unexplored. This work employs theoretical and experimental methods to investigate the effects of irradiation on defect formation and segregation and the subsequent effects on transport in carefully engineered interfaces in both oxide and nitride materials. Bicrystals of pure and Cr-doped $(U,Th)O_2$ are fabricated using hydrothermal methods and superlattices of single crystalline nitrides are formed using a new molecular beam epitaxy chamber. The first order surrogates of ZrN/GaN have been chosen for investigation prior to actinide nitride synthesis. As localized interfacial modes play an important role in energy transport across interfaces, even in the absence of defects, these interfaces will be examined prior to irradiation to gather a baseline. A large suite of characterization techniques are employed to determine the types defects that arise, where/if segregation or annihilation occurs, and the effects on the resultant thermal and electrical transport.

II-S1-10: ENABLING ANION REDOX THROUGH CATION VACANCIES AND THE ORIGIN OF FIRST-CYCLE ACTIVATION AND VOLTAGE HYSTERESIS IN LI-RICH SULFIDE MATERIALS

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[1]California Institute of Technology, [2]University of Southern California, [3]University of California Santa Barbara, [4]Univeristy of California San Diego

Conventional Li-ion battery intercalation cathodes leverage charge compensation formally associated with transition metal redox. Employing anions in the charge compensation mechanism, termed anion redox, can yield higher capacities beyond the traditional limitations of intercalation chemistry. Here, we aim to understand the structural considerations enabling reversible anion redox in Li-rich sulfides. Using Li_2TiS_3 as a model system, we present both first-principles simulations and experimental data showing cation vacancies are required for anion redox. We also aim to understand the origins of the first-cycle activation and voltage hysteresis in Li-rich sulfides. By examining the discharge mechanism of $LiTi_{0.75}\square_{0.25}S_2$, we show Ti is over-reduced and S is not fully reduced back to S^{2-} during discharge. Voltage hysteresis is caused by trapped $(S_2)^{2-}$ and the formation of amorphous regions during discharge. This system offers fundamental insights to deepen our understanding of structure-property relationships governing the activation of reversible anion redox in Li-rich sulfides.

II-S1-11: MECHANISMS CONTROLLING THE ENERGY BARRIER FOR ION TRANSPORT IN POLYMER ELECTROLYTES

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We will present our work on understanding mechanisms controlling the energy barriers for ion hopping in conducting polymers. Polymer electrolytes usually show Arrhenius-like temperature dependence of the conductivity relaxation time (characteristic time of local ion rearrangements) at temperatures below their glass transition Tg. However, our analysis reveals that the Arrhenius fit of this regime leads to unphysically small prefactors, $\tau_0 \ll 10^{-13}$s. Imposing a value of 10^{-13}s for this parameter renders the fairly unexpected result that the energy barrier for charge transport in these polymers has strong temperature dependence even below Tg. Our study also revealed significant temperature variations of the dielectric permittivity and the instantaneous shear modulus in the glassy state of these polymers. Using the Anderson and Stuart model, we demonstrate that these variations provide strong justifications for the temperature variation of energy barriers for ion hopping. Most importantly, the proposed approach reveals that the energy barrier controlling ion hopping in polymer electrolytes is significantly (∼30−40%) lower than that estimated using the traditional Arrhenius fit. These new insights call for revisions of many earlier results based on apparent Arrhenius fits, and the proposed new approach can provide more accurate guidance for the design of solid-state electrolytes with enhanced ionic conductivity. Ongoing works using data science and a statistical mechanics-based theory will be discussed for the purpose of designing anions leading to a room temperature ionic conductivity 1 mS/cm in single ion conducting polymer electrolytes.

II-S1-12: UNDERSTANDING HETEROGENEOUS ICE NUCLEATION ON FELDSPAR FROM FIRST PRINCIPLES

[CCS - CSI] Pablo M. Piaggi[1], Annabella Selloni[1], Athanassios Z. Panagiotopoulos[1], Roberto Car[1], Pablo G. Debenedetti[1]
[1]*Princeton University*

The formation of ice in the atmosphere plays a key role in the climate of our planet. Although ice can form directly from liquid water at deeply supercooled conditions, the presence of foreign particles can aid ice formation at much warmer temperatures. Over the past decade, experiments have highlighted the remarkable efficiency of feldspar minerals as ice nuclei compared to other particles present in the atmosphere. However, the exact mechanism of ice formation on feldspar surfaces has yet to be fully understood. Here, we develop a first-principles machine-learning model for the potential energy surface aimed at studying ice nucleation at microcline feldspar surfaces. The model is able to reproduce with high-fidelity the energies and forces derived from density-functional theory (DFT) based on the SCAN exchange and correlation functional. We use this model to drive molecular dynamics simulations in different fully-hydroxylated terminations of the (100), (010), and (001) surfaces of microcline exposed to liquid water. Our calculations suggest that flat, defect-free surfaces of microcline do not promote ice nucleation. We suggest that defects or chemical processes at the surface of microcline may play a crucial role in the formation of ice.

II-S1-13: WATER CONFINED IN CARBON NANOTUBES: STRUCTURE, DYNAMICS, AND REACTIVITY FROM MACHINE LEARNING MOLECULAR DYNAMICS SIMULATIONS

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Confinement has a major impact on the structure and transport of fluids in single-digit nanopores (SDNs). For example, water confined in sub-nm carbon nanotubes (CNTs) exhibits unusual ice phases and orders of magnitude enhancement in proton diffusion relative to the bulk solution. Although this system has been extensively studied with computer simulations, conventional approaches lack either the accuracy of first-principles potential energies or the efficiency of parametric force fields. To address this knowledge gap, we develop a general platform for simulating water in CNTs with quantum accuracy on time and length scales beyond the reach of conventional first-principles approaches. We apply this framework to investigate the infrared spectra and transport mechanism of monoatomic and water ions in sub-nm CNTs. Our simulations reveal a strong correlation between the disruptive effects of confinement on the H-bond network of water and its infrared absorption spectra, providing new atomic-level interpretation of experimental spectra. We also provide new understanding on the mechanism of ion diffusion, including the reactive transport of water ions through the Grotthuss mechanism in the confined media. The machine learning models constructed in this work can be further extended to simulate other physically-relevant events, paving the way to the study of nanofluidics with first principles-based atomistic simulations.

II-S1-14: PROTON CONDUCTION AND INTERFACIAL KINETICS IN PROTONIC SYNAPSE DEVICES

[EFRC – HEISs] Heejung Chung[1], Jordan Meyer[1], Ju Li[1], Bilge Yildiz[1]
[1]*Massachusetts Institute of Technology*

In comparison to standard architectures, electrochemical random-access-memory (ECRAM) can enable orders of magnitude reduction in computing energy consumption. In prior work (DOI: 10.1038/s41467-020-16866-6), we fabricated fast protonic devices with very small energy consumption, but only at prohibitively large operating voltages. To reduce kinetic limitations responsible for the high voltages, efforts are now focused on understanding and accelerating proton conduction in metal oxides and charge transfer at the interfaces.

In ternary oxides, proton diffusion is rate-limited by hopping between proximate O...O pairs, where energy barriers are believed to be lower for hops across shorter O...O distances. However, our results show that very short distances (<2.7 Å) correlate with high energy barriers (>1 eV). To explain this, we introduce a property called thermal shrinkage, or expected reduction in O...O distance from thermal vibrations. Closer O...O pairs typically have low thermal shrinkage, indicating low flexibility. We found that only compact and flexible O...O pairs have low energy barriers. These results used preliminary calculations with machine-learning potentials and will be validated using density functional theory. We are also exploring whether existence of rigid-unit modes indicates higher proton conductivity.

For enhancing interface proton and electron transfer, potential strategies include using metals to catalyze the proton reduction reaction or metal oxides described by acid-base scales. Sub-monolayer coatings were sputtered at the HfO_2-WO_3 electrolyte-channel interface of ECRAM

devices. Kinetics of conductance modulation was then explored in modified ECRAM devices. Next steps include shifting to a thinner, more proton-conductive electrolyte, to reduce electrolyte resistance and isolate interface effects.

II-S1-15: STRUCTURE AND SOLVATION DYNAMICS OF DEEP EUTECTIC SOLVENTS

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AFFILIATED TALK – II-T1-6: Structure and Solvation Dynamics of Deep Eutectic Solvents

Deep eutectic solvents (DESs) are mixtures of hydrogen bond donor (HBD) molecules and hydrogen bond acceptor (HBA) molecules that are characterized by a significant depression of the melting point compared to that of its individual constituents. With their versatile properties, DESs hold great promise as next-generation electrolytes for electrochemical energy storage solutions. In this study, we investigate the influence of varying the HBA, HBD, HBA/HBD molar ratios, and co-solvents on the structure and dynamics of DES ethaline, a 1:2 molar ratio mixture of choline chloride (ChCl) and ethylene glycol (EG). When examining the influence of HBA/HBD molar ratio, femtosecond transient absorption spectroscopy reveals two distinct time components. Both components indicate that solvation dynamics are enhanced with increasing ChCl composition up to 16.67 mol% but are slowed down for 33 mol% ChCl. Additionally, molecular dynamics simulations shed light on the role of co-solvents, specifically water molecules, in DESs. Higher concentrations of water co-solvent promote longer Grotthuss mechanism chain lengths within the DES. The H_3O^+ ion, briefly stabilized by Cl^-, interacts with ethylene glycol, indicating a disruption of the hydrogen bond network in the DES. Our results reveal that substituting ChCl with ChF as the HBA enhances the relaxation dynamics of DES. The ^{19}F-NMR spectrum of ethalineF unveils two distinct chemical environments surrounding the fluoride ion, namely EG···F (freely dissolved F^- in EG) and Ch···F (choline-bound F^-). Consequently, by altering the O-H spacing and alkyl chain length of EG, it becomes possible to fine-tune the polarity and solvation dynamics of DESs.

II-S1-16: CORRELATIVE ANALYSIS OF COORDINATION COMPLEXES OF NI(II) IN MOLTEN SALTS USING A COMBINATION OF X-RAY AND OPTICAL SPECTROSCOPIES AND SIMULATIONS

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As MSR fuel salt ages in service, fission, corrosion, and radiolytic products accumulate in addition to the original actinide fuel loading. Proper management of the Molten Salt Reactor (MSR) fuel

salt for reliable operation requires understanding of the solubilities, insolubilities, and volatilities of the broad array of elements contained in the salt. One of MSEE's focuses is to understand how the solute species interacts with the host molten salt at atomic-level and affect the salt properties such as solubilities, redox properties, and volatilities. We studied the speciation (coordination number and geometry) of the Ni^{2+} cation in molten salts because nickel is a major component of the alloys used for salt circulation loops in MSRs and a common corrosion product. Speciation of nickel in molten chloride salts is very sensitive to its environment, making it an excellent probe of solute-salt interactions. We characterized Ni^{2+} solvation in a wider array of salts as function of composition and temperature KCl-$ZnCl_2$, LiCl-KCl, NaCl-$MgCl_2$ and LiCl-$ZnCl_2$ using a multimodal approach combining X-ray and optical spectroscopy, and classical and ab initio molecular dynamics. We studied its speciation and variation molten salt systems and developed a novel approach of combining the multivariate curve resolution - alternating least squares (MCR-ALS) analysis of the XAS data to deconvolute the coexisting coordination complexes. Our studies indicate that the speciation and local structural heterogeneity demonstrated by Ni(II) ions in various molten salts systems is directly related to the solvent composition, owing to the polarizing power of the solvent metal cations.

II-S1-17: DESIGNING AND OPTIMIZING SEMICONDUCTING POLYMERS AS CATHODE BINDERS IN LITHIUM ION BATTERIES

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Cathodes of current lithium-ion batteries (LIBs) consist of the electrochemically-active material, conductive additives, and binders that are designed to be chemically and mechanically durable during lithium intercalation and deintercalation. By utilizing conjugated polymers as binders, we can add electrical conductivity to this list of properties, allowing for reduced resistive losses and faster charging. Here we demonstrate that dihexyl-substituted poly(3-4-propylenedioxy-thiophene) (PPrODOT-Hx_2) can serve as an ideal, easily synthesized conducting binder with good electronic conductivity. Its ionic conductivity can be further improved by make copolymer of PPrODOT-Hx_2 and a poly(3-4-propylenedioxy-thiophene) with oligoether sidechains. Ratios of Hex:OE up to 65:35 can function as battery binders, with the most stable cycling observed for the 75:25 copolymer. The oligoether sidechains increases the ionic conductivity, but decreases the electronic conductivity, a result that stems from a reduction in crystallinity in electrochemically doped copolymers with large EO fractions. Polymer elasticity can also be improved by the incorporation of conjugation break spacers, which are randomly spaced aliphatic segments copolymerized into the PPrODOT-Hx_2. Long spacers or higher spacer fraction results in pore binder performance, but shorter spacer length (6- or 8-carbons) at only 5% incorporation results in improved binder performance. Finally, we examine solvent swelling in these binders, which are in contact with electrolytic solvent. Swelling improves the ionic conductivity and decreases the electronic conductivity. Extra charges introduced by electrochemical doping during cycling leads

to potential dependent swelling increases. Using a range of polymers, swelling can be measured using an electrochemical quartz microbalance and correlated with polymer crystallinity.

II-S1-18: ADVANCES IN THE EFFECTS OF IONIZING RADIATION ON THE STABILITY AND REACTIVITY OF MOLTEN SALTS

[EFRC – MSEE] Alejandro Ramos-Ballesteros[1,2], Kazuhiro Iwamatsu[3], Santanu Roy[4], Ruchi Gakhar[1], Phillip Halstenberg[5], Michael E. Woods[1], Bobby Layne[3], Jay A. LaVerne[2] , Simon M. Pimblott,[1] James F. Wishart[3], and Gregory P. Holmbeck[1]
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AFFILIATED TALK – II-T1-5: Advances in the Effects of Ionizing Radiation on the Stability and Reactivity of Molten Salts

Molten salts are proposed as liquid fuels and coolants in a new fleet of nuclear reactors with operational and safety advantages over present reactor designs. Salt mixtures containing monovalent and divalent metal cations are of particular interest because of their tunable Lewis acidity-basicity that can be used to control the solubility of dissolved metal ions in the reactor. However, these salt mixtures will be exposed to intense, multi-component ionizing radiation fields within the reactor environment, leading to unanticipated changes in the physical and chemical properties of the system. Consequently, understanding the underlying chemical effects of radiolysis on the salt is essential for the reliable, efficient, and sustainable operation of molten salt reactors. Assembling this fundamental understanding necessitates the identification of initial and steady-state salt radiolysis products and characterizing their respective chemistries over multiple time and distance regimes. To this end, we have employed solid (gamma ray) and molten (electron pulse) salt irradiation techniques to isolate these species and interrogate their chemical behavior with a combination of electron paramagnetic resonance, diffuse reflectance, and integrated transient optical absorption spectroscopy techniques. Here we present our most recent findings on radiation-induced processes in complex salt mixtures, including: *(i)* the radiolytic reduction of uranium trichloride; *(ii)* the aggregation of nickel nanoparticles in irradiated lithium potassium-zinc chloride eutectic; and *(iii)* the influence of magnesium and potassium cation ratios on the transient behavior of the solvated electron in molten chloride mixtures.

II-S1-19: IMAGING PHOTOEXCITED STATES AT THE 1 NM SCALE

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Imaging photoexcited states at the nanometer scale offers fundamental insights about photoexcitation and recombination pathways, with potential applications that bridge the gap between electron-light interactions and electron-ion interactions. However, imaging photoexcited states at the 1 nm scale is non-trivial. Traditional optical imaging techniques are limited by the Abbe diffraction limit to around 0.5 µm for visible light. Optical super-resolution techniques can achieve ~10-50 nm scale resolution using a variety of approaches such as centroid localization of

stochastic emission, scanning using a near field evanescent optical source and so o. However, 1 nm scale imaging is not yet routine. In 2020 we demonstrated a novel photoexcited state imaging technique called PAMELA – PhotoAbsorption Microscopy using Electron Analysis, where optical excitation modulated secondary electron emission in an SEM. In those proof of principle experiments, we demonstrated ~10-20 nm spatial resolution photoexcited state imaging and identified that laser induced photovoltage was the mechanism that modulated secondary electron emission. Here we use a recently developed SE detector in a Nion HERMES STEM, which has recently demonstrated atomic (<0.2 nm) resolution. We have added laser illumination to this system and are able to focus the laser light onto a 20 x 40 µm spot on the sample. Using this system, we demonstrated ~1 nm resolution PAMELA imaging on Silicon nanoparticles. We expect PAMELA to lead to new insights about light matter interactions at the 1 nm scale.

II-S1-20: COMBINED IPAS AND IN-SITU TEM EFFORTS TO PROBE DEFECT EVOLUTION IN NUCLEAR MATERIALS

[EFRC – FUTURE] Thai Hang Chung[1], Riley C. Ferguson[1], Adric C. L. Jones[1], Matthew Chancey[2], Hyosim Kim[2], Angelica L. Morales[3], Djamel Kaoumi[3], Yongqiang Wang[2], Blas P. Uberuaga[2], Farida A. Selim[1]
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Fundamental Understanding of Transport Under Reactor Extremes (FUTURE) targets the gaps in knowledge regarding the mechanisms of coupled irradiation and corrosion. FUTURE has developed a multiscale research portfolio to achieve a comprehensive understanding of material response under these extremes on the experimental and modeling front. Amongst these developments is a novel experimental capability, *in situ* positron annihilation spectroscopy (*i*PAS). Coupled to an ion accelerator, *i*PAS is a probe that provides non-destructive depth- and time-resolved monitoring of ion induced atomic scale defects with a sensitivity of ~0.1 ppm. With this remarkable sensitivity, *i*PAS reveals the formation of non-equilibrium defects during irradiation and their impact on material heterogeneities as well as their evolution. Ultimately, *i*PAS will complement *in situ* Transmission Electron Microscopy (TEM), and Atom Probe Tomography (ATP) to identify critical transport processes. *i*PAS is used in conjunction with TEM which reveals larger defects unresolvable by PAS (and vice versa). The defect size as a function of dose/temperature from atomic clusters (resolved by PAS) to nm/um size (resolved by TEM) are needed to inform and benchmark cluster dynamics/phase field meso-scale models with the validation of all-inclusive experimental data across multiple scales. Here we show examples of *ex situ* PAS and *in situ* TEM results on interesting defect interactions in multiphase materials and discuss how *i*PAS may reveal the mechanisms behind them. Finally, an update on the *i*PAS development status including challenges emerged from magnetic field interference and buncher upgrades to produce sub-ns pulsed positron beam for lifetime spectroscopy are presented.

II-S1-21: ORDERING OF BICONTINUOUS MICROEMULSIONS ON HYDROPHILIC AND AMPHIPHILIC SUBSTRATES

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Recent developments in the study of microemulsions have shown that they can be utilized for electrochemical applications such as redox flow batteries. Insights into the structure and dynamics of these systems is needed to understand and direct their electrochemical behavior. While bulk solution measurements have provided insight, the surface layers' purity and thickness will influence the electrode accessibility of redox-active species and the ion transport required to satisfy the electroneutrality condition. Neutron reflectivity experiments using a series of deuterated water (D2O)/Tween-20/Toluene ME compositions on hydrophilic and amphiphilic surfaces provide the interface structure between an electrode and the bulk ME. The surface structures formed by these solutions demonstrate layered structures near the hard electrode surface. These lamellar-type layers transition from the surface to the bulk microemulsion as a series of mixed layers that contain oil, water, and surfactant consistent with a perforated lamellae structure. We employed molecular dynamics simulations to corroborate the neutron reflectivity findings further and used a common coarse-grained (CG) forcefield to explore its ability to reproduce microemulsion phase diagrams. To perform a quantitative comparison of the accuracy of the CG model, we compared energetics as a function of microemulsion composition obtained to a detailed all-atom simulation of systems with planar biphasic systems. Next, we investigated the effect of surface polarity on the layering of bicontinuous microemulsion components. The surface polarity and ME composition direct the ordering and purity at the surface and affect the final performance of an electrochemical device that utilizes MEs as the electrolyte.

II-S1-22: TWO-DIMENSIONAL INFRARED SPECTROSCOPY OF VIBRATIONAL PROBES AT THE ELECTROCHEMICAL INTERFACE

[EFRC – AMEWS] Melissa Bodine[1], Vepa Rozzyev[1,2], Alanna Felts[3], George C. Schatz[3], Jeffrey W. Elam[2], Andrei Tokmakoff[1], and Nicholas H. C. Lewis[1]
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A molecular understanding of the structure and fluctuations of the double layer in an active electrochemical cell is essential for the complete understanding of the physical and chemical processes that drive the reactivity and heterogeneous catalysis. So far, there are few experimental methods that allow us to probe the dynamics on the scale of molecular motions in this complex environment. Here we describe the development of a new approach for 2D IR spectroscopy of vibrational probes at the electrochemical interface which provides a route towards this goal. We have developed a layered electrode which is compatible with 2D IR spectroscopy and suitable for electrochemical measurements and have developed a simple model that explains the complex spectroscopy of molecular monolayers interacting with the plasmonic activity of the electrode, including the influence of the bias potential. We have also simulated this system to elucidate the structuring of the monolayer and the ions at a variety of conditions, which allow us to link the vibrational spectroscopy to the molecular details. This approach will allow us to study the structural dynamics and molecular interactions near the electrode in active electrochemical devices in new ways, to reveal how these properties impact performance and reactivity.

II-S1-23: MODELING MINERAL DISSOLUTION AND PRECIPITATION IN FRACTURED MEDIA ACROSS SCALES

[EFRC – GMCS] Jeffrey Hyman[1], Matthew Sweeney[1], Qinjun Kang[1], Min Liu[1], Bill Carey[1], Hari Viswanathan[1], Peter Kang[2], Vaughan Voller[2]
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Effectively modeling the interplay among fluid flow, solute transport, mineral dissolution, and precipitation in fractured media remains a primary challenge. To this end, we present two numerical modeling studies at different scales. In the first, we present a pore-scale study of coupled fluid flow, solute transport, and mineral dissolution/precipitation in 3D fractured carbonate rocks. The injected fluid can dissolve the carbonate and release carbonate ions into the solutions, which react with Ba2+ resulting in barium carbonates (BaCO3) precipitation. Simulations with a wide range of Pe and Da numbers are carried out to systematically study their effects on dissolution/precipitation patterns and on evolution of fracture geometry, porosity, and permeability. The results show that the coupled physicochemical process is strongly dependent on the Pe and Da. In the second study, we perform a set of reactive transport simulations in three-dimensional fracture networks to characterize the impact of geochemical weathering on flow channelization at the 10s of meter scale. The fractures are partially filled with quartz, which is gradually dissolved under steady flow until quasi steady-state conditions are obtained. We compare the initial unweathered and final weathered states of the flow field using flow and transport observations. We observe that the weathered fracture networks provide less resistance to flow and exhibit increased flow channelization. Future work will characterize the net effect of precipitation and dissolution to determine how much carbon mineralization can occur in complex 3D fracture networks under different flow and transport conditions.

II-S1-24: VERTICALLY ALIGNED NANOSTRUCTURES AND COMBINATORIAL THIN FILMS: MODEL PLATFORMS FOR STUDIES OF INTERFACIAL HYDROGENIC FLUXES

[EFRC – HEISs] Yong-Yun Hsiau[1], Alexia Popescu[1], Supriyo Majumder[2], Camille Layden[2], Zhi Li[2], Paul Chery[2], Patrick Donahue[2], Nicola H. Perry[1], Chris Wolverton[2], Michael J. Bedzyk[2], Sossina M. Haile[2]
[1]*University of Illinois at Urbana-Champaign;* [2]*Northwestern University*

Charge and mass transfer reactions at the gas-electrode and electrode-electrolyte interfaces often limit the overall performance of electrochemical devices. A fundamental understanding of the physical and chemical factors influencing transport kinetics of charged species across interfaces will guide future applications of these materials. Vertically Aligned Nanostructures (VANs) are uniquely suited to the study of charge transport across and along solid-gas and solid-solid interfaces, while compositionally-graded thin films allow for rapid evaluation of the kinetics of charge transfer at the gas-solid interface of many compositions. In this work, we report preliminary results on two VANs systems and a compositionally-graded film system: a protonic/mixed oxide-ionic and electronic $BaZr_{0.9}Y_{0.1}O_{3-\delta}/Pr_{0.1}Ce_{0.9}O_{2-\delta}$ VAN, a protonic/hydridic-electronic $BaZrO_3/SrTiO_3$ VAN, and protonic-to-triple-conducting compositionally-graded thin films of $BaZr_{0.9}Y_{0.1}O_{3-\delta}$ - $BaFe_{1-x}(Zn,Y)_xO_{3-\delta}$. The morphology, relative orientation of the phases, and epitaxy-induced strain are measured using transmission electron microscopy (TEM) and X-ray diffraction

(XRD) measurements. Chemically resolved, atomic-scale surface and interface structures are studied before, after, or during treatment employed to induce hydrogen incorporation, using techniques including crystal truncation rod (CTR) and X-ray standing wave (XSW) excited X-ray photoelectron spectroscopy (XPS) or X-ray fluorescence (XRF) measurements. The oxidation state of the composing elements is probed via XPS and X-ray absorption spectroscopy (XAS). In concert, these experiments set the stage for future studies of hydrogenic and/or electronic transport across solid-solid and gas-solid interfaces using techniques such as AC impedance spectroscopy, 2D optical transmission relaxation, and electrical conductivity relaxation measurements.

II-S1-25: BEYOND 3RD ORDER ANHARMONICITY

[EFRC – TETI] Chris Marianetti[1], Shuxiang Zhou[2], Chao Jiang[2], Hao Ma[3], Enda Xiao[1], Michael Manley[3], David Hurley[2]
[1]Columbia University, [2]Idaho National Laboratory, [3]Oak Ridge National Laboratory

AFFILIATED TALK – II-T1-3: Probing Higher Order Phonon Anharmonicity in Ceramic Nuclear Fuels under Temperature and Pressure Extremes

Phonons play a critical role in thermal transport in both insulating and metallic nuclear fuel materials. The de facto standard for computing phonon thermal transport involves solving the Boltzmann transport equation using scattering probabilities constructed from cubic phonon interactions and leading order perturbation theory. However, such a procedure will likely not be satisfactory at high temperatures where nuclear reactors operate. Therefore, we are enhancing phonon thermal transport calculations in several ways. First, both cubic and quartic phonon interactions are computed using our precise irreducible derivative methods. Second, we are executing self-consistent perturbation theory to construct scattering probabilities, whereby infinite classes of scattering events are summed, yielding a non-perturbative result. Third, we have included interband scattering processes which we have demonstrated to be quantitatively important at high temperatures. We applied our methodology to UO_2, a Mott insulator, which builds upon our previous work which demonstrated that DFT+U was able to produce both a qualitative and quantitative description of the ground state properties of UO_2. Our first-principles calculations provide an accurate description of experimentally measured thermal transport, and elucidate the role of nonpertubative effects. We also study nitride nuclear fuels, which are metals, where phonon thermal transport is less straightforward to experimentally isolate due the electronic thermal transport.

II-S1-26: INSIGHTS INTO THE STRUCTURE AND ION TRANSPORT PROPERTIES OF POLYMER AND HYBRID ELECTROLYTES USING NMR TOOLS

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[1]University of California, Santa Barbara; [2]University of Tennessee.

Polymer electrolytes are promising materials for solid-state batteries, flow batteries, fuel cells, and electrolyzers, and for many other energy relevant applications. The key challenge for the

development of next-generation polymer electrolytes is the lack of a microscopic (site-to-site hopping)-to-macroscale (bulk diffusion) understanding of the underlying mechanisms of ion transport, resulting in a dearth of materials design rules to improve their conductivity and ion selectivity. NMR is a powerful, element-specific tool with the ability to probe both the atomic level structure and the dynamics of a wide variety of material classes. When it comes to dynamics, pulsed-field gradient NMR (PFG NMR) and relaxometry (T1, T1ρ) have been found to provide insights into ion transport and ion-ion correlations. ^{19}F and ^{6}Li solid-state MAS NMR reveal local chemical structures in single-ion conducting, dual-ion-conducting, and polymer-ceramic composite electrolytes. Furthermore, variable temperature ^{7}Li PFG NMR exhibits differences in the Li-ion diffusions in hybrid electrolytes compared to pristine polymers and how temperature influences the diffusion phenomenon.

II-S1-27: A-SITE OCCUPANCY EFFECTS ON STRUCTURE, PHASE STABILITY AND IONIC CONDUCTIVITY OF $K_xMg_{x/2}Ti_{8-x/2}O_{16}$ HOLLANDITE MATERIALS

[EFRC – CHWM] Nakeshma Cassell[1], Nancy Birkner[1], Shraddha Jahdav[1], Amir Mofrad[4], Theodore Besmann[4], Jake W. Amoroso[3], Joseph Schaeperkoetter[4], Scott T. Misture[4] and Kyle S. Brinkman[1]
[1]Clemson University; [2]Savannah River National Laboratory; [3]Alfred University; [4]University of South Carolina

Titanate-based hollandite ceramics are of particular interest as fast ionic conductors and promising hosts for immobilization of radioactive cesium. The latter, owing to their remarkable radiation resistance, chemical durability and high thermodynamic stability, is the focus of the current work. $K_xMg_{x/2}Ti_{8-x/2}O_{16}$ ($1.24 \leq x \leq 2$) hollandite samples were synthesized using solid-state route and solgel method to investigate the effect of structure, ionic conductivity and thermodynamic stability as a function of A-site (K) occupancy. X-ray Diffraction (XRD) determined that the as-synthesized K-hollandite samples formed single phase tetragonal structure. The ionic conductivity, as measured using electrochemical impedance spectroscopy, decreases as the A-site becomes more occupied. Conversely, the stability increased with A-site occupancy. Titanate hollandite, of the form $K_xMg_{x/2}Ti_{8-x/2}O_{16}$ were measured using high-temperature oxide melt solution calorimetry. The enthalpies of formation are strongly exothermic indicating that they are thermodynamically stable relative to their constituent oxides. The thermodynamic results showed a trend of increasing stability as x changes in $K_xMg_{x/2}Ti_{8-x/2}O_{16}$. Previous studies have demonstrated increased stability as the Cs content increases and a similar trend was observed for the K-bearing hollandite samples. The measured enthalpies of formation ($\Delta H_{f,ox}$) were in good agreement with density functional theory (DFT) predictions. Understanding the correlation between structure, ionic conductivity and phase stability will lead to the design of new energy materials.

II-S1-28: ADVANCING MEMBRANE PERFORMANCE FOR WATER-ENERGY APPLICATIONS: CHARGED AND NEUTRAL SOLUTE TRANSPORT IN CONFINED AQUEOUS ENVIRONMENTS.

[EFRC – AMEWS] Joan Montes de Oca[1], Wen Chen[1,2], Feng Gao[2], Jamila Eatman[1,2], Juan J. de Pablo[1,2], Paul F. Nealey[1,2], Seth B. Darling[1,2]

[1]*University of Chicago;* [2]*Argonne National Laboratory*

Membrane separation performance in water-energy applications is often dictated by charge- and size-based mechanisms. We explore challenges induced by these mechanisms through combining precision membrane fabrication and molecular dynamics simulations. Mesoporous silicon nitride membranes (SiN_x) were fabricated with a narrow pore-size distribution and high pore density with pore wall properties tuned via atomic layer deposition. These membranes exhibit superior ion mobility compared to conventional ion-exchange membranes, accommodating complete ion hydration and fully developed electrical double layers. Our simulations reveal a novel transport mechanism in charged membranes that could alleviate concentration polarization. This process, termed "electrostatic funneling," is initiated when a concentration disparity arises between the membrane's internal environment and the external solution. This disparity triggers an electrostatically guided ion movement to preserve the membrane's internal charge density. The extent of this funnel can influence both the membrane's and the electrolyte's resistance. These SiN_x membranes can also serve as an isoporous membrane platform to precisely control neutral solute transport. We introduce a "number of attempts" as the average number of times a feeding solute encounters pores of a membrane during a filtration process. This principle, not explicitly considered in the literature, influences neutral solute transport significantly as small solutes may eventually permeate through the membrane with sufficient attempts. In the case of an isoporous membrane, the large number of attempts could sharpen a typical "S-shape" rejection curve, bringing it closer to an idealized "step-function" rejection curve.

II-S1-29: ISOPOROUS TETRABLOCK POLYMER MEMBRANES: SYNTHESIS AND FABRICATION OF STRONG, TOUGH ULTRAFILTRATION MEMBRANES

[EFRC – M-WET] Noah Wamble[1], Adam Mann[1], Benjamin Pedretti[1], Louise Kuehster[1], Mostafa Nassr[1], Matthew Landsman[2], Christian de la Fuente[1], Gregory Su[2], Gabriel Sanoja[1], Nathaniel Lynd[1], Benny Freeman[1], Glenn H. Frederickson[3]
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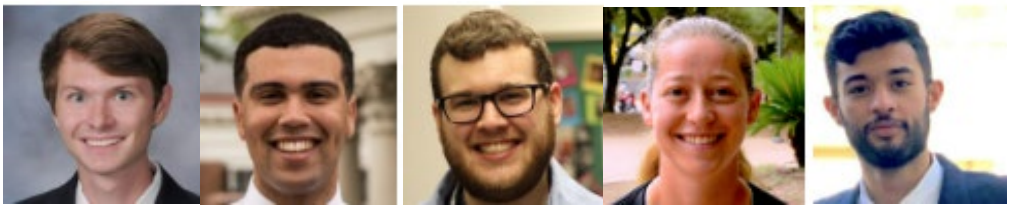
Precise ultrafiltration separations require membranes with controlled pore size distributions. Self-assembly and nonsolvent induced phase separation (SNIPS) can produce membranes with unparalleled separation performance, but they are typically mechanically weak due to the poorly entangled polystyrene used as the matrix block of these membranes. Additionally, SNIPS is a complex, highly nonequilibrium process that is poorly understood fundamentally, which limits its use in transformational manufacturing of membranes. This project combines synthesis, characterization, and simulations to better understand the basic science of SNIPS. Mechanically robust, isoporous membranes were cast from solutions of polystyrene-b-poly(isoprene)-b-polystyrene-b-poly(4-vinylpyridine) (SISV) tetrablock polymers. Small angle X-ray scattering (SAXS) was used to evaluate solution self-assembly of the tetrablock polymers, and SNIPS was used to prepare isoporous membranes. A tough membrane matrix is formed via an additional mechanism of energy dissipation through rubber toughening resulting from the rubbery poly(isoprene) block between the glassy polystyrene blocks. The work to fracture under uniaxial elongation until failure

is two orders of magnitude higher for SISV relative to polystyrene-b-poly(4-vinylpyridine) (SV) deblock copolymers, 708 and 2.6 kJ/m^3, respectively. The fracture strength of SISV is an order of magnitude larger than that of SV. Liquid water permeation experiments of SISV conducted up to 4.0 bar of transmembrane pressure yielded water fluxes with a steady state permeance of up to ca. 2200 LMH/bar, nearly six times those of track etched membranes of similar pore size.



(from left) Noah Wamble, Adam Mann, Benjamin Pedretti, Louise Kuehster, and Mostafa Nassr

II-S1-30: FABRICATION OF LARGE-SCALE, MECHANICALLY ROBUST LOW-DENSITY SILICA SOLIDS WITH A CONTINUOUS MESOPOROUS FRAMEWORK

[EFRC – MUSE] Ahmed Elnashar[1], Will Nguyen[1], Lianbo Hu[1], Jinfeng Zhao[2], Subhash H. Risbud[2], John McLennan[1], Milind D. Deo[1], Michael H. Bartl[1]
[1]University of Utah; [2]University of California at Davis

A novel supramolecular assembly-based multi-step technique is presented for the fabrication of a large-scale and mechanically robust silica material with a continuous mesoporous structure. In contrast to previously developed mesoporous solids and monoliths, the material presented here consists of an ordered mesoporous framework without the presence of unwanted macroporous networks or cracks. The newly developed process involves three main steps: 1) Synthesis of a mesostructured silica powder with a SBA-16 type ordered framework using typical supramolecular assembly methods. 2) Consolidation of the powder into an inch-sized robust pellet using spark plasma sintering (SPS). 3) Transformation of the unwanted macroporous network formed during the consolidation process into an ordered mesoporous structure. The last step was done by repeated infiltration of the macropores with a silica sol containing structure-directing polymers, which assemble into the same SBA-16 type cubic mesostructured phase present in the original silica powder. The resulting material is characterized using various techniques, including pore and surface analysis methods, electron microscopy, X-ray scattering, and a range of mechanical tests. The combined characterization methods revealed a highly permeable silica solid with a surface area exceeding 270 m^2/g from a predominantly cubic mesoporous network and a low degree of macropore inclusions. Despite having a low density of only ~1 g/cm^3, the fabricated pellets exhibit robust mechanical properties comparable to sandstone rocks. This novel material opens new avenues for studying flow and thermodynamic properties in nanoconfinement, and offers new possibilities for sorption, catalysis, and separation applications.

II-S1-31: IMPROVEMENT OF ATOMISTIC MODELING FOR CONFINED FLUID PROPERTIES: TRANSLATING FROM THE STATISTICAL TO CONTINUUM SCALE

[EFRC – MUSE] Seyed M. Hatamlee[1], Brennon L. Shanks[2], Michael P. Hoepfner[2], Jiaoyan Li[1]
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AFFILIATED TALK – II-T1-7: Experimentally-Informed State Dependent Atomic Forces in Real Fluid Ensembles

Predictive multiscale modeling and molecular thermodynamic theories are critical to provide needed insight into confined fluid properties due to a lack of available and consistent experimental data. However, several knowledge gaps exist in the development of such predictive models. Firstly, atomistic simulations have demonstrated poor representation of local fluid structure and are predominantly benchmarked to available macro-fluid properties (e.g., density). Secondly, atomistic simulations are time-consuming and efficient equations of state approaches are desired. In this poster, we first present a novel solution to the century-old "inverse problem" where experimental neutron diffraction measurements are used to extract accurate pair potentials to improve the prediction of local atomic forces and properties. We demonstrate by analyzing experimental diffraction results that the forces between atoms in krypton fluids varies as a function of state and are less attractive and more deformable as the temperature increases. These measurements enable potentially transformative new applications of neutron scattering to improve molecular modeling directly and provide a novel pathway to assess local atomic forces in real fluid ensembles. We then discuss a representative investigation to explore the translation of atomic simulations to equation of state modeling for binary mixtures of methane-heptane and CO2-heptane using Monte Carlo simulations. The results reveal a decrease in the critical points of the mixtures and enable optimization of equation of state approaches. Coupled together, these studies highlight the need for additional and fundamental development of accurate pair potentials and approaches and simulation methods to reliably predict fluid properties and phase behavior in confinement.

II-S1-32: THEORY AND EXPERIMENTS ON MICRO-POROELASTIC MODELS OF MAFIC AND ULTRAMAFIC ROCKS

[EFRC – GMCS] Yifan Yang[1], Dawei Xue[1], Giuseppe Buscarnera[1], Pouyan Asem[2], Emmanuel Detournay[2], Joseph Labuz[2]
[1]Northwestern University; [2]University of Minnesota

This collaborative work involves the development of micro-poroelastic constitutive laws aimed at capturing hydro- chemo-mechanical induced deformation of mafic and ultramafic rocks that are of interest to CO2 storage via mineralization. Two constitutive laws based on different homogenization schemes, Hashin-Shtrikman and Mori-Tanaka, are presented. The goal is to describe mineralization-induced deformation resulting from interactions between matrix and secondary carbonate minerals while accounting for the effect of (i) microcrack and pore characteristics, and (ii) stiffness, morphology, and volume of the carbonate minerals forming within them. First, the models are evaluated using benchmark hydromechanical tests on Westerly blue granite, a low porosity crystalline rock. Second, our hydromechanical test results using nonpolar pore fluid on an ultramafic rock (serpentinized Oman harzburgite) are used to evaluate

the accuracy with which each poromechanical model captures the dependence of the bulk modulus on aspect ratio of equant and microcrack-like features.

II-S1-33: BOEHMITE SURFACE CHEMISTRY EXPLAINS SOLUTION CHEMISTRY-DEPENDENT MODES OF AGGREGATION

[EFRC – IDREAM] Lili Liu[1], Tingting Liu[2], Elias Nakouzi[1], Benjamin A. Legg[1], William Smith [1,3], Xin Zhang[1], Aurora E. Clark[4,1], Gregory K. Schenter[1], James J. De Yoreo[1,5], Jaehun Chun[1], Andrew G. Stack[2]
[1]Pacific Northwest National Laboratory; [2]Oak Ridge National Laboratory; [3]Washington State University; [4]University of Utah; [5]University of Washington

The ability to predict nanoparticle aggregation and attachment requires a rigorous understanding of the interplay between crystal structure, particle size, surface chemistry, solution composition and interparticle forces. Here, we used an integrated suite of experimental, theoretical and simulation methods to examine the effect of pH and salt solution on the aggregation of boehmite nanoplatelets, a system relevant to legacy nuclear waste processing. Liquid-phase transmission electron microscopy (LPTEM) data and particle-scale calculations show that surface protonation produces heterogeneous surface charges, leading to facet-dependent aggregation behavior. The LPTEM results also demonstrate that increasing salt concentrations produce more strongly bound aggregates in both sodium nitrate ($NaNO_3$) and potassium nitrate (KNO_3) suspensions, as well as ion specific effects, with more "stable" aggregates present in $NaNO_3$. Classical molecular dynamics simulations informed a mechanistic understanding of the effect of salt on particle aggregation; the addition of salt reduces the energy barriers for particle aggregation by disrupting the bonding network of water in the interlayer. We also found a mode of crystal-face specific aggregation that is independent of surface charge, through which aggregation by basal–basal surface attachment is more favorable than aggregation by edge–edge attachment. These results demonstrate that mineral-water interfacial chemistry, especially for interacting nanoparticles, plays a critical role in determining the extent and anisotropic nature of aggregation. This molecular-based understanding of aggregation processes will improve our predictive capability for processing legacy radioactive waste and for other applications, such as controlled synthesis of materials via particle assembly.

II-S1-34: EFFECT OF IRON AND CHROMIUM DOPANTS ON RADIATION-INDUCED PROCESSES IN GIBBSITE

[EFRC – IDREAM] Hanna Hlushko[1], Alejandro Ramos-Ballesteros[1], Yatong Zhao[2], Micah P. Prange[2], Xin Zhang[2], Brant M. Jones[3], Thomas M. Orlando[3], Kevin M. Rosso[3], Carolyn I. Pearce[3,4], Jay A. LaVerne[1]
[1]University of Notre Dame; [2]Pacific Northwest National Laboratory; [3]Georgia Institute of Technology; [4]Washington State University

Aluminum, one of the main metal ions in legacy radioactive waste, is present as oxyhydroxide solid phases, including gibbsite ($Al(OH)_3$). Under ionizing radiation in these highly alkaline environments, gibbsite platelets experience radiolysis inducing subsequent redox reactions between components of the waste. Cations, like iron (Fe(III)) and chromium (Cr(III)), also present in the waste, can be incorporated into gibbsite platelets, influencing their radiolytic behavior and

dissolution. This work focuses on incorporating Fe(III) and Cr(III) ions into gibbsite, and exploring the effect of dopants on radiolytic behavior under gamma radiation. The gibbsite was synthesized using a hydrothermal method, and 0.5% or 5% of Fe(III) and Cr(III) were incorporated at the stage of crystallization. The crystalline structure and composition of synthesized materials were characterized with X-ray diffraction, X-ray photoelectron spectroscopy, and extended X-ray absorption fine structure spectroscopy. Samples were then irradiated with cobalt-60 gamma irradiation up to 20 kGy. Stable radical formation was detected with electronic paramagnetic resonance (EPR). The molecular products of radiolysis, induced by electron beams with different electron energies, were analyzed with in situ mass spectrometry. EPR spectra revealed oxygen paramagnetic centers growing in the gibbsite with an increase in radiation dose. The presence of metal ions incorporated in gibbsite nanoplatelets suppressed the formation of oxygen paramagnetic centers. Simultaneously, reduction of Cr(III) to Cr(II), as well as Fe(III) to Fe(II) was observed in diffuse reflectance UV-vis spectra and changes in EPR signal. Higher concentrations of Fe(III) in the sample were required to reach similar scavenging as with Cr(III).

II-S1-35: REDUCING THE ENERGY BARRIER FOR PROTON TRANSPORT IN POLYMERS UNDER ANHYDROUS CONDITIONS

[EFRC – FaCT] Amit Bhattacharya[1], Michelle L. Lehmann[2], Zitan Huang[3], Harrison Cassady[3], Tomonori Saito[2], Raphaële Clément[1], Ralph Colby[3], Michael A. Hickner[4], Alp Kurbay[5], Valentino Cooper[2]
[1]University of California, Santa Barbara; [2]Oak Ridge National Laboratory; [3]Penn State University; [4]Michigan State University; [5]University of Illinois, Urbana-Champaign.

AFFILIATED TALK – II-T1-8: Reducing the energy barrier for proton transport in polymers under anhydrous conditions

Proton exchange membrane fuel cells are a promising technology that would enable our vehicles to be powered by a clean renewable energy source. For efficient performance, these fuel cells need to operate under anhydrous conditions, however this significantly reduces proton mobility. Our goal is to understand the underlying mechanisms and molecular interactions that facilitate proton hopping transport in anhydrous systems through a combined experimental and computational approach. We have developed a Python script to search molecular databases for potential proton-hopping molecules. We have also compiled our own database of proton conducting polymers in non-aqueous systems. The results of this, along with new compounds created using the cheminformatics package RDKit are used to perform DFT analysis. The results of this will be fed into a machine learning system for identification of targets for synthesis and experimental testing.

Concurrently, we have evaluated the ionic conductivity and other dielectric properties of pure azole molecules and azole-phosphonic acid mixtures using broadband dielectric spectroscopy (BDS). The measurements show that pure azole molecules have a high conductivity after melting, and that their conductivity, dielectric properties, and viscosity are all similar in the melt state. Then the conductivity for several azole-phosphonic acid mixtures were investigated using BDS. The azole-phosphonic acid mixtures exhibited a much higher conductivity than that of the pure azole molecules due to the additional proton provided by the acid. The mixtures show conductivity values in the range of 100 mS/cm.

II-S1-36: WHY DOES DISSOLVING SALT IN WATER DECREASE ITS DIELECTRIC PERMITTIVITY

[CCS – CSI] Chunyi Zhang[1,2], Shuwen Yue[1], Athanassios Z. Panagiotopoulos[1], Michael L. Klein[2], Xifan Wu[2]
[1]*Temple University;* [2]*Princeton University*

AFFILIATED TALK – II-T1-2: Why does dissolving salt in water decrease its dielectric permittivity

The static dielectric permittivity of sodium chloride solution decreases as more salt is dissolved. This phenomenon is referred to as dielectric decrement. For nearly one century, this phenomenon has been widely explained by dielectric saturation theory, which invokes saturation in the dielectric response of the individual solvent water molecules. However, the dielectric saturation theory lacks the collective dipolar response picture of water. Moreover, the local electric field induced by ions should be calculated using quantum mechanics instead of a classical description. In this work, we elucidated the microscopic origin of dielectric decrement in salt water at the level of quantum mechanics by employing state-of-the-art neural network methods and density functional theory. Our simulated dielectric permittivity as a function of solute concentration agrees well with the experimental results. The present results unambiguously determine that the dielectric decrement should mostly be attributed to the suppressed dipolar correlation among solvent water molecules as the solute concentration increases. Specifically, around the solvated ions, the tetrahedral H-bond structure is replaced by approximately spherical hydration shells. The intrusion of these hydration shells interrupts the H-bond-induced correlations among the molecular dipoles, resulting in the observed dielectric decrement.

II-S1-37: COUPLED PHASE BEHAVIOR AND TRANSPORT IN COMPLEX CONFINED NANOPOROUS NETWORKS

[EFRC – CMC-UF] Lingfu Liu[1], Saman Aryana[1]
[1]*University of Wyoming*

AFFILIATED TALK – II-T1-1: Coupled Phase Behavior and Transport in Complex Confined Nanoporous Networks

Confinement has a profound impact on the phase behavior, flow, and transport of gases due to copious interactions between the gas molecules and those of the confining solid. Shale systems are an example of a natural environment with an abundance of nanoconfined features interspersed with much larger features in complex geometric configurations that make classical homogenization techniques ineffective. This poster reviews our work as part of the CMC-UF on the intricate micro and meso-scales physics, including our contributions to computational tools bridging these scales to gain insight into macro-scale and system-level behavior in shale and tight subsurface formations. We will discuss using fluidic systems to investigate flow behavior in complex pore networks, the limitations of these systems due to the need to incorporate nano-sized features, and our developed numerical infrastructure as an alternative to lab experiments. Our numerical experiments utilize finely tuned, optimized implementations of the lattice-Boltzmann (LB) method, coupled with intermolecular force representations, capturing phase behavior and adsorption under confinement. Once tuned against molecular simulation data, LB implementations simulate the impact of confinement, adsorption, and complex geometries on gas

storage and flow in complex confined pore networks. Our ongoing work involves exploring artificial intelligence to scale up the computational domains we can simulate, aiming to reach sizes akin to macroscale Representative Elementary Volumes.

II-S1-38: PHASE FIELD-VOLUMETRIC LATTICE BOLTZMANN MODEL OF ION UPTAKE IN POROUS NUCLEAR WASTE FORM MATERIALS UNDER CONTINUOUS FLOW

Zirui Mao[1], Xiaoyu Zhang[2], Yulan Li[1], Vanessa Proust[4], Alban Gossard[4], Thomas David[5], Robert Montgomery[1], Agnes Grandjean[4], Huidan Yu[2], Hans-Conrad zur Loye[3], and Shenyang Hu[1]
[1]Pacific Northwest National Laboratory; [2]Indiana University-Purdue University Indianapolis; [3]University of South Carolina; [4]CEA, DES, ISEC, DMR; [5]Univ. Grenoble Alpes, CEA, LITEN, DTNM

In the continuous flow experiments and engineering applications of porous nuclear waste form materials, the flow field within the mesopores of sorbent particles plays a crucial role in radionuclide diffusion and ion uptake kinetics, thus impacting the overall performance of the waste form material. This study employs the volumetric lattice Boltzmann method (VLBM) to accurately and efficiently calculate the steady velocity field inside the pores. The obtained velocity field is then utilized to calculate the convection of ions in the steady flow. Also, a phase field (PF) model of ion uptake is used to describe the ion diffusion and the interface reaction occurring at the solid-liquid interface. The integrated PF-VLBM model was applied to study the influence of thermodynamic and kinetic properties, as well as flow field conditions and pore structures, on ion uptake kinetics. The results indicate three distinct stages in the ion uptake kinetics of porous materials. In the first stage, the kinetics are predominantly controlled by the flow field and ion diffusivity in the liquid phase. In the second stage the kinetics are primarily governed by ion diffusivity in the solid phase. In the third stage the system researches a dynamic equilibrium without net uptake at the interface. It is also found that porous structures significantly affect the efficiency of ion uptake. The simulation results can help to understand the physics behind the observed ion uptake kinetics in experiments and to facilitate the development of constitutive equations that can account for heterogeneous microstructures in engineering performance codes.

II-S1-39: THE INFLUENCE OF LITHIUM ALLOYS AND COMPOUNDS ON NUCLEATION AND GROWTH OF LITHIUM AT SOLID-STATE ELECTROLYTE INTERFACES: SAKAMOTO, MCDOWELL, MITLIN, MUKHERJEE

[EFRC – MUSIC]: Stephanie Sandoval[1], Catherine Haslam[2], Bairav Vishnugopi[3], Jeff Sakamoto[2], David Mitlin[4], Partha Mukherjee[3], Matthew McDowell[1]
[1]Georgia Institute of Technology; [2]University of Michigan; [3]Purdue University; [4]University of Texas, Austin
AFFILIATED TALK – II-T1-10: Mechanochemical Phenomena at the Alkali Metal/Solid Electrolyte Interface

"Anode-free" or zero-lithium-excess solid-state batteries feature high energy density since there is no active material at the anode upon assembly. While beneficial effects of interfacial layers at the anode-solid electrolyte interface have been demonstrated, the mechanisms through which they influence lithium plating/stripping are unclear. The MUSIC team has undertaken a coordinated effort to understand the influence of lithium alloys and compounds present at solid-

state electrochemical interfaces on lithium growth and stripping mechanisms. Thin (100 nm) silver and gold layers at Li_6PS_5Cl/lithium interfaces are shown to improve Coulombic efficiency and resistance to short circuiting, even though FIB-SEM imaging and synchrotron X-ray tomography shows that the alloys form solute regions or particulates that detach from the current collector during plating. *In situ* electrochemical impedance spectroscopy reveals that the alloys return to the interface and mitigate contact loss at the end of stripping, avoiding a critical vulnerability of anode-free cells. Gold clusters in contact with $Li_7La_3Zr_2O_{12}$ are further shown to reduce nucleation overpotential and enhance uniformity of lithium growth during plating, while also enabling low-impedance initial contacts to be formed. Li_2Te is also demonstrated to promote nucleation and uniform growth due to its preferential wetting behavior with lithium. Continuum modeling shows that i) alloys can be lithiated/delithiated in response to local overpotentials due to current constrictions, and ii) that interfacial wetting behavior can determine morphological evolution. The teams are further working together to understand how the competition between the electrochemistry of alloy layers and lithium itself determines interfacial evolution. Overall, this work has advanced our understanding of electrochemical nucleation, growth, and dissolution at solid-state electrochemical interfaces.

II-S1-40: STATUS OF ICE III R&D FOR SIMULTANEOUS IRRADIATION-CORROSION RESEARCH

[EFRC – FUTURE] Franziska Schmidt[1,2], Hyosim Kim[1], Matthew Chancey[1], S. Scott Parker[1], Peter Hosemann[2], Yongqiang Wang[1], Bethany E. Matthews[3], Djamel Kaoumi[4], Daniel K. Schreiber[3], Nan Li[1], Benjamin K. Derby[2], Kayla H. Yano[3]
[1]Los Alamos National Laboratory; [2]University of California Berkeley; [3]Pacific Northwest National Laboratory; [4]North Carolina State University

Corrosive nuclear environments present unique demands on material performance where structural alloys must be resistant to simultaneous corrosion and radiation damage. Novel Gen-IV nuclear reactor coolants and their inherent higher operating temperatures present a host of new scientific questions that cannot be fully addressed by sequential pre-irradiation and subsequent corrosion experiments. As part of the FUTURE EFRC, we are tackling this issue with the Irradiation and Corrosion Experiment (ICE). In this poster we will present progress made in the design and performance of ICE III to study the combined effects of irradiation and corrosion in model oxide-forming (heavy liquid metals) and dissolution dominant (molten salt) environments. Recent progress for integrating in-situ sample monitoring with X-ray emission spectroscopy (PIXE) will be highlighted. We will also discuss various experimental challenges that have had to be overcome with our designs for heavy liquid metal and molten salt environments, highlighting the environment-specific design similarities and differences. Ex situ and in situ results for the corrosion behavior of bulk samples under irradiation in ICE III will be shown in the context of small-scale irradiation-corrosion results as well as results considering the effects of radiation and corrosion separately produced across the EFRC.

II-S1-41: NUCLEATION OF ALUMINUM HYDROXIDE POLYMORPHS FROM ALKALINE SODIUM ALUMINATE SOLUTIONS

[EFRC – IDREAM] Hsiu-Wen Wang[1], Emily T. Nienhuis[2], Maxime Pouvreau[2], Trent R. Graham[2] , Jacob G. Reynolds[3], Lili Liu[2], Xiaoxu Li[2], Gregory K. Schenter[2], Aurora E. Clark[4,2], Kevin M. Rosso[2], Carolyn I. Pearce[2,5]

[1]Oak Ridge National Laboratory; [2]Pacific Northwest National Laboratory; [3]Washington River Protection Solutions, LLC; [4]University of Utah; [5]Washington State University

AFFILIATED TALK – II-T1-9: New Reactive Force Fields Explore Molecular Reactivity in Concentrated Electrolytes

A processes-based framework for molecular-scale understanding of speciation and reactivity during homogeneous nucleation and crystal growth is needed to predict structural chemistry and solubility of metal hydroxides and related minerals. This is relevant to processing of radioactive wastes, stored at Department of Energy legacy nuclear sites, that contain large quantities of aluminum in solution and in solid aluminum (oxy)hydroxide phases, along with molar concentrations of sodium hydroxide, nitrate, and nitrite. Here, we unravel the crystallization pathways of protonated and deuterated aluminum hydroxide ($Al(OH)_3$) polymorphs in metastable alkaline sodium aluminate solutions using: (i) neutron total scattering and cryogenic transmission electron microscopy for in situ analysis of phenomena associated with homogeneous nucleation; and (ii) ex-situ characterization of the precipitates using ^{27}Al magic angle spinning nuclear magnetic resonance spectroscopy, Raman spectroscopy, X-ray diffraction, and scanning electron microscopy. We hypothesize that nucleation of aluminum hydroxide/deuteroxide proceeds through transformation of an initially formed amorphous precursor phase, and via a structurally precise single-layer aluminum hydroxide prenucleation species. The single layer nanosheets ultimately stack to form aluminum hydroxide/deuteroxide comprised of gibbsite and bayerite. We developed an efficient reactive force field to predict nucleation and growth mechanisms during crystallization and identify favorable reaction pathways. The integration of experimental measurements and molecular dynamics simulations is facilitating this mechanistic understanding of nucleation and growth of both amorphous and crystalline phases. Based on this, we can develop predictive models for particle-based pathways of crystallization applicable to radioactive waste processing, carbon dioxide sequestration, electrical energy storage, and solar energy capture.

II-S1-42: ELUCIDATION OF NON-CRYSTALLINE PHASES CRITICAL TO ELECTROCHEMICAL FUNCTION OF MONO AND BI-METALLIC MANGANESE BASED CATHODES IN ZINC-ION BATTERIES

[EFRC – *m2m#s*] Jason Kuang[1], Steven (Tyler) King[1], Daren Wu[1], Zachary R. Mansley[2], Lisa M. Housel[1,2], Nahian Sadique[1], Lu Ma[2], Steven N. Ehrlich[2], Hui Zhong[2], David C. Bock[2], Esther S. Takeuchi[1], Amy C. Marschilok[1], Yimei Zhu[2], Shan Yan[2], Lei Wang[2], Kenneth J. Takeuchi[1,2]

[1]Stony Brook University; [2]Brookhaven National Laboratory

Large-scale battery systems should be safe, low cost, reliable and sustainable. Aqueous secondary aqueous zinc-ion batteries are promising candidates, however the complexity of the chemistry results in conflicting reports of operation principles, making rational improvements challenging. In contrast to rocking chair lithium-ion batteries which are dominated by insertion with retention of the host framework, the cathode evolution upon aqueous zinc battery cathode (dis)charge

often involves multiple changes of phase and state. In this presentation, investigations coupling operando synchrotron X-ray diffraction (XRD) and X-ray absorption spectroscopy (XAS) with complementary electron microscopy and Raman spectroscopy to lend mechanistic insight will be described, including elucidation of non-crystalline phases critical to electrochemical function of mono and bi-metallic manganese based cathode materials.

II-S1-43: STRUCTURAL EVOLUTION OF MANGANESE OXIDES IN NON-AQUEOUS LITHIUM AND AQUEOUS ZINC BATTERIES: ATOMIC LEVEL INSIGHT VIA ELECTRON MICROSCOPY AND DENSITY FUNCTIONAL THEORY

[EFRC – *m2m#s*] Thanh Le[1], Zachary Mansley[1], Sung Yoo Kim[1], Lijun Wu[1], Shi-Ze Yang[1], Killian Tallman[2], Alexander B. Brady[2], Shan Yan[1], Daren Wu[2], Lisa M. Housel[1], Jianping Huang[2], Lei Wang[1], Xiaobing Hu[1], Sooyeon Hwang[1], Jessica L. Durham[2], Feng Xu[1], Xiao Tong[1], Eric Dooryhee[1], Esther S. Takeuchi[1,2], Lei Wang[1], Kenneth Takeuchi[1,2], Amy Marschilok[1,2], Ping Liu[1], Yimei Zhu[1]
[1]Brookhaven National Laboratory; Stony Brook University[2]

Manganese oxides have a rich structural diversity and are conceptually appealing as battery cathode materials due to their low cost, environmentally abundant, and nontoxic nature. Despite their promising electrochemistry, their reaction mechanisms have remained elusive. In non-aqueous lithium based batteries, Jahn-Teller effects at the manganese(III) center can induce local distortions which manifest in significant structural rearrangements, making both insertion and conversion based redox possible. Aqueous zinc-based batteries present additional challenges for atomistic characterization and theory, with multiple ions available as participants for insertion (proton and zinc) and an additional redox pathway beyond insertion and conversion (dissolution/deposition). In this presentation, we describe progress toward understanding the structural evolution of manganese oxide cathodes via transmission electron microscopy and density functional theory, including comparisons and contrasts of behavior in non-aqueous lithium and aqueous zinc battery systems.

II-S1-44: ROLE OF SOFT MATERIALS IN THE ELECTROCHEMISTRY OF METAL OXIDE COMPOSITE NEGATIVE ELECTRODES IN LITHIUM AND SODIUM BASED BATTERIES

[EFRC – *m2m#s*] Miguel A. Gonzalez[1], Godze Barim[2], Donghee Gueon[1], Judith Alvarado[2], Eongyu Yi[2], W. Henry Freer[5], Meng Wang[1], Calvin Quilty[3], Seunghyun Jeon[5], Thomas Fuller[5], Kenneth J. Takeuchi[3,4], Esther S. Takeuchi[3,4], Amy C. Marschilok[3,4], Marca M. Doeff[2], Elsa Reichmanis[1].
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The electrochemistry of batteries is impacted by electrode composition and structure, where chemistry and engineering of soft materials can have significant impacts. The role of a polymeric binder is to create chemomechanical stability over two length scales: (1) the particle scale to modulate the impact of local volume change by creating an adhesive layer at the particle surface and (2) the mesoscale to provide structural stability among the composite electrode components during cycling. For example, binders with high carboxylic acid and/or hydroxyl content can induce favorable adhesive interactions via hydrogen, covalent, and/or van der Waals bonding to the

native surface layer of the active material surface. The systems can be further tuned through design of multicomponent binders using constituents with differing properties. Specific chemical functionality with interaction to the redox active material surface can be beneficial in maintaining electrode integrity to accommodate the inherent volume changes associated with electrochemical activity during (de)lithiation and (de)sodiation, as we will highlight in this presentation.

II-S1-45: EXPLORING STRUCTURE-PROPERTY RELATIONSHIPS IN HETEROGENEOUS POROUS MATERIALS THROUGH EXPERIMENTAL AND NUMERICAL METHODS

[EFRC-MUSE] Seo Young Ahn[1], Abdullah Arafat[1], Rahul Reddy Kancharla[2], Adri Van Duinn[3], Robert Wheeler[4], Valerio Pascucci[5], Pania Newell[1]
[1]University of Utah; [2]Idaho National Laboratory; [3]Pennsylvania State University; [4]Air Force Research Lab; [5]University of Utah

Heterogeneous porous materials with irregular pore shapes play a significant role within the natural world, exerting a profound impact on diverse processes and phenomena, including the mechanical responses of various systems. In this poster, we introduce pioneering insights, encompassing: (I) innovative *4D* micro-pillar compression test, (II) design of novel micro-architected porous materials followed by *in-situ* pico-indentation, and (III) molecular dynamic (MD) simulations of amorphous porous silica containing irregular pore shapes. The overarching goal of these studies is to systematically discover the intricate structure-property relationships in heterogeneous porous materials. For the first study, specimens with diameters around 35 microns were prepared via focused ion beam (FIB) milling. These specimens underwent quasi-static loading on a holding stage, with machine learning tools aiding in reconstruction and advanced visualization tools facilitating volumetric evolution analysis along the stress-strain curve. For the second study, we used nanoscribe to create three categories of micro-architected samples: idealistic, semi-realistic, and realistic, where we controlled porosity, pore shape, and pore location. Then through the use of *in-situ* pico-indenter within Scanning Electron Microscopy (SEM), we investigated the role of pore morphology on the overall elastic response of each sample. Our findings indicated that while resolving pore morphology is vital, simplification of complex systems may still yield accurate results in the elastic region. Furthermore, we showed that macroscopic theory can be applied to micro-porous structures. In the last study, we investigated the atomistic response of amorphous silica by creating simulation boxes with different irregular pore shapes subject to uniaxial tension test using MD simulation. Our results highlighted the correlation between modulus and fracture energy release rate with the pore shape index. These findings provide valuable insights into how realistic porous materials behave under mechanical loading and can inform the design of stronger, more durable, and more efficient materials and structures for various applications.

Poster Session 2

II-S2-01: UNDERSTANDING THE STRUCTURE AND STABILITY OF MOLECULAR COMPLEXES IMMOBILIZED ON CONDUCTING METAL OXIDE SUBSTRATES FOR ELECTROCATALYTIC WATER REMEDIATION

[EFRC – AMEWS] Karen Mulfort,[1] Carolyn Williams,[1] Bidushi Sarkar,[1] H. Atallah,[1] Jacob Kupferberg,[1] Paul Fenter,[1] Pietro Papa Lopes,[1] Alex B.F. Martinson[1]
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Our team seeks to develop stable and selective electrocatalyst materials for water remediation, and electrode-immobilized molecular catalysts present a versatile platform to understand electrocatalytic activity, selectivity, and mechanisms by synthetically tailoring the active site structure, outer coordination sphere, and surface anchoring group. However, there is a knowledge gap regarding the stability of electrode-immobilized molecular complexes, particularly with respect to the kinetics and mechanism of degradation or desorption from the surface. In this work we have synthesized two prototype molecular complexes with carboxylic acid and phosphonic acid groups that enable metal oxide substrate immobilization. Synchrotron X-ray reflectivity measurements of molecularly-modified TiO_2 and Al_2O_3 substrates show that the interfacial structure is nearly identical for the two different anchoring groups, although the experimentally obtained molecular film thickness is nearly twice that expected from a uniform monolayer, suggesting that the initially adsorbed complexes form bilayers or other aggregates. In situ ICP analysis was used to measure the temporal evolution of dissolved metals in solution in contact with the TiO_2 substrates as a function of solution pH to quantify the desorption rate of the metal center. We observe that the phosphonic acid anchor provides higher stability across the pH range than the carboxylic acid, and conclude that protonation of the interface is likely the key contributor to complex desorption. These studies will provide the design principles for hybrid electrocatalytic materials using molecular complexes based on earth-abundant elements which are stable and efficient under the conditions required to degrade aqueous contaminants.

II-S2-02: USING TRANSMISSION X-RAY MICROSCOPY TO UNDERSTAND VOLUME EXPANSION IN NANOPOROUS ALLOY ANODES

[EFRC – SCALAR] Kodi Thurber,[1] David Nana Agyeman-Budu,[2] Joseph Mazzetti,[1] Johanna Nelson Weker,[2] Sarah H. Tolbert[1]
[1]*University of California Los Angeles,* [2]*Stanford Linear Accelerator Center*

In battery materials, redox reactions often result in significant chemical and structural change, which can prevent recharging or shorten battery lifetime. This is particularly true in alloy anodes, which are a favored candidate to replace traditional graphite anode due to their ability to accommodate several Li+ per unit cell, and perform multi-electron redox. Unfortunately, accompanying volume expansions >250% lead to crack formation and capacity fade. Here, we utilize nano-porous alloy anodes in combination with transmission X-ray microscopy (TXM) to visualize volume expansion and crack formation and propagation during cycling with a goal of developing systems that can reversibly accommodate large volume changes. TXM allows for imaging of particle features as small as 50 nm and as large as 30 microns, and sample can be

continuously imaged during cycling to asses chemiophysical transformations. Using 2D TXM, we have found that intermetallic phases with two elements that lithiate at different potentials (SbSn, for example) show pores that reversibly shrink upon lithiation to accommodate the added volume, while single elements like Sn show pore fracture. Hierarchical porosity in SbSn appears to further stabilize the pore system over many cycles. Materials with amorphous intermediates, like nanoporous Sb cycled with Na, also show highly reversible volume changes with reduced cracking. To gain a higher level of structural information, a flooded capillary cell geometry, capable of operando 3D tomographic reconstructions has been developed. While this geometry is applicable to any battery system, it is well suited for analyzing structural change in alloy anodes.

II-S2-03: $LaCl_3$-NaCl MIXTURES AND THE CONCEPT OF A "SPACER SALT"

[EFRC – MSEE] Matthew S. Emerson[1], Shobha Sharma[1], Santanu Roy[2], Vyacheslav S. Bryantsev[2], Alexander S. Ivanov[2], Ruchi Gakhar[3], Michael E. Woods[3], Leighanne C. Gallington[4], Sheng Dai[2,5], Dmitry S. Maltsev[2], Claudio J. Margulis[1]
[1]University of Iowa, [2]Oak Ridge National Laboratory, [3]Idaho National Laboratory, [4]Argonne National Laboratory, [5]University of Tennessee, Knoxville

Lanthanides are important fission products in molten salt reactors and understanding their structure and that of their mixtures is relevant to nuclear and separation technologies, for example the separation of rare earth species. Because of their structural similarity, lanthanide salts can also serve as surrogates to interrogate the structural features of actinide salts. Our recently published work[1] aimed to resolve the following very important questions: "Is it correct to think of long-lived octahedral coordination structures for La^{3+}? What is the nature as a function of temperature of networks and intermediate-range order particularly upon dilution of the trivalent ion salt? Is the so-called scattering first sharp diffraction peak (FSDP) for neat $LaCl_3$ truly indicative of intermediate-range order? If so, why is there a new lower-q peak when mixed with NaCl? Are X-ray scattering and Raman spectroscopy results fully consistent and easily described by simulation results?"[1] In this poster we show that not only is the coordination of La^{3+} both temperature and concentration dependent but also that multiple coordination states coexist in the melt. We also show that a FSDP in X-ray scattering develops upon mixing in NaCl that is due to correlations between anion-decorated La^{3+} complexes or networks that are spaced by the lower valency salt. Our team's Raman calculations and experiments finally put to rest the long-standing historical interpretation of such experiments as proof of octahedral coordination given that simulations predicting a larger coordination number for La^{3+}, in fact multiple coordination states, well reproduce the Raman spectra.

II-S2-04: PHONON LINEWIDTHS IN URANIUM NITRIDE AT HIGH TEMPERATURES: EXPLORING PHONON-PHONON AND ELECTRON-PHONON

[EFRC – TETI] Michael Manley[1], Hao Ma[1], Enda Xiao[2], Chris Marianetti[2]
[1]Oak Ridge National Laboratory, [2]Columbia University

As part of the TETI EFRC, we are investigating the microscopic origin of thermal transport in advanced oxide and metallic nuclear fuels, including uranium dioxide and uranium nitride (UN). Thermal transport is directly related to reactor efficiency, as well as reactor safety, and is arguably one of the most important material properties. Neutron scattering measurements of the phonon group velocities and lifetimes (inverse of phonon linewidths) provide a direct measure of the microscopic mechanisms underlying the lattice thermal transport. A key aim of this center will be to benchmark advanced theoretical calculations that account for strong 5*f*-electron correlations against the neutron scattering measurements. We have analyzed phonon dispersion of UN measured using the CNCS and SEQUOIA instruments at the Spallation Neutron Source (SNS) of Oak Ridge National Laboratory. At low temperatures (5K to 300K), it is observed that measured phonon dispersion is in good agreement with theoretical results. Unfortunately, their phonon linewidths could not be extracted due to the limitation of instrumental resolution. However, it is critically important to obtain phonon linewidths of UN because they play an important role in understanding its thermal conductivity and is related to phonon-phonon and electron-phonon scattering rates. In addition, this is fundamentally interesting and can serve as benchmarking data for theoretical calculations. Therefore, we plan to measure acoustic phonon linewidths of UN at higher temperatures, where theoretical calculations indicate that they should be broad enough to resolve using the CNCS or HYSPEC instruments at the SNS.

II-S2-05: THERMAL ENERGY TRANSPORT UNDER IRRADIATION

[EFRC – TETI] David H. Hurley[1], Marat Khafizov[2], Chris Marianetti[3], Miaomiao Jin[4], Michael Manley[5], Zilong Hua[1], Brelon May[1], Krzysztof Gofryk[1], Yanwen Zhang[1], Amey Khanolkar[1], Yongfeng Zhang[6], Matthew Mann[7], Kaustubh Bawane[1], Chao Jiang[1], Farida Selim[8], Elizabeth Sooby[9], Linu Malakkal[1], Boopathy Kombaiah[1], Shuxiang Zhou[1]
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In nuclear fuel, irradiation-induced defects scatter thermal energy carriers (electrons and phonons), greatly reducing the capacity of the fuel to transport heat to the coolant for eventual electricity generation. This reduction significantly impacts fuel performance, safety margins, and the amount of usable energy. However, in some special cases, microstructure evolution can lead to local increases in thermal conductivity. The Center thus adopts the **vision** that a first-principles understanding of thermal transport addressing the complexity of irradiation defects will provide the tools to control thermal transport.
Our vision is examined from the perspective of two thrusts. The first tackles phonon mediated thermal transport in advanced oxide fuels (thorium oxide mixed with uranium). The second thrust emphasizes electron mediated thermal transport in advanced nitride fuels (uranium nitride and thorium nitride). To meet our vision we have defined four research goals that represent significant challenges in the field of thermal transport:

1. *Extend computational and experimental framework to temperature extremes*

2. *Accurately measure electron-phonon coupling*
3. *Characterize the spectrum of defects and model defect carrier interactions*
4. *Understand defect segregation at interfaces and thermal transport across interfaces*

Tackling the computational complexity is a far-reaching challenge. Our approach involves beyond DFT methods to understand the role of 5*f* electrons, mesoscale models of defect evolution, and transport models targeting the fundamental mechanisms that control thermal transport. These modeling approaches will be complemented by a well-defined set of electron- and phonon-structure measurements and transport measurements in ion-irradiated model fuels having well-characterized microstructures.

II-S2-06: NANOFLUIDIC PLATFORMS FOR ADDRESSING KNOWLEDGE GAPS AT THE WATER-ENERGY NEXUS

[EFRC – CENT] Yu-Ming Tu[1], Rahul Prasanna Misra[1], Matthias Kuehne[2], Hananeh Oliaei[3], Cody L. Ritt[1], Samuel Faucher[1], Kyle Sendgikoski[4], Xintong Xu[5], John Cumings[4*], Arun Majumdar[5*], Narayana Aluru[3*], Daniel Blankschtein[1*], and Michael S. Strano[1*]
[1]Massachusetts Institute of Technology; [2]Brown University; [3]University of Illinois Urbana-Champaign; [4]University of Maryland; [5]Stanford University

AFFILIATED TALK – II-T2-6: Nanofluidic Platforms for Knowledge Gaps at the Water-Energy Nexus

Fluids confined inside single digit nanopores (SDNs) with pore dimensions comparable to the size of the fluid molecules can exhibit thermodynamic properties, including phase transitions, which differ remarkably from those in the bulk phase. Here, we develop a high-throughput platform utilizing carbon nanotubes (CNTs) as SDNs to precisely characterize environmental coupling effects and investigate fluid phase transitions under strong confinement. Using local laser heating *in vacuum*, we discovered thermally reversible radial breathing mode (RBM) downshifts of CNTs by an extraordinary 10 to 15%, which is attributed to a reversible increase in damping and can be described using the harmonic oscillator model across 93 different Raman scans. Additionally, immersing CNTs opened by focused ion beam in water reveals phase transitions with concave-up trajectories dominated by the internal fluid desorption (adsorption) at high (low) temperatures. To model water phase transitions, we have developed an equation of state (EOS), aided by molecular simulations carried out in a hybrid statistical mechanical ensemble, where the confined water is maintained in quasi-chemical and thermal equilibrium with separate chemical potential and thermal reservoirs, respectively, under non-isothermal conditions. Importantly, this thermodynamic theory entails a self-consistent determination of the phase transition temperature as a function of the water-CNT interactions and CNT diameters, thereby enabling an accurate characterization of the enthalpy of phase change through fitting to the experimental data. Overall, our combined experimental and theoretical study demonstrates the exceptional promise of CNTs as precision systems for various nanofluidic applications at the water-energy nexus.

II-S2-07: HIGH-RESOLUTION X-RAY SCATTERING AND SPECTROSCOPY RESOLVES THE STRUCTURE OF CONCENTRATED SOLUTIONS

[EFRC – IDREAM] Yihui Wei[1], Emily T. Nienhuis[2], Roberto A. Colina Ruiz[2], Sebastian T. Mergelsberg[2], J. David Bazak[2], Trent R. Graham[2], Hsiu-Wen Wang[3], Aurora E. Clark[1,2], Jacob G. Reynolds[4], Gregory K. Schenter[2], Carolyn I. Pearce[2,5]
[1]University of Utah; [2]Pacific Northwest National Laboratory; [3]Oak Ridge National Laboratory; [4]Washington River Protection Solutions; [5]Washington State University

Highly concentrated and saturated electrolyte solutions are common in industrial processes, including the management of liquid radioactive waste stored in tanks at Department of Energy legacy nuclear sites. A precise understanding of how solution composition and density influence salt nucleation mechanisms in these complex electrolytes is required to predict their behavior. A major knowledge gap is the lack of fundamental understanding of medium- to long-range aqueous solution structures at high concentrations. This knowledge gap prevents the development of predictive models and tools. Here, we use a multimodal experimental and theoretical approach to develop structure-function relationships for concentrated nitrate and nitrite solutions, establishing the physicochemical links between solution structure and solution composition, diffusivity, viscosity, and reactivity. We proposed a new structural model for concentrated sodium nitrate ($NaNO_3$) and sodium nitrite ($NaNO_2$) solutions, developed using X-ray pair distribution function analysis, that predicts the formation of extended ion coordination clusters. We are further testing this model by measuring the small-angle X-ray scattering (SAXS) and X-ray absorption spectroscopy (XAS) of pure and mixed concentrated solutions. SAXS separately resolves the structure of solute and solvent contributions to the overall structure, whereas XAS measures the element-specific local electronic structure of the solution components and reveals differences in coordination geometry. Using this approach, we can distinguish the fundamental controls of cation and anion chemistry on different components of the solution structure. Future work will integrate these findings with measurements of solution viscosity, solution density, and cation diffusion.

II-S2-08: UNDERSTANDING FLUID FLOW IN MESOPOROUS SILICA: PORE STRUCTURE AND CONFINEMENT EFFECT

[EFRC – MUSE] Yidong Xia[1], Zachary Diermyer[1,2], Rahul Kancharla[1], Ahmed Hamed[1], Jiaoyan Li[2], Milind Deo[3], Seyed M. Hatamlee[2], Luiz Emilio[3]
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The MUSE EFRC has significantly advanced the scientific understanding of the flow and transport behaviors of nano-confined fluids through novel modeling & simulation approaches and instrumented experimental measurements. This poster will comprehensively showcase the findings and broader impact in three areas: 1) flow measurement, 2) flow simulation, and 3) electron tomography. For flow measurements, we show how measured data deviates from the expected Darcy's Law values in naturally occurring interconnected porous networks in Vycor porous glass and in nanofabricated channels. For flow simulation, we show the importance of pore shape in resource recovery in nanoconfined channels, as well as the perceived reduction in permeability from a flow perspective, due to the confinement effect. For electron tomography, we

show that intra-particle pore size is comparable to the inter-particle pore size in sintered mesoporous silica nanoparticles, indicating the transport behavior of fluids within these materials should consider both intra- and inter-particle pore geometry and size distribution.

II-S2-09: EFFECTS OF FLUID FLOW, MIXING, AND SATURATION INDEX ON MINERAL DISSOLUTION AND PRECIPITATION

[EFRC – GMCS] Michael Chen[1], Weipeng Yang[1], Huan Peng[1], Sang H. Lee[1], Peter K. Kang[1], Vaughan Voller[1], Emmanuel Detournay[1], Bill Carey[2], Hari Viswanathan[2]
[1]*University of Minnesota;* [2]*Los Alamos National Laboratory*

While carbon sequestration by mineral carbonation has been successfully observed at CarbFix in Iceland and other sites, many questions remain on how to leverage carbonation processes to maximize carbonation efficiency. Specifically, it is unclear how the interplay of pore-scale flow, mixing, and saturation index control larger-scale mineral dissolution/precipitation patterns. While the literature is replete with studies investigating a subset of these factors, limited work has integrated them into a relevant framework for mineral carbonation. Our primary goal is to establish fundamental understanding of these linked processes such that one can predict and engineer mineral carbonation regimes necessary to successfully implement this critical technology. To this end, we established a novel experimental platform to address the following questions: 1. How does fluid inertia and solute mixing control mineral precipitation and clogging at fracture intersections? 2. How does coupled fluid flow and dissolution-driven convection control dissolution patterns? 3. How does the interplay between fluid flow, solute mixing, and saturation index control spatiotemporal patterns of mineral precipitation? Through direct experimental visualization of precipitation and dissolution coupled with flow, we demonstrate how the coupled processes alter mineral reaction rates and patterns. Precipitation experiments show how fluid flow and local saturation index fundamentally alters precipitation dynamics, while dissolution experiments show how local variations in under-saturation create convective flows that dramatically alter dissolution patterns. These results lay the foundation for future work, which will realize our goal of delineating major mineral carbonation regimes.

II-S2-10: IDENTIFICATION OF TIME AND LENGTH SCALES FOR CARBON MINERALIZATION PROCESSES

[EFRC – GMCS] Vaughan Voller[1], Michael Chen[1], Weipeng Yang[1], Huan Peng[1], Peter Kang[1] Lawrence Boampong[2], Qinjun Kang[2], Bill Carey[2], Jeffrey Hyman[2], Hari Viswanathan[2]
[1]*University of Minnesota;* [2]*Los Alamos National Laboratory*

The aim of this work is to identify the key scalings that control the mineralization of CO2 in mafic rock masses. This is achieved through the development and application of a simple but complete model of the fate and transport of a supersaturated CO2 charged fluid moving unidirectionally through a basalt rock. Under the assumptions that a first order heterogeneous precipitation dominates the mineralization process and that the initial conditions in the rock are uniform, the developed model consists of three coupled equations describing the (i) fate and transport of the precipitation reactant in the aqueous phase, (ii) spatial varying rate of change of the porosity,

hydraulic conductivity, and specific surface area due to the precipitation, and (iii) resulting temporal and spatially varying fluid discharge. The model operates until "shut-off," the point at which precipitation clogs the pores and cuts off the fluid flow. A dimensional analysis of the model provides universal time and space scalings that can be used to characterize the duration, extent, and capacity of field scale carbon mineralization processes.

II-S2-11: UNDERSTANDING AND CONTROLLING STRESS NON-UNIFORMITIES DURING NUCLEATION AT SOLID-STATE ELECTROCHEMICAL INTERFACES

[EFRC – MUSIC] Neil P. Dasgupta[1], Micah Thorpe[1], Michael Thouless[1], Mengyao Zhang[1], Stephanie Sandoval[2], Matthew McDowell[2], C. Haslam[1], Jeff Sakamoto[1]
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Nucleation phenomena at solid-solid interfaces between an ionically conductive ceramic electrolyte phase and an electronically conductive current collector exhibit unique chemo-mechanical coupling that dictate key properties including nucleation areal density, nuclei morphology, and interfacial adhesion. In particular, during nucleation, both externally applied (e.g. via stack pressure) and internal (e.g. owing to adhesion) stresses dynamically evolve. The implications of this nucleation behavior, and how it influences the morphological evolution as electrodeposition transitions to the growth phase, are not well understood for emergent solid-state systems based on ceramic ion conductors. In this study, we explore the role of stress inhomogeneities on the nucleation and growth behavior as new phases precipitate at solid-solid interfaces, using metal/ceramic interfaces as a model system. A multi-modal suite of *in situ/operando* and *ex situ* analytical methods are employed to quantify the nucleation density, nuclei morphology, and eventual coalescence into a dense secondary phase. In particular, it is observed that a non-uniform initial stress state along the interface can promote dramatically different nucleation morphologies, which is quantified using synchrotron x-ray tomography. A continuum-scale mechanical model is introduced that accounts for the stress evolution as a function of these inhomogeneous boundary conditions. Finally, it is shown that by tuning the boundary conditions using elastomeric bodies, the stress-distribution along the interface can be rationally controlled, facilitating improved uniformity of both nucleation and growth of alkali metals.

II-S2-12: MECHANOCHEMICAL STABILITY OF NASICON MEMBRANES TO ENABLE AQUEOUS SODIUM LONG DURATION ENERGY STORAGE TECHNOLOGY

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The accelerated adoption of EVs creates the necessary impetus to augment the electrical grid. While renewable technologies such as wind and solar can provide electrical power, complimentary electrical energy storage is needed to provide continuous operation. One promising

electrochemical grid battery is a class of long duration energy storage (LDES) based on aqueous Na electrolyte. However, enabling higher voltage and high coulombic efficiency aqueous Na-based chemistries requires a single-ion solid electrolyte that physically isolates the anolyte from the catholyte. NASICON of the nominal formula $Na_3Zr_2(SiO_4)_2PO_4$ is a promising ceramic electrolyte exhibiting fast ion conduction (~4 mS/cm) and is believed to be stable in water. In principle, NASICON satisfies many criteria to enable advanced LDES, however, in practice knowledge gaps remain. Achieving membrane area specific resistance (ASR) targets of ~5 Ohms.cm^2 requires thicknesses in the 100 micron range. Since NASICON is a ceramic and is known to be brittle (~ 1.5 MPa.m$^{-0.5}$), mechanical integrity during operation becomes increasingly difficult as the membrane area increases or the aspect ratio decreases. Moreover, NASICON is frequently known to consist of multiple crystalline phases and a glass phase. Owing to the stress and strain resulting from the thin (low aspect-ratio) format, combined with the unknown chemical stability of each constituent creates an environment that commonly causes stress-corrosion cracking (SCC) in ceramics. SCC is a process whereby the combination of stress and chemical reactions at a crack tip accelerate crack propagation. The MUSIC team is conducting one of the first analyses of stress-corrosion cracking in ceramics for LDES.

II-S2-13: MOLTEN SALT DEALLOYING CORROSION OF METALS: MECHANISMS AND IRRADIATION EFFECTS

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AFFILIATED TALK – II-T2-8: The Duality in Damage: Multi-Scale Investigations into Corrosion and Irradiation Effects in Salt-Facing Nuclear Reactor Materials

Metal alloys in contact with molten salts can corrode via a dealloying process, wherein the less noble metal elements are selectively dissolved as the salt infiltrates the alloy and generates a porous structure. The conditions for dealloying are set by the chemistry of the salt, the electrochemical potential controlled by either applied potential or oxidizer concentration, and the microstructure of the alloy - all of which are expected to evolve under effects of irradiation. However, a fundamental understanding of how these factors synergistically control corrosion remains incomplete. Computational and experimental efforts within FUTURE are undertaken to advance understanding of these mechanisms, using NiCr alloys in contact with molten LiF-NaF-KF salt as a model system. The thermodynamic and kinetic conditions for dealloying have been established using a series of electrochemical diagnostics, including linear sweep voltammetry, electrochemical impedance spectroscopy, and chronoamperometry. These conditions are used to parameterize a phase field model, validated against corrosion morphologies observed from advanced structural and characterization methods. Combined modeling and experiment reveal (a) how compositional heterogeneities at the metal/salt interface underly a morphological instability that precedes salt attack into the alloy, and (b) the mechanisms by which structural heterogeneities in the alloy (namely, grain boundaries and dislocations) act as preferential sites

for salt infiltration. This understanding provides the basis for future work that will leverage simultaneous irradiation-corrosion experiments (ICE) developed within FUTURE to characterize irradiation effects on corrosion behavior.

II-S2-14: MORPHOLOGICAL AND STRUCTURAL EVOLUTIONS OF METAL-MOLTEN SALT INTERFACES

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The structure of solids at interfaces with strongly reactive media defines the properties of a variety of materials. Understanding interfacial evolution has immense importance in energy applications. The interfaces and their changes are particularly of interest when the materials are subject to extreme environments such as molten salts. The potential use of molten salts in sustainable energy facilities such as molten salt reactors, concentrated solar power plants, energy storage, 2D materials, and molten salt batteries has been a subject of intense research. The high-temperature, highly reactive fluidic environment often leads to an actively evolving interface whose properties are not well understood due to the paucity of experimental and theoretical tools for their characterization. We studied the evolution of Cr in molten KCl-$MgCl_2$ via time-resolved synchrotron X-ray nano-tomography, absorption spectroscopy and diffraction, combined with density functional theory and *ab initio* molecular dynamics simulations. Cr is present in structural materials in which corrosion is a concern for molten salt applications. We revealed a reaction/dissolution of Cr forming pores and formation of δ-A15 Cr changing the Cr coordination environment in molten salt in the initial stage of the reaction. Computational simulations were conducted to compare the stability of bcc and δ-A15 Cr and the interfacial behavior of the stable facets for different Cr phases with affinities for Mg^{2+}, K^+, and Cl^- ions. Overall, we not only developed a suitable model system for such investigation, but also devised a multimodal strategy for probing the morphological, structural, and chemical evolution of solids at interfaces.

II-S2-15: HYDROGEN IN ENERGY AND INFORMATION SCIENCES (HEISS)

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HEISs aims to advance the fundamental understanding and discovery of the behavior of multihued hydrogen in inorganic solids of earth-abundant elements, where 'hydrogen' includes all charge states of the element: H^+ (proton), H^0 (atom), and H^- (hydride ion). The transport and incorporation

characteristics of hydrogen are distinct from those of other elements owing to its small mass and its ambipolar nature. Dominant transport via tunneling at ambient temperatures is possible for protons, and kinetic isotope effects are appreciable. Its redox flexibility is accompanied by a dramatic change in ionic/atomic radius, from effectively 0 for H^+, to 0.6 Å for H^0, and 1.1 Å for H^-. Beyond its special place in physical chemistry, hydrogen is of high societal importance in energy technologies (fuel cells, electrolyzers) and of growing importance in energy-efficient computing (electrochemical synaptic systems). In both arenas, the relevant devices are limited by hydrogen kinetics, whether it be electrochemical reaction at an interface or diffusion through the bulk, and whether the material be an electrolyte, a semiconductor, or functionally a metal. Leveraging the interdisciplinary expertise of the team, which spans from chemistry to materials science, and applied physics to nuclear engineering, HEISs undertakes comprehensive studies, both experimental and computational, to assess hydrogen transport through **bulk** materials, across and along solid-solid **interfaces**, and incorporation at gas-solid **surfaces**. HEISs further exploits **novel stimuli** - light, stress, and extreme electric field - as routes to manipulate and enhance hydrogen dynamics.

II-S2-16: ACTINIDE-BASED METAL-ORGANIC FRAMEWORKS (AN-MOFS)

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To manage radioactive species, radionuclide sequestration, storage, separation, and sensing are four emergent areas that must be addressed in the upcoming years. Metal-organic frameworks (MOFs) are a potential candidate for addressing these challenges. Due to their porosity, high surface area, and tunability, MOFs can be considered a particularly promising class of sorbent materials that can display an aptitude for sequestering radionuclides. First, we focused on tuning defect-controlled leaching kinetics of MOFs which revealed a remarkable re-adsorption process using cerium cations as a surrogate for plutonium cations. In addition, we probed the adsorption of radioactive americium cations for the first time. Utilizing a series of zirconium-based MOFs, we determined that >99% of transuranic ^{241}Am radionuclides could be captured and retained in the crystalline matrix even after one week. Our results showcase the possibility to control cation release kinetics in MOFs as a function of MOF defects through postsynthetic linker installation and installation of cation chelating agents, such as a crown-ether-based organic linker. Further, we developed a trend in the physicochemical properties of a series of heterometallic U/Th-containing frameworks as a function of metal ratio for the first time. We also shed light on the possibility of utilizing the uranium-containing MOF as precursor to probe the preparation of heterometallic U/Pu-analogs. Overall, the presented detailed structural analysis, kinetics, and thermochemical stability studies showcase MOFs as a viable nuclear wasteform material.

II-S2-17: INVESTIGATION OF STRUCTURAL AND MICROSTRUCTURAL TRANSITIONS IN SOL-GEL SYNTHESIZED PHOSPHATE-BASED GEOPOLYMERS DURING THERMAL TREATMENT

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Geopolymers have attracted considerable interest due to their versatile applications as coating materials, fire-resistant materials, composites for infrastructure reinforcement, aircraft, and automobile interiors, etc. Geopolymers are considered environmentally friendly alternatives to Portland cement owing to their low carbon dioxide emissions, relatively low cost and comparable mechanical strength. The mechanical strength in these geopolymers is attributed to $AlPO_4$ phases formed in their matrix. The geopolymers are synthesized using a sol-gel approach by mixing $Si_2Al_2O_x$ with phosphoric acid (H_3PO_4) to obtain the geopolymers with composition having Si:Al:P ratio of 1:1:1. The viscous mixture is cured at room temperature and 80 °C to obtain hard enamel-like solid geopolymers, labeled as GP-25 and GP-80, respectively, in the study. GP-25 and GP-80 are thermally treated up to 990 °C while acquiring the wide-angle scattering data to delineate the structural evolution in these materials. During heating, the berlinite phase of $AlPO_4$ persists at high temperature, while it emerges after 200 °C in case of GP-25 and around 120 °C for GP-80. Tridymite phase of SiO_2 is also noted in both GP-25 and GP-80 at high temperatures. Moreover, intermediate phases, such as P_2O_5, variscite ($AlPO_4.2H_2O$), AlP_3O_9, and $Si_5O(PO_4)_6$ are noted during the thermal treatment at lower temperatures (<300 °C). Understanding the evolution of Si-Al linkages during the synthesis and thermal treatment of geopolymers, and formation of Al-P linkages are essential to develop predict controls over the chemistry of these geopolymers. To obtain an atomistic-scale understanding of this evolution process, we are employing molecular dynamics simulations using the ReaxFF reactive force field. In these ReaxFF simulations, a system with a periodic boundary condition consisting of $Al_2Si_2O_7$ and Phosphoric acid (H_3PO_4) has been modeled. We extended a previously developed LiTiAlPOH ReaxFF parameter set with Si-parameters and subsequently studied the formation of $AlPO_4$ at different temperatures (1000 K – 1500 K – 2000 K). Analyzing the results of the initial simulations shows an increasing trend in radial distribution function (RDF) between Aluminum and Phosphorus atoms which indicate the formation of Al-O-P linkages and subsequently the formation of $AlPO_4$ – which agrees with the experimental trends. The insights gained from this study will advance the fundamental understanding of the effects of composition of geopolymers and curing conditions and will also help in developing the next generation of construction materials.

II-S2-18: FLUID BEHAVIOR, MASS TRANSFER, AND SORPTION IN NANOPOROUS MATERIALS – EXPERIMENTAL OBSERVATIONS AND MODELING AT MOLECULAR AND CONTINUUM SCALES

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Nanoconfined fluids are important in many environmental and engineering processes. Here, we study via experiments and molecular dynamics simulations, nanoconfined ethane, of interest in

hydrocarbon production and gas separations. Its pore critical properties and self-diffusivity are known, but the relationship between molecular organization and phase behavior is not. We examine the impact of pore wall proximity, pore size, and temperature on the nanoconfined ethane structure, and report an energetically favorable molecular rearrangement in the adsorption layer. These studies support the further development of adsorbate phase density models to convert excess to absolute adsorption and may lead to more accurate gas-in-place estimates and the efficient design of adsorbents and membranes. Gas transport and storage in low-permeability organic-rich shales poses an array of challenges due to complex pore morphology, a broad range of pore sizes, and heterogeneous structure. Here, tandem experiments with inert (He) and adsorbing (Kr and CO_2) gases were performed. Transport parameters, from the He experiments, were used to model the Kr and CO_2 experiments, by properly accounting for differences in fluid properties and transport mode. The predictions and experiments are in excellent agreement. Gas dissolution and diffusion in liquid hydrocarbons confined in nanopores, is important during extraction processes from unconventional formations. Here, we measured methane diffusion in n-decane, n-hexadecane, and their mixture in a mesoporous material with pore size of 4 nm. We observe that binary diffusivities, measured in the bulk phase, are sufficient to predict the ternary system behavior both in bulk and in confinement.

II-S2-19: POLYMER-CERAMIC COMPOSITE ELECTROLYTES: EFFECT OF PARTICLE SIZE ON BULK AND INTERFACIAL ION TRANSPORT

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Significant efforts have been made to develop composite electrolytes combining polymer matrix with Li-ion conducting ceramics for feasible construction of solid-state batteries. Li-ion transport in composite electrolytes depends on the interface between polymer/ceramic, Li-ion solvation in the polymer matrix, surface structure of ceramics and the interaction between polymer and ceramics. Therefore, the electrolyte composition and interfacial region significantly affect the ion transport in composites. In this work, we study the effect of ceramic particle size and structure on bulk and interfacial ion transport in the polymer-ceramic composite electrolytes composed of $Li_{0.34}La_{0.56}TiO_3$ (LLTO) nanorods and a single-ion-conducting polymer electrolyte. LLTO nanorods with relatively low LLTO content (TiO_2-LLTO) and high LLTO content (LLTO nanorod) have been synthesized. Transmission electron microscopy (TEM) is used to investigate the size and surface structure of these LLTO nanomaterials. Broadband dielectric spectroscopy (BDS) reveals that the total ionic conductivity in these polymer-ceramic composites increases with the addition of both the LLTO nanorods and TiO_2-LLTO, compared with neat polymer electrolyte. The LLTO nanorods show more pronounced enhancement of the ionic conductivity at 30 °C. For comparison, composites made from a commercial source of LLTO with micrometer size particles do not show enhancement in conductivity. The effect of LLTO particle size on Li-ion transport kinetics of bulk and interfaces is discussed. We ascribe the enhanced conductivity to faster Li^+ transport in the interfacial polymer layer surrounding the ceramic particles.

II-S2-20: UNDERSTANDING THE ELECTROCHEMICAL ACTIVITY AND STABILITY OF INDIUM OXIDE FOR SELECTIVE ELECTROCATALYTIC DEGRADATION OF WATER CONTAMINANTS AND REACTIVE OXYGEN SPECIES GENERATION

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Our team seeks to develop active, stable, and selective electrocatalyst materials for water remediation. Doped indium oxide is a highly conductive and oxidatively stable electrode with exceedingly low activity for water oxidation, thereby providing new opportunities for remediation of aqueous pollutants through selective reactive oxygen species (ROS) generation or direct oxidation of pollutants. We have developed a rapid route to the fabrication of conductive, high surface area In_2O_3 frameworks. However, there is a knowledge gap regarding the stability of high surface frameworks at high electrode potentials, the selectivity for ROS generation, and the activity of In_2O_3 for degradation of perfluoroalkyl substances (PFAS) as a function of surface (defect) site and nanoconfinement. In this work, we fabricate planar and nanoscale conductive oxide frameworks and establish their electrochemical activity and stability both experimentally and with ab-initio simulations. Specifically, we use computed electronic and vibrational properties of indium oxide water interfaces to interpret and guide experiments. Rotating ring disk electrode (RRDE) experiments at selected ring potentials enable quantification of the formation of ROS as a function of In_2O_3 polarization, while coupling with an Inductively Coupled Plasma Mass Spectrometer (ICP-MS) to offer real-time information about the rates of In dissolution as function of electrode preparation, polarization, electrolyte choice.

II-S2-21: INFLUENCE OF IRRADIATION ON THE KINETICS OF OXIDATION IN CORROSIVE ENVIRONMENTS

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The sustainability of metals and alloys as structural materials in oxidizing environments is only possible by the formation of passivating oxide layers which serve as a barrier to prevent further corrosion. The effectiveness of passivating films is governed by the transport of oxygen and/or metal atoms through them as mediated by defects in the crystal structure. During irradiation, additional defects induced by displacement may change the nature of these mass transport processes, potentially accelerating or suppressing oxidation kinetics, and thereby altering the corrosion susceptibility of alloys in radiation environments. In this work we combine atom probe tomography (APT), heavy ion irradiation, and a variety of modeling capabilities to assess changes in mass transport in oxides resulting from radiation exposure in hematite (Fe_2O_3), magnetite (Fe_3O_4), and iron chromate ($FeCr_2O_4$), the principal oxides which form on ferritic/martensitic steels at nuclear reactor operating temperatures. Isotopically labelled oxide films grown with molecular beam epitaxy (MBE) were analyzed after thermal aging and/or ion irradiation by using APT

measurements of isotope redistribution to quantify changes in diffusion behavior. The experiments conform to a multi-scale mass transport model informed by density functional theory (DFT) calculations. Ongoing work targets accelerated mass transport at surfaces and grain boundaries, including a new *in situ* APT reactor capability allowing direct oxidation of APT needles, and molecular dynamics simulations of oxide-oxide interfaces. Together these capabilities advance our understanding of oxidation in extreme environments and predict the extent corrosion will change during irradiation exposure.

II-S2-22: THE ROLE OF PORE CHEMISTRY IN WATER AND ION TRANSPORT THROUGH UIO-66: A COMPREHENSIVE EXPERIMENTAL AND MOLECULAR MODELING APPROACH

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The effect of pore chemical groups on water and ion transport through membranes is a critical knowledge gap for developing ultra-precise separation technologies. This ongoing study leverages highly customizable pore chemistry of UiO-66, a water stable metal-organic framework, to explore the role of functional group interactions in water and ion transport. While previous work is limited by ambiguous transport pathways of multi-crystalline platforms, we are building novel single-crystal devices of UiO-66 modified by linker functional groups to directly relate ion transport and pore chemistry. Ion-functional group interactions are being assessed through isothermal titration calorimetry to elucidate the effect of binding energy on transport results. A multi-pronged computational approach is used to mechanistically explore water and ion transport in functionalized UiO-66 pores. Water self-diffusion coefficients were assessed via grand-canonical Monte-Carlo and equilibrium molecular dynamics simulations, revealing an order of magnitude decrease compared to bulk water at 1 atm and 300 K. Water and functional group binding affinities were calculated via density functional theory and show a preference for hydrogen-bonding groups. Furthermore, partitioning and pressure-driven transport is being assessed through non-equilibrium molecular dynamics simulations of a slab-like UiO-66 membrane. Preliminary results characterize NaCl transport through two orientations of UiO-66: a zirconium-exposed and linker-exposed surface. Na^+ preferentially partitions over Cl^- in both membrane orientations. However, the zirconium-exposed orientation blocks Cl^- passage 20-fold compared to the linker-exposed surface. We are continuing this combination of simulations and single-crystal experiments to generate relationships between binding affinity, diffusion coefficients, and partitioning of water and ions in UiO-66.

II-S2-23: RADIOLYSIS IN EXTREME ENVIRONMENTS

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Understanding elementary steps following ionization in aqueous systems provides a framework for radiation-matter interactions in chemistry and biology. A microscopic understanding of reaction mechanisms in the physicochemical time regime is missing because standard techniques, such as electron paramagnetic resonance and UV spectroscopy, lack time or spectral resolution. A powerful two-color sub-femtosecond time-resolved X-ray pump/probe scheme developed at the LCLS provides a new tool to systematically understand the electronic and nuclear dynamics following outer-, inner-valence, and core ionization in aqueous systems. Building on earlier work focused on outer-valence ionization, we used this new $\omega/2\omega$ scheme to investigate liquid water radiolysis following full valence-band ionization via X-ray transient absorption. The X-ray pump produced outer- and inner-valence holes, and the probe covered valence-hole absorption and oxygen K-edge. Time delays from 0.6 -50 fs allow one to capture many ultrafast dynamical processes. Here we report on the shortest time delay, 0.6 fs. As the first all X-ray attosecond pump/probe transient absorption study in condensed phase, it was imperative to establish the nature of detected signals. Theory revealed the importance of electron-induced ionization and dephasing on sub-femtosecond timescales. That established the validity of obtaining spectral snapshots on timescales shorter than the free-induction decay, and, of using time-independent quantum chemistry methods. Multireference configuration interaction calculations on neutral and singly-ionized tetrahedrally-coordinated water clusters reproduced observed transient absorption for sparse ionization. This work establishes attosecond X-ray pump/probe transient absorption methodologies in condensed phase and sets the stage for further investigations at LCLS and EuXFEL with more complex solutions.

II-S2-24: HYDRIDE INCORPORATION IN $SrTiO_3$ AND COMPUTATIONALLY PREDICTED $xBaZrO_3$-(1-x)$SrTiO_3$

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AFFILIATED TALK – II-T2-5: New Routes to Hydrogen Incorporation in $SrTiO_3$

While proton incorporation in acceptor-doped $BaZrO_3$ and related perovskites has long been established, recent literature indicates that undoped titanate perovskites can incorporate hydride species, forming, for example, $SrTiO_{3-x}H_x$ (STO: H^-). Key to broadening the study of these materials is the development of a readily tuned synthesis approach. Here we pursue a two-step reduction process under hydrogen atmospheres, designed to first reduce the base material ($SrTiO_3$) and subsequently incorporate hydride anions. Thermogravimetric analysis (TGA) reveals that the first step successfully produces $SrTiO_{2.82}$. Electron energy loss spectroscopy following the second step suggests an impact of the processing steps on the Ti environment, indicating that either the Ti does not exhibit its ideal octahedral coordination or the average oxidation state lies between 3+ and 4+. ^1H solid-state NMR shows significant differences between pristine STO and STO: H^-, with a

stronger peak in the latter at 1 ppm. Additionally, a peak at 5 ppm, tentatively attributed to surface H+ species, is substantially lower in STO: H^- than in the (nominally) pristine material. The totality of the results suggests STO: H^- has been obtained.

Along with expanding synthetic routes, we aim to establish the chemical rules for hydride vs proton incorporation via study of the $BaZrO_3$-$SrTiO_3$ system. Computational results indicate strain may stabilize solid solutions of otherwise immiscible BZO-STO. To this end, machine learned potentials based on density-functional theory calculations are being developed to simulate the growth of strained solid solution films.

II-S2-25: FUNCTIONALIZED CONFINED TWO-DIMENSIONAL CHANNELS FOR SEPARATION AND SELECTIVITY

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AFFILIATED TALK – II-T2-3: Ion transport in MoS_2 nanochannels

The design of synthetic channels with superior selectivity for any desired target ion remains a significant challenge due to limited understanding of the interplay between aqueous fluid containing the target and the solid interface. Two-dimensional (2D) materials offer new opportunities for controlling separation and selectivity, with interlayer spacings from angstroms to nanometers. We have created 2D platform channels with three complimentary classes of materials: transition metal dichalcogenides (TMDCs), phyllosilicate minerals, and MXenes. (i) ***TMDCs***: We have synthesized a confined angstrom-scale 2D channel based on MoS_2 functionalized with acetate, and we have observed anomalous and cooperative ion transport within this channel. Molecular dynamics (MD) simulations were also conducted to investigate the interplay between ions, revealing the significant role of long-range interactions in influencing counterion pairing. (ii) ***Phyllosilicate minerals***: We have devised a route to tunable ion-transport properties for vermiculite membranes (VMs) by the introduction of alkanediamine molecules to cross-link the layers, which also enhances membrane stability. (iii) ***MXenes***: We have designed hierarchically engineered MXenes with novel MXene morphologies, surface terminating groups, and hybrid organic-inorganic material systems; we have also investigated the role of material structure (across multiple length scales) impact separation properties. Based on this material platform and advanced characterization and modeling, we aim to elucidate the impact of various factors such as interlayer spacing, ion binding mode, dehydration, and electrostatic interactions on water and ion permeabilities and selectivities. These insights will provide constructive guidance for the precise design of selective 2D materials.

II-S2-26: FUNDAMENTAL MECHANISTIC UNDERSTANDING OF ELECTROCATALYTIC SULFUR REDUCTION REACTION

[EFRC – SCALAR] Leyuan Zhang,[1] Dongfang Cheng,[1] Rongli Liu,[1] Ziyang Wei,[1] Philippe Sautet,[1] Xiangfeng Duan[1]
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The sulfur reduction reaction (SRR), a complex 16-electron process, is central for high capacity in Li-S batteries. Despite considerable interest, the fundamental mechanism and the SRR molecular pathways remain elusive. By combining electrocatalysis, cyclovoltammetry (CV), and operando Raman studies, we reveal two main stages from S_8 to Li_2S, with Li_2S_4 as the separating intermediate. Density functional theory (DTF) calculations propose a detailed molecular pathway for the first stage, with the simulated CV and key species (S_8, Li_2S_8, Li_2S_6, and Li_2S_4) matching experimental results. Kinetic studies show that the first stage is relatively easy with low activation energy, whereas the subsequent conversion of the polysulfides into insoluble Li_2S_2/Li_2S has a much higher activation energy, contributing to the accumulation of soluble polysulfides that exacerbate polysulfide shuttling. Nitrogen and sulfur dual-doped holey graphene considerably improve the SRR kinetics, lowering the activation energy for the second stage. DFT calculations indicate that doping tunes the p-band centre of the active carbons to optimize adsorption strength and electroactivity. To further explore the catalytic performance, we find the co-doping of nonmetal and metal heteroatoms can show a synergetic effect on facilitating the 16-electron sulfur reaction. The Fe-N-S co-doping can be an effective strategy to promote the reduction reaction of both long- and short-chain polysulfides. The Fe-N site can be the major active center for the long-chain polysulfide reaction while the C site adjacent to S sites is mainly responsible for the short-chain polysulfide reaction. Finally, we demonstrate the Li-S coin cell can show a stable cycling at a high areal capacity.

II-S2-27: FUTURE: FUNDAMENTAL UNDERSTANDING OF TRANSPORT UNDER REACTOR EXTREMES

[EFRC – FUTURE] Mark Asta[1], Peter Hosemann[1], Aaron A. Kohnert[2], Daniel K. Schreiber[3], Farida A. Selim[4], Sandra D. Taylor[3], Blas P. Uberuaga[2], Kayla H. Yano[3]
[1]University of California Berkeley; [2]Los Alamos National Laboratory; [3]Pacific Northwest National Laboratory; [4]Bowling Green State University

Nuclear energy systems are some of the most hostile and extreme built by humans. A multitude of harsh conditions exist simultaneously, pushing the materials to non-equilibrium and acting in concert to degrade the performance of the materials that comprise the system. These extremes include irradiation and corrosion. Individually, these are two of the greatest materials science challenges as they are truly multiscale. For example, irradiation spans from subatomic effects at the femtosecond time scale to macroscopic consequences on the time scale of decades. On the other hand, corrosion mechanisms differ depending on if the corrosive environment is a molten salt versus an oxygenated system that induces oxide formation. In actuality, these are not independent within the reactor. Rather, materials are simultaneously subjected to both irradiation and corrosion. To obtain a descriptive and ultimately predictive understanding of materials evolution in nuclear energy systems, we need to understand the coupled extreme environments of irradiation and corrosion. Our research is focused on the impact that material heterogeneities – the disruptions of perfect order present in all materials – have on this evolution. These include structural heterogeneities such as grain boundaries and dislocations, phase heterogeneities in which multiple phases are present, and compositional heterogeneities where chemical species are

distributed non-uniformly. At the same time, radiation damage and corrosion both induce new heterogeneities in the material, leading to dynamic feedback between the response and structure. By combining modeling and experiment, FUTURE targets the fundamental mechanisms responsible for the non-equilibrium evolution of materials under combined irradiation and corrosion.

II-S2-28: ACCELERATING THE DESIGN OF CONCENTRATED HYDROGEN BONDED ELECTROLYTES USING ACTIVE LEARNING AND HIGH THROUGHPUT EXPERIMENTAL SCREENING

[EFRC – BEES2] Dinis O. Abranches,[1] William Dean,[2] Miguel Muñoz,[2] Wei Wang[3], Yangang Liang[3], Burcu Gurkan,[2] Edward J. Maginn,[1] Yamil J. Colón[1]
[1]University of Notre Dame; Case Western Reserve University; [3]Pacific Northwest National Laboratory

Concentrated hydrogen bonded electrolytes (CoHBEs), including deep eutectic solvents (DESs) formed commonly from liquid mixtures of solid hydrogen bond donors (HBDs) and acceptors (HBAs), offer high tunability for specific applications such as energy storage. While their tunability stems from the ease of changing precursors and relative compositions, measuring physical and electrochemical properties across large composition and temperature ranges is tedious, error-prone, and represents a bottleneck in the advancement of CoHBEs for flow batteries. As such, active learning (AL) methodologies based on Gaussian Processes (GPs) were developed in this work to minimize the experimental effort necessary to design DESs and characterize their phase diagrams with organic mixtures towards the development of CoHBEs. The prediction of the VLE behavior for ternary mixtures using only three experimental points is demonstrated, as well as properties such as single-ion activity coefficients for which there are no classical thermodynamic models available. We confirmed the ability of AL to greatly reduce the amount of data needed (e.g., by as much as 80% for viscosity predictions) to obtain accurate models by combining it with a high throughput experimental (HTE) screening tool. This case study featured CoHBEs based on choline chloride HBA, ethylene glycol and aniline HBDs, and various co-solvents and redox active species of interest for flow batteries. By leveraging the combined approach of AL and HTE, future predictions of electrochemical stability, accessible redox active concentrations, and redox potentials will accelerate the development of energy storage systems with CoHBEs.

II-S2-29: NANOFLUIDICS: TRANSPORT IN CHIRALITY-CONTROLLED CARBON NANOTUBE PORINS (CNTPS) AND FLUORESCENCE ULTRASHORT NANOTUBES (FUNS)

[EFRC – CENT] Sidi Zhao[1,2], Rahul Prasanna Misra[3], Yuhao Li[1], Haoran Qu[4], Alice Gillen[1], Jeffrey Fagan[5], YuHuang Wang[4*], Daniel Blankschtein[3*], Aleksandr Noy[1,2*]
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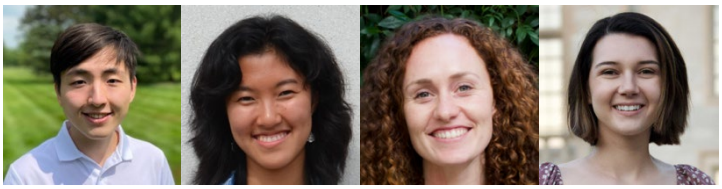
Carbon nanotubes (CNTs) are promising model systems to investigate the role of the electronic properties of the channel wall on ion and water transport. CNTs of different chiralities can be synthesized which are either metallic or semiconducting depending on the band gap. Here, we

prepared short chirality-separated pure (6,5), (7,4), and (7,5)/(8,4) CNT porins (CNTPs), which vary in electronic properties yet are almost identical in diameter. Single channel conductance from potassium ion transport through these CNTPs indicates that the electronic properties have a weak effect on ion transport, whereas water transport is relatively faster in metallic than in semiconducting CNTs. These results were rationalized using molecular dynamics simulations based on the ion-CNT and water-CNT polarization interactions, including the calculation of the water friction coefficient inside metallic and semiconducting CNTs. Additionally, sodium and lithium ion transport through different chirality CNTPs were also studied. In addition to intrinsic electronic properties, we also investigated the role of the functional group and defects on the CNT wall. We measured ion transport through fluorescence ultrashort nanotubes (FUNs) – functionalized channels with defective walls dispersed by surfactants such as CHAPS and SDOC. Although the single channel conductance using different surfactants were similar, these channels exhibited significantly lower conductance compared to the pure (6, 5) CNTPs in both CHAPS and SDOC surfactant. Overall, our study highlights the role of the electronic properties of the CNT wall, including defects, and functional groups, on the nanofluidic transport of water and ions through single channel CNTs.

II-S2-30: PROBING WATER STRUCTURE AND SOLUTE TRANSPORT IN ZWITTERIONIC MEMBRANE MATERIALS

[EFRC – M-WET] Justin Yun[1], Sally Jiao[1], Audra J. DeStefano[1], Suzana Ivandic[2], Benny D. Freeman[2], M. Scott Shell[1], Rachel A. Segalman[1], Craig Hawker[1]
[1]University of California, Santa Barbara; [2]University of Texas at Austin

Surfaces decorated with zwitterionic groups have excellent antifouling properties. As such, incorporation of zwitterionic functionalities is a promising strategy for the development of novel, fouling-resistant water purification membrane materials. However, our ability to tune and optimize selectivity while minimizing fouling is limited because we lack a fundamental understanding of how chemical functionality influences ion transport in the membrane and solute affinity for membrane surfaces. In particular, the structure and dynamics of water is hypothesized to mediate the interaction between such zwitterionic surfaces and both charged and uncharged solutes, but the underlying mechanism remains unresolved. Here, we synthesize PEGDA/PEGMEA/zwitterion random copolymer networks with systematically varied cation/anion charge density, zwitterionic group loading, and water volume fraction. We perform ion transport studies showing that salt permeability is affected by water content and cation size. Concurrently, simulations of zwitterionic surfaces, in comparison with uncharged chemistries, demonstrate that zwitterionic groups uniquely perturb water's triplet angle structure, resulting in distinct hydration structures that increase the free energetic penalty associated with rearrangement of water's structure upon solute adsorption. Taken together, these studies bring together synthesis, characterization, and molecular simulations to highlight the importance of nanoscopic and systematic characterization of water and solute behavior in such membrane materials.



(from left) Justin Yun, Sally Jiao, Audra J. DeStefano, and Suzana Ivandic

II-S2-31: ATOMISTIC INVESTIGATION OF RADIATION-INDUCED DEFECTS AND THEIR IMPACT ON THERMAL TRANSPORT IN ThO_2

[EFRC – TETI] Miaomiao Jin[1], Beihan Chen[1], Marat Khafizov[2], Chao Jiang[3], Linu Malakkal[3], Yongfeng Zhang[4], Kaustubh K. Bawane[3], Boopathy Kombaiah[3], David H. Hurley[3]
[1]Pennsylvania State University; [2]The Ohio State University; [3]Idaho National Laboratory; [4]University of Wisconsin-Madison

Radiation-induced defects constitute the foundation of radiation-assisted microstructural evolution and degradation of thermal transport in nuclear fuels. In this poster, we present an investigation of a spectrum of defects ranging from point defects to dislocation loops, and their impact on thermal transport in thorium dioxide (ThO_2). We have identified a number of defects to be generated due to radiation primary damage. The energy-preferable defect (cluster) configurations are identified and explored with both first-principles calculations and self-developed machine learning interatomic potential. For example, defect clusters tend to approach charge neutral, with a particular exception of cuboctahedral interstitial clusters which embrace a high symmetry but a high unbalanced charge. On the experimental scale of microscopy, we investigate the dislocation loop structures and reveal the mechanisms of how the Frank dislocation loop unfaults to a perfect loop, which is of significance to explain the microstructural characteristics under irradiation. To understand how the defects affect thermal transport, the enhanced phonon scattering is assessed via thermal conductivity models against values obtained by extensive molecular dynamics simulations of systems with point defects, small defect clusters, and dislocation loops. Furthermore, we particularly probe the impact of point defects via phonon relaxation time and phonon modal contribution to conductivity based on both Green's function method and dynamical methods, to reveal the importance of high-order anharmonicity in defect-bearing systems. These results facilitate a fundamental understanding of radiation-induced defects and their impact on thermal transport in ThO_2.

II-S2-32: MODELING ION EXCHANGE IN FAUJASITES: A METHODS STUDY USING DENSITY FUNCTIONAL THEORY

[EFRC – CHWM] An T. Ta[1], Ayoub Daouli[2], R. Seaton Ullberg[1], Vanessa Proust[3], Agnès Grandjean[3], Michael Badawi[2], Simon R. Phillpot[1]
[1]University of Florida, [2]University of Lorraine, [3]CEA, DES, ISEC, DMRC, Univ Montpellier

AFFILIATED TALK – II-T2-2: Modeling Ion Exchange in Faujasites: A Methods Study Using Density Functional Theory

Zeolites are popular candidates as capture materials for removing harmful cesium radionuclides (e.g., cesium-137) from used nuclear waste because of their relatively low cost, radioactive stability, and effective performance. Faujasites are among the zeolite types under consideration and are made up of two building units (sodalite and d6mr), which results in a framework that possesses specific exchange sites in its super and inner cages. In this study, approaches implementing various reference states (e.g., gaseous, implicit solvation, explicit solvation) were evaluated to determine the most appropriate technique for modeling ion exchange in faujasites using density functional theory (DFT). It was found that the consideration of both implicit and explicit solvation leads to the most reliable results. Exchange energies for Li^+, K^+, and Rb^+ with Na-X zeolites were considered and validated with available experimental data.

II-S2-33: BRIDGING THE GAP BETWEEN MACROSCALE ELECTROLYTE PERFORMANCE AND MICROSCOPIC DYNAMICS AT ELECTRODE INTERFACES USING ADVANCED ELECTROANALYSIS AND COMPUTATIONAL MODELING

[EFRC – BEES2] Vaishnavi Sree Jeganathan[1], Armando Santiago-Carboney[2], Peisen Qian[2], Quincy Spitzer[1], Zeynep Bagbudar[1], Brian Doherty[3], Robert Warburton[1], Mark Tuckerman[3], Jesse Wainright[1], Rohan Akolkar[1], Joaquín Rodríguez-López[2]
[1]Case Western Reserve University; [2]University of Illinois; [3]New York University

To fully realize superior flow battery concepts based on concentrated hydrogen-bonded electrolytes (CoHBEs), exceptional charge transport in their bulk must be met by facile charge transfer at electrode interfaces. In this poster, we describe ongoing technical efforts to accurately determine heterogeneous rates of electron transfer, transport, and reactive parameters of redox couples, interactions between redox species and the electrolyte, and electrode–electrolyte interfacial dynamics. For example, we have established a methodology to use SECM approach curves in high-viscosity CoHBEs to probe the hypothesis that proton transport networks quantitatively impact electron transfer processes involving redox probes and surfaces involving PCET and different degrees of H-bonding. We have started the comparison of classical redox mediators, such as ferrocenes and viologens, to PCET systems, such as quinones. Furthermore, the introduction of IDAs to accurately measure generation and collection processes enables the exploration of the extent to which interactions between H-bonded electrolytes and redox pairs and electrodes will affect transport and interfacial processes, such as adsorption and precipitation. We also build on previous works on surface-enhanced spectroscopy and new tricks for improving interfacial signals at graphitic electrodes to correlate electrochemical to molecular interfacial dynamics. Finally, computational modeling in BEES2 informs new directions toward understanding the impact of the energetics of adsorbed states and molecular functions at electrodes that could

be distinctively leveraged at CoHBE systems. Overall, these techniques and models will enable critical insight regarding redox phenomena and help us bridge a knowledge gap on improving charge transport and charge transfer in these promising electrolytes.

II-S2-34: DENSIFICATION AND SOLID STATE BATTERIES

[EFRC – MUSIC] Kelsey B. Hatzell[1], MinGi Jeong[1], Partha P. Mukherjee[2], Bairav S. Vishnugopi[2], Kaustubh G. Naik[2], Jeff Sakamoto[3], Yet Ming Chiang[4], Thea Yan[4]
[1]Princeton University; [2]Purdue University; [3]University of Michigan; [4]Massachusetts Institute of Technology

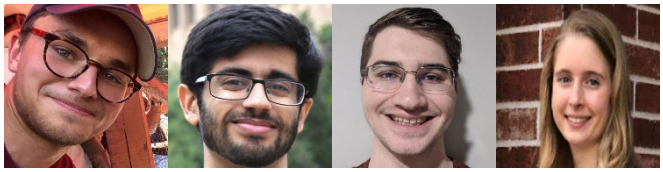
Manufacturing of solid-state batteries remains an open challenge. Most solid electrolyte materials are sensitive to moisture and operate at elevated pressures. High pressure is necessary to maintain contact between electrodes and solid electrolytes during operation and enable efficient transport. Ambient temperature and pressure densification of solid state electrolytes and electrodes is desirable for scalable manufacturing of solid state batteries. The MUSIC team has been examining the fundamental densification mechanisms in solid state electrolytes and cathodes. Chemo-mechanics and densification of composite cathodes is studied using combined energy dispersive x-ray diffraction, electrochemistry and modeling. Imaging of solid state cathodes demonstrates how pressure and solid electrolyte particle size impact compaction of cathodes and solid electrolytes. Cold sintering, where a fluid is passed through a electrolyte to guide densification, is also studied in this thrust. Halide electrolyte densification is shown to be highly impacted by solvent properties (e.g. viscosity, boiling point, dielectric properties, etc.).

II-S2-35: FUNDAMENTAL DESIGN PRINCIPLES OF HIGHLY SELECTIVE MEMBRANES FOR WATER TREATMENT

[EFRC – M-WET] Everett S. Zofchak[1], Rahul Sujanani[2], Nico Marioni[1], Aubrey Quigley[1], Venkat Ganesan[1], Rachel A. Segalman[2], Benny D. Freeman[1]
[1]University of Texas at Austin; [2]University of California, Santa Barbara
AFFILIATED TALK – II-T2-1: Mechanisms Underlying Mixed Salt Partitioning in Uncharged Poly(ethylene oxide)-based Membranes

Selective polymer membranes are critical in established and emerging water treatment processes (e.g., desalination, resource recovery). Many new applications require precise separation of specific ions (e.g., Li^+) from concentrated solute mixtures, yet current membranes exhibit limited ion-ion selectivity due to non-specific polymer-ion interactions. Additionally, our current understanding of ion transport in membranes is informed by single salt studies, yet separations are necessarily performed in complex mixtures. The design of highly selective membranes is hindered by poor understanding of the molecular interactions underpinning ion transport in polymers challenged with electrolyte mixtures. We performed experimental and computational studies to systematically probe the effects of hydration and mixed salt interactions on ion transport. Measurements in polymers exposed to humid air showed that ion transport rates depend weakly on water content at low water activity but depend strongly on water content at high water activity. Complementary simulations provided molecular level insights, suggesting ion

transport is governed by polymer dynamics at low water content and by water dynamics at high water content. Mixed ion partitioning experiments performed at a fixed ionic strength facilitate comparison of single and mixed salt partitioning. Systematic deviations were observed between the single and mixed salt cases. Molecular dynamics simulations coupled with equilibrium thermodynamic modeling indicate these differences arise from: (1) differences in ion affinity for the membrane and (2) electrostatic interactions between ions in a predictable manner. Together, the synergistic combination of synthesis, characterization and simulations provide new fundamental insights for designing membrane materials for advanced ion separations.



(from left) Everett Zofchak, Rahul Sujanani, Nico Marioni, and Aubrey Quigley

II-S2-36: PROBING EFFECTS OF CONFINEMENT ON ETHANE PHASE CHANGES VIA NMR SPECTROSCOPY

[EFRC – CMC-UF] Erik R. Smith[1], Samantha J. Harris[1,x], Kyle Rehmeier[1,y], Teresa Lehmann[1,*], Vladimir Alvarado[1,*]
[1]*U. of Wyoming,* [x] *formerly Samantha J. Tower,* [y] *formerly Kyle Covington*

Confinement can alter fluid phase behavior due to interfacial interactions. Departure from bulk thermodynamic behavior encompasses phenomena such as capillary condensation. This condensation occurs whenever a liquid condenses from a gas, when the gas alone should exist. We have shown that High-Field Nuclear Magnetic Resonance (HF-NMR) responds to phase changes in porous materials. Results in microporous materials show that chemical shift can be used to determine the phase transition, because densification alters the local magnetic environment through effects of shielding. In this work, we summarize evidence of capillary condensation in mesoscopic materials as well as the influence of surface wettability on this phenomenom. Various porous materials, covering several scales, from macro to nanoscale, were used in experiments. Wetting conditions, i.e. gas, water or oil wet, were created by applying a silane or a silazane coasting. Solution-state nuclear magnetic resonance (NMR) was used to collect ethane chemical shift data. Chemical shift spectra revealed auxiliary peaks and line broadening attributed to capillary condensation. Our findings highlight how important wettability is in ethane gas condensation. Finally, condensation occurred at pore sizes larger than expected in the case of gas-wet systems.

II-S2-37: ZWITTERIONIC ADDITIVES FOR REDUCING ENERGY BARRIERS AND ENHANCING IONIC CONDUCTIVITY IN SINGLE ION CONDUCTING POLYMER ELECTROLYTES

[EFRC – FaCT] Jodie Lutkenhaus[1], Hongwei Li[1], Catalin Gainaru[2], Panagiotis Christakopoulos[2], Rajeev Kumar[2], Md Anisur Rahman[1], Michelle Lehmann[1], Tomonori Saito[1], Ralph Colby[3], Alexei P. Sokolov[2]

[1] *Texas A&M University;* [2] *Oak Ridge National Lab;* [3]*Penn State University*

Zwitterionic molecules are promising additives for the purpose of enhancing ionic conductivity in single ion conducting polymers. These molecules contain both positive and negative charge groups, and it is expected that zwitterionic additives will reduce the energy barriers for ion hopping due to an enhancement of local dielectric constants. Here, we present our work on understanding the effects of oligomeric and polymeric zwitterions in reducing energy barriers and, in turn, enhancing ionic conductivity of single ion conducting polymer electrolytes. Effects of glass transition temperature and structural changes in the blends containing zwittterions will be discussed.

II-S2-38: MULTISCALE NUCLEAR-ELECTRONIC ORBITAL QUANTUM DYNAMICS IN COMPLEX ENVIRONMENTS

[CCS – NEOQD] Mathew Chow[1], Aodong Liu[2], Eleftherios Lambros[2], Xiaosong Li[2], Sharon Hammes-Schiffer[1]
[1]Yale University; [2]University of Washington

AFFILIATED TALK – II-T2-7: Multiscale Nuclear-Electronic Orbital Quantum Dynamics in Complex Environments

Multiscale descriptions of quantum dynamics are critically important for modeling and understanding complex chemical processes at the interface of energy conversion, storage, and transfer. The nuclear-electronic orbital (NEO) method provides an effective and elegant way to introduce nuclear quantization directly into quantum chemistry calculations, enabling the capture of zero-point energy, hydrogen tunneling, and other nuclear quantum effects not included in conventional electronic structure calculations. The NEO method is particularly useful for studying nonadiabatic processes, such as photoinduced proton transfer and proton-coupled electron transfer, which often occur in solution or in extended, heterogeneous environments. A multiscale treatment is required to accurately model the chemical complex of interest as well as its surrounding environment. In our work, the NEO method has been integrated into a solvent environment using both a simple, yet powerful polarizable continuum model (PCM) embedding, as well as an atomistic hybrid quantum mechanical/molecular mechanical (QM/MM) strategy. Our calculations demonstrate that the environment can quantitatively polarize the nuclear density, providing important insight into how energy-related proton transfer processes behave in solution. Furthermore, the NEO QM/MM approach, coupled with the state-of-the-art MB-pol water model, can capture atomically resolved solvent effects on the quantized nuclei and the coupled nuclear-electronic dynamics. These methods are implemented in ChronusQ, an open-source quantum chemistry package allowing the democratization of these advances towards US energy leadership. Finally, our outreach program develops a STEM educational pathway for students from University of Hawai'i to participate in a research experience for undergraduates in computational chemical sciences.

II-S2-39: COUPLED TRANSPORT, REACTIVITY, AND MECHANICS IN FRACTURED SHALES

[EFRC – CMC-UF] M. P. Murugesu[1], B. Vega[1], C. M. Ross[1], T. Kurotori[1,3], T. J. L. Druhan[2], A. R. Kovscek[1]

[1]*Stanford University;* [2] *University of Illinois Urbana-Champaign;* [3]*currently Imperial College London*

Shales are low-permeability caprocks that confine fluid, such as CO_2, nuclear waste, and hydrogen, in storage formations. Stress-induced fractures in shale caprocks provide pathways for fluid to leak and potentially contaminate fresh water aquifers. Fractured shales are also increasingly considered as resources for CO_2 sequestration, enhanced geothermal, and unconventional energy recovery. Injecting reactive fluids into shales introduces chemical disequilibrium, causing an onset of a series of dissolution and precipitation reactions. The reactions have rapid kinetics and significant impact on porosity and permeability; consequently, flow and storage properties of formation rocks. This study unveils these highly coupled transport and reactivity mechanisms by tracking and visualizing the reaction-induced alterations in the matrix, microcracks, and fractures of shales over time. We conducted pH 4 and 2 brine injection experiments in a naturally fractured Wolfcamp shale sample while simultaneously imaging the dynamic processes using x-ray computed tomography (CT). CT images are validated by finer resolution images obtained using micro-CT and scanning electron microscopy. We also tracked the sample permeability and fluid chemistry using brine permeability and inductively coupled plasma mass spectrometry, respectively. Findings show that fluid primarily flowed through fractures, dissolving reactive minerals and mobilizing fines on fracture surfaces. Dissolution of fracture asperities under confining stress led to fracture sealing favorable for CO_2 storage. Clogging in narrow fracture pathways, caused by fines accumulation, diverted fluid flow into matrix pores.

II-S2-40: EXPLORING THE PATH TO HIGH PERFORMANCE BEES RFBS: TEMPOILS, COHBES AND BEYOND

[EFRC – BEES2] Brian Barth[1], Madisson McMichael[2], Houston Smith[3], Ananya Banik[3], David Powers[3], Emily Pentzer[3], Adam Imel[1], Shane Foister[1], Tom Zawodzinski[1,2]
[1]*University of Tennessee;* [2]*Oak Ridge National Laboratory;* [3]*Texas A&M University*

Breakthrough Electrolytes for Redox Flow Batteries (RFBs) are the critical target of our EFRC. We demonstrated the first microemulsion redox flow battery in BEES1, but this system left much to be desired in terms of performance. Both energy and power density (ED and PD) were low relative to conventional systems. We are exploring several strategic directions to densify our energy and power. To improve on our first microemulsion electrolytes, we formulate and characterize highly conductive acidic microemulsions, which incorporate large quantities of oil. We demonstrate surprising phase behavior: despite large ionic strength, all four Winsor phases are observed through tuning emulsifier hydrophobicity. Microemulsions near the Winsor I/IV boundary are close to 50% toluene but exhibit conductivities greater than 200 mS/cm. We analyze new concepts including redox-active pure oils in microemulsions and CoHBEs, in which proton conductive and redox-active functions are combined to increase ED. We utilize phase-transfer catalyzed reactions for multi-gram, high-yield alkylation of 4-hydroxy TEMPO without the need for column chromatography. By this approach, we prepare 4-(dodecyloxy)TEMPO which is capable of solubilizing unmodified TEMPO for a pure redox-active oil phase at a concentration of 5M! Improving PD requires substantial work to understand the interactions of constituents with RFB components. We report the results of such interactions with electrodes and membranes and their

effects. SDS added in mM concentrations has no effect on proton transport through the membrane but substantially changes reaction rates. Kinetics can be enhanced via surfactant additives, depending on the chemistries of the surfactant, electrode, and electrolyte.

II-S2-41: REFRACTORY TRANSITION METAL OXIDES AS ELECTRODES IN LITHIUM-ION BATTERIES

[EFRC – SCALAR] Ashlea Patterson,[1] Yunkai Luo,[2] Yucheng Zhou,[2] Laurent Pilon,[2] Bruce Dunn,[2] Ram Seshadri[1]
[1]*University of California, Santa Barbara,* [2]*University of California, Los Angeles*
AFFILIATED TALK – II-T2-4: Refractory Transition Metal Oxides as Electrodes in Lithium-Ion Batteries

Refractory transitions metal oxides include oxides of metals such as zirconium (Zr), niobium (Nb) and molybdenum (Mo) that typically have high melting temperatures. These oxides, particularly of Nb, are also key components in oxide materials that can take up and release lithium rapidly in electrochemical energy storage systems, with voltages that make them suitable as anodes that can be paired with a high voltage cathode material. A large body of research from the SCALAR EFRC has emerged on these materials, including design principles for these compounds to function as high-power electrodes capable of fast charging/discharging, the role of crystal structure and composition in ensuring such fast charge/discharge, the role of metallicity and insulator-to-metal transitions with lithiation to enable current to be delivered quickly, the role of multielectron redox on the transition metal.

We will present recent work on new Wadley-Roth compounds from the Na–Nb–O family that are effective at high-rate, high-capacity redox and describe subtle compositional differences in certain bronze compounds with related structures that dramatically impact cycling stability and high-rate-performance.

An important aspect of SCALAR research that has informed our understanding of these anode oxide materials had involved of the use of calorimetry and entropy potential measurements as a function of lithiation and delithiation. These measurements permit distinct regimes in the electrochemistry to be identified even when there are no structural signatures.

II-S2-42: BRINGING WAVEFUNCTIONS AND DENSITIES TOGETHER FOR EXASCALE FIRST PRINCIPLES SIMULATION

[CCS – PsiXC] Bikash Kanungo[1], Soumi Tribedi[1], Jeff Hatch[1], Vikram Gavini[1], Paul Zimmerman[1]
[1]*University of Michigan*

The two most widely used *ab initio* strategies for chemical and materials simulations are wave function and density functional theories (WFT, DFT). These methods were developed along parallel, but fundamentally different pathways. Among their differences are limits in applicability: WFT can be tuned to arbitrary accuracy, but scales poorly, while DFT is highly scalable, but strategies to obtain further accuracy are ambiguous. This project seeks to better intertwine WFT and DFT by creating new mechanisms for WFT to inform the design of more accurate DFT functionals, and for the resultant DFT to improve the computational efficiency of WFT.

This poster introduces two key components of this effort, and describes how they will be combined into a synergistic strategy to improve both the scalability and the accuracy of first principles simulations. First, finite element methods—which provide a systematic and complete basis set—are used alongside a density inversion algorithm to convert electron densities into accurate exchange-correlation potentials. Second, new algorithms for full configuration interaction will give WFT benchmark results for challenging, strongly correlated models. The two components—when used together—will facilitate the training of new density functionals using the exact 3D exchange-correlation potential. The new functionals are aimed at capturing strong correlation effects using the DFT ansatz, with the goal of achieving WFT-like accuracy.

II-S2-43: INSIGHTS INTO ELECTROCHEMICAL BEHAVIOR AND BATTERY DEGRADATION MODES VIA INTEGRATION OF PHYSICS BASED MODELING AND EXPERIMENT

[EFRC – *m2m#s*] Karthik S. Mayilvahanan[1], Zeyu Hui[1], Andrew Nicoll[2], Arun Kingan[2], Jwal R. Soni[1], Xiao Tong[4], David C. Bock[3,4], Alan Gen Li[1], Tianwei Jin[1], Matthias Preindl[1], Yuan Yang[1], Kenneth J. Takeuchi[2,3], Amy C. Marschilok[2,3], Esther S. Takeuchi[2,3], Alan C.West[1]
[1]Columbia University; [2]Stony Brook University; [3]Brookhaven National Laboratory

Degradation phenomena in Li-ion batteries are highly complex, coupled, and sensitive to use history and operating conditions. In this study, we show how tracking model parameters in continuum-level physics-based models can be useful in testing hypotheses for degradation mechanisms. Exemplary analyses are presented, including a cell revival process combined with parameter estimates over the course of cycling to extract valuable insights into cathode evolution, and approaches to evaluate the contribution of individual degradation modes to performance losses and provide estimates of the energy-power correlation of cells after cycling. The presented approaches are expected to be broadly applicable for degradation analysis of electrodes.

II-S2-44: DESIGN PRINCIPLES FOR REGULATING ELECTRODEPOSITION AT METALLIC ALUMINUM AND ZINC BATTERY ANODES VIA INTERFACIAL CONTROL

[EFRC – *m2m#s*] Jingxu Deng[1,2], Tian Tang[1], Qing Zhao[1], Yue Deng[1], Wenzao Li[3], Jiefu Yin[1], Patrick J. West[3], Killian R. Tallman[3], Xiao Tong[4], Shuo Jin[1], Qing Zhao[1], Regina Garcia-Mendez[1], Kenneth J. Takeuchi[2,3], Esther S. Takeuchi[2,3], Amy C. Marschilok[2,3], David C. Bock[3,4], Lynden A. Archer[1].
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Although Li-based batteries have established a dominant role in the current energy-storage landscape, post-Li chemistries (for example, Al or Zn) are emerging as promising candidates for next-generation rechargeable batteries. Electrochemical cells using Al or Zn metal as the negative electrode are of interest for their potential low cost, intrinsic safety, and sustainability. However, the way surface chemistry influences reactions occurring thereupon has been a long-standing question of broad scientific and technological interest. Here, we consider the relation between the surface chemistry at interfaces and the reversibility of electrochemical transformations at rechargeable battery electrodes; and show that such knowledge provides a powerful tool for

designing key materials in highly reversible battery systems based on Earth-abundant, low-cost metals.

Day 3 – September 26, 2023

Poster Session 1

III-S1-01: TAILORING CORRELATED OXIDES FOR EFFICIENT NEUROMORPHIC COMPUTING DEVICES

[EFRC – Q-MEEN-C] Sarmistha Das[1], Shenli Zhang[2], Rourav Basak[1], I-Ting Chiu[3], Mingzhen Feng[3], Uday Goteti[1], Min-Han Lee[1], Junjie Li[1], Henry Navarro[1], Alexandre Pofelski[4], Yongjin Shin[2], Tianxing Wang[1], Ravindra Bisht[5], Robert Dynes[1], Alex Frañó[1], Giulia Galli[2], Shriram Ramanathan[5], Ivan K. Schuller[1], Yayoi Takamura[3], and Yimei Zhu[4]
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Correlated oxides, such as the perovskite oxides are promising candidate materials for neuromorphic systems due to the wide range of functional properties that they exhibit, ranging from ferromagnetic, antiferromagnetic, and ferroelectric phases, as well as abrupt metal-to-insulator transitions (MITs). In recent years, the control of the anion concentration has proven to be a highly effective means of modulating their functionality as the ABO_3 perovskite structure can transform to several perovskite-related phases including oxygen-deficient perovskite ($ABO_{3-\delta}$), Grenier (GN, $ABO_{2.7}$), brownmillerite (BM, $ABO_{2.5}$), and Ruddlesden-Popper ($A_{n+1}B_nO_{3n+1}$, *n*=integer) phases. In this work, we explore the versatility of this approach through a combination of experimental and first-principles calculations. We find that the extent of the "topotactic" transformations that are observed, strongly depends on the identity of the *B*-site cations (*B* = Co, Mn, and Fe). The structural complexity of these phases leads to cooperative distortions of the constituent BO_6 octahedral and BO_4 tetrahedral-coordinated layers, leading to ferroelectricity in the GN ferrites. In addition, the perovskite/BM interface in the cobaltite system is predicted to display metallic conductivity between two insulating phases due to the combined effects of orbital reconstruction and interfacial charge transfer. Finally, the introduction of defects through He irradiation of the nickelates is shown to stabilize to a low temperature metallic phase, thus preventing the MIT to an insulating ground state. Due to the charged nature of the oxygen ions involved in these processes, these approaches hold great promise for voltage-controlled perturbation of their functionality as required for neuromorphic computing devices.

III-S1-02: CHEMICAL VAPOR DEPOSITION GROWTH OF CUBIC UWBG SEMICONDUCTORS INCLUDING DIAMOND AND CUBIC BORON NITRIDE

[EFRC – ULTRA] Timothy Grotjohn[1] , Robert Nemanich[2] , Fernando Ponce[2] , Mary Ellen Zvanut[3] , Arunima Singh[2] , Srabanti Chowdhury[4] , Richard Wilson[5] , Alexander Balandin[5]
[1]Michigan State University; [2]Arizona State University; [3]University of Alabama at Birmingham; [4] Stanford University; [5]University of California-Riverside

Diamond and cubic boron nitride (CBN) for power electronics are grown by plasma-assisted CVD. The EFRC work on diamond is to understand and reduce dislocation defects and to get uniform and controlled doping levels that lead to diamond with high thermal conductivity, high carrier mobilities and high electric field breakdown strength. The EFRC work on CBN is to grow it with sp^3 phase purity and at appreciable growth rates. The technical goals driven by the co-design effort

include deposition of undoped and doped diamond with no or low dislocation density and uniform doping levels of desired thickness. To achieve these goals and because measured values of electric field breakdown are often less than expectations, a deeper understanding of defects and doping is needed to advance the technology beyond that achieved through past research. The technical goal for CBN is to grow on diamond substrates CBN pure layer of 100's nm thickness. CBN from a co-design perspective has high thermal conductivity and can be doped n-type. Synthesis of diamond is performed with advances being explored in dislocation reduction and doping control via various structural properties, dislocation and defect characterization techniques including nano-scale cathodoluminescence, TEM microscopy, electron paramagnetic resonance, Raman and Brillouin spectroscopy, and time-domain thermoreflectance. Photoconductive and electrical properties are being measured at high electric fields to understand breakdown in diamond. CBN growth is being studied versus variations in growth conditions via TEM microscopy and other techniques.

III-S1-03: DYNAMICALLY RECONFIGURABLE VANADIUM OXIDE ELECTROCHEMICAL DEVICES

[EFRC – reMIND] Brian Zutter,[1] Sangheon Oh,[1] Saul Perez-Beltran,[2] Andres Lopez-Meza,[2] Brayan Arenas Blanco,[2] Vahid Attari,[2] Arunabha M. Roy,[2] Allison Arabelo,[2] Kenna Ashen,[2] Alexander Strasser,[2] Xiaofeng Qian,[2] Raymundo Arroyave,[2] Anton Levlev,[3] Josh Sugar,[3] Timothy D. Brown,[1] John Anderson,[1,4] Sean R. Bishop,[5] Patrick Finnegan,[5] Suhas Kumar,[1] Elliot J. Fuller,[1] R. Stanley Williams,[2] Perla B. Balbuena,[2] Alec A. Talin[1]

[1]Sandia National Laboratories—Livermore; [2]Texas A&M University; [3]Oak Ridge National Laboratory; [4]Stanford University; [5]Sandia National Laboratories—Albuquerque

Devices that provide real-time hardware reconfigurability will greatly expand the capabilities of an analog computing network. Here we demonstrate vanadium oxide electrochemical devices, which can be reconfigured to function as switches for signal routing and demultiplexing, tunable synapses and somas, and variable-frequency oscillators. We combine two synapses and a neuron together into a small network, and demonstrate a reconfigurable AND/OR logic gate with no active components. These devices exhibit excellent retention under short circuit, with accelerated aging studies showing less than 1% loss of their state in 14 years at room temperature. To understand the switching and retention mechanisms of these devices we combine Raman spectroscopy, scanning-transmission electron microscopy, and time-of-flight secondary ion mass spectroscopy measurements with first principles informed models. We find that the transformations and the coexistence of multiple phases of vanadium oxide are responsible for the electronic changes and the long-term state retention. Mesoscopic phase field analyses illustrate the effect of electrical biases on the oxygen concentration profile in the vicinity of the VO_2-V_2O_5 interface. First-principles calculations further reveal the minimum energy pathway and low kinetic barrier of phase transformation as well as the underlying electronic structure changes along the pathway. These devices can provide a foundation for adaptive neuromorphic networks that can be scaled and reconfigured on-demand.

III-S1-04: CENTER FOR MANY-BODY METHODS, SPECTROSCOPIES, AND DYNAMICS FOR MOLECULAR POLARITONIC SYSTEMS

[CCS – MAPOL] Simragni Banerjee[3], Nick Bauman[1], Jonathan Foley[2], Niranjan Govind[1], Karol Kowalski[1], Xiaosong Li[3], Ruby Maderna[2], Daniel Mejia-Rodriguez[1], Erdal Mutlu[1], Ajay Panyala[1], Himadri Pathak[1], Nam Vu[2]
[1]*Pacific Northwest National Laboratory;* [2]*University of North Carolina-Charlotte;* [3]*University of Washington-Seattle*
AFFILIATED TALK – III-T1-7: Towards Accurate Polaritonic Potential Energy Surfaces With Cavity Quantum Electrodynamics Complete Active Space Configuration Interaction Theory

There is a critical need to optimize complex chemical reaction processes to reduce waste and cost, ultimately achieving environmentally friendly clean-energy solutions. The notion of photonic reagents, tailored light fields that work in concert with molecules to control chemical reactivity, has captivated the imagination of scientists and led to fundamental studies involving light-matter interactions. Polaritons emerge when photons and molecules are confined in cavities, dramatically enhancing their interactions. Polaritonic chemistry represents an exciting reimagining of chemical transformations with photons, promising reliable ways to precisely control molecular energy flow, thus offering alternate routes to direct and manipulate molecular motion and function towards specific ends.

Our ability to understand and predict the properties of complex polaritonic phenomena relies on the development of predictive first-principles methodologies. The vision of our MAPOL center is to (1) develop a suite of theoretical frameworks, spanning low-order to high-level many-body methods to model novel chemical phenomena involving molecular polaritonic systems, (2) deliver open-source software implementations of these methods that can harness Department of Energy (DOE) leadership-class computational facilities in the US, (3) apply our developments to interpret, guide, and design innovative experiments to enhance fundamental understanding of polaritonic chemistry, and (4) nurture a community of practitioners in computational molecular sciences as part of our outreach efforts.

III-S1-05: A MULTIFUNCTIONAL QUANTUM MATERIALS PLATFORM BASED ON THE MAGNETIC SEMICONDUCTOR CRSBR

[EFRC – Pro-QM] Y. J. Bae[1], D. G. Chica[1], J. Cenker[2], E. J. Telford[1], K. Xie[2], M. E. Ziebel[1], K. Lee[1], A. H. Dismukes[1], N. P. Wilson[2], G. M. Diederich[2], D. J. Rizzo[1], A. S. McLeod[1], T. Cao[2], D. Xiao[2], J.-H. Chu[2], A. N Pasupathy[1], D.N. Basov[1], C. R. Dean[1,*], X. Xu[2], X.-Y. Zhu[1], X. Roy[1]
[1]*Columbia University;* [2]*University of Washington*

Multifunctional 2D materials offer unique opportunities to engineer programmable quantum states. To this end, Pro-QM researchers designed a new materials platform to explore these phenomena based on CrSBr, a 2D semiconductor that combines a direct bandgap in the near-IR region, giving rise to Wannier excitons and tunable electrical conductivity, with robust intralayer ferromagnetic and interlayer antiferromagnetic order, which persists down to the few-layer limit (*Advanced Materials*, **2022**). The interplay between these multiple functions has produced several breakthroughs within the center. In a series of collaborative publications, we reported the strong

and tunable coupling of the magnetic order of CrSBr to its electronic band structure (*Nature Materials*, **2021**), charge transport properties (*Nature Materials*, **2022**) and strain (*Nature Nanotechnology,* **2022**). The dual functionalities of CrSBr also led to the first demonstration of strong coupling between excitons and coherent spin waves (or magnons) (*Nature*, **2022**). Such magnon-exciton coupling enabled the first linear optical access to magnons, quantum transduction between microwave (~0.1 meV) and near-IR (~1 eV) photons. The strong exciton-magnon coupling also resulted in the recent discoveries of emerging magnon modes in twisted CrSBr unprecedented magnon nonlinearity, with stunning observations of 2nd and 4th harmonics, as well as difference frequency generation (DFG) of the magnons (*Nature Nanotechnology*, **2023**). The exceptionally strong magnon nonlinearity likely results from coupling of magnon to the electronic structure. Overall, our work illustrates in striking terms how unique quantum phenomena can emerge when multiple functions couple strongly in a 2D material.

III-S1-06: MAGNETIC FIELD CONTROL OF QUANTIZED HYBRID POLARITONS

[EFRC – Pro-QM] Lukas Wehmeier[1,2*], Suheng Xu[3], Makoto Tsuneto[1], Michael Dapolito[1,3], Rafael A. Mayer[1], Zengyi Du[1], Rui Pu[1], Xinzhong Chen[1,3], Wenjun Zheng[1], Ran Jing[1], Zijian Zhou[1], Kenji Watanabe[4], Takashi Taniguchi[4], Qiang Li[1,5], Alexey B. Kuzmenko[7], G. Lawrence Carr[2], Michael M. Fogler[8], Xu Du[1], D.N. Basov[3], Mengkun Liu[1,2]

[1]Stony Brook University; [2]Brookhaven National Laboratory; [3]Columbia University; [4]National Institute for Materials Science, Japan; [5]Brookhaven National Laboratory; [7]University of Geneva, Switzerland; [8]University of California at San Diego

Pro-QM studied a new collective excitation mode, referred to as magnetoexciton-phonon polariton, rooted in the strong coupling between inter-Landau level excitations in magnetized charge-neutral graphene and phonon polaritons in hexagonal boron nitride (hBN). Via real-space imaging using a newly developed magneto infrared nanoscopy, we demonstrate magnetic field control of the propagation of the hybrid polaritons and their polaritonic coupling strength, enabling one to tune in and out of the strong coupling regime at will. This is not only achieved through the optically allowed inter-Landau-level transitions but also the far-field forbidden ones, suggesting a relaxation of selection rules for near-field interaction. Importantly, the quantized magneto-polariton modes exhibit discrete and well-defined excitation energies, providing a means to probe the local graphene Fermi velocity with an accuracy of 1%, revealing intriguing many-body physics in charge-neutral graphene. Our work establishes magnetic-field-regulated strong coupling in charge-neutral graphene as a novel platform for controlling quantized polaritonic excitations at the nanoscale.

III-S1-07: CRYSTAL GROWTH AND DISCOVERY OF MAGNETIC TOPOLOGICAL MATERIALS

[EFRC – CATS] Tyler J. Slade[1,2], Brinda Kuthanazhi[1,2], S. X. M. Riberolles[1,2], Joanna Bławat[3], Ross McDonald[3], B. G. Ueland[1,2], Lin-Lin Wang[1], Sergey L. Bud'ko[1,2], R. J. McQueeney[1,2], Paul C. Canfield[1,2]

[1]Ames National Laboratory; [2]Iowa State University; [3]Los Alamos National Laboratory

Topological materials feature unique electronic structures with symmetry protected states that give rise to remarkable properties including high magnetoresistance and the quantum Hall effect. Because magnetic order can alter a materials symmetry, magnetism expands the diversity of possible topological states and may provide a way to externally control the quantum properties. CATS Thrust 1 has objectives to discover and characterize magnetic topological materials. Here, we present an overview of these efforts using two different approaches. 1) CATS uses DFT calculations to identify candidate topological materials containing non-moment bearing alkali earth or rare earth elements and next attempt to prepare crystals of isostructural analogues with moment bearing rare earths; and 2) CATS searches for entirely new topological phases by adding magnetic 3*d* transition metals into melts based on eutectic compositions of high-*Z* elements and main group elements (i.e. Pt–P). This poster highlights successful examples of each approach, encompassing the discovery of tunable magnetic states in $EuCd_2As_2$, characterization of three successive magnetic transitions in $EuIn_2$, and an overview of the crystal growth, neutron diffraction, and *T*–*H* magnetic phase diagram of $ErMn_6Sn_6$. We furthermore present the discovery and basic magnetic properties of two new ferromagnetic materials, $CrPt_5P$ and $MnPd_5P$, which belong to the sparsely studied XPt_5P family. We show the nonmagnetic XPt_5P compounds have Dirac points and flat bands in their electronic structures, and that the magnetism of $MnPd_5P$ can easily be tuned between anti- and ferromagnetic states with chemical substitution.

III-S1-08: NONPERTURBATIVE STUDIES OF FUNCTIONAL MATERIALS UNDER NONEQUILIBRIUM CONDITIONS

[CMS – NPNEQ] Xavier Andrade[1], Alfredo Correa[1], Tadashi Ogitsu[1], Sangeeta Rajpurohit[2], Liang Z. Tan[2], David Prendergast[2], Felipe Jornada[3], Aaron Altman[3], Aaron Lindenberg[3], Ilana Porter3, Jiaojian Shi[3], Yuan Ping[4], Andrew Greider[4], Rafi Ullah[4], Wuzhang Fang[4].
[1]Lawrence Livermore National Laboratory, [2]Lawrence Berkeley National Laboratory, [3]SLAC/Stanford University, [4]University of Wisconsin Madison

AFFILIATED TALK – III-T1-1: studying the impact of interactions on nonlinear optical processes using real-time ab-initio based simulations

The CMS Software Center for Nonperturbative Studies of Functional Materials Under Nonequilibrium Conditions (NPNEQ) started in September 2019 with the goal of developing and ditributing an open source real-time time-dependent density functional-theory (RT-TDDFT) code optimized for the current and future DOE Leadership Class HPC systems. The RT-TDDFT software named INQ has been developed and released with the functionalities for calculating ground state electronic structure and time propagation, where in addition to excellent performance on GPU, reproducibility of physical quantities associated with both ground state and excited states were demonstrated for the selected reference problems. The INQ code is written from scratch and designed specially to leverage GPU computing power. We are currently implementing GPU-optimized exact-exchange and spin-orbit-coupling, which will dramatically improve the fidelity of excited state simulation in the nonperturbative limit. Along with INQ, we developed and applied the time-dependent tight-binding (TD-TB) method and found a novel magnetic phase transition. During the second phase, we will focus on improving the fidelity of quantum dynamics simulations of spin-electron-ion coupled systems by implementing and validating new features to address

known issues associated with quantum coupling and relaxation behaviors. We will also develop a machine learning TD-TB method to extend the accessible time and length scales. Our software validation will be performed based on scientific research, including non-linear optics and magnonics. Our outreach leverages LLNL-CCMS summer school, TMF Users Meeting, Ultrafast X-ray summer school, Rutgers TDDFT Workshop, CECAM, Electronic Structure workshop, and the U.S.-Africa DFT school.

III-S1-09: NEUROMORPHIC OPTOELECTRONIC PHENOMENA IN QUANTUM MATERIAL HETEROSTRUCTURES

[EFRC – Q-MEEN-C] Henry Navarro[1], Shaobo Cheng[2], Coline Adda[1], Kumar Vinjeet[3], Jasleen Kaur[1], Chi Chen[1], Min-Han Lee[1], Xing Li[2], Alexandre Pofelski[2], Qingping Meng[2], Chenyu Zhou[2], Zishen Wang[1], Mingzhao Liu[2], Ali C. Basaran[1], L. Heki[3], Jon A. Schuller[3], Yimei Zhu[2], Marcelo Rozenberg[4], Shyue P. Ong[1], and Ivan K. Schuller[1]

[1] University of California San Diego; [2]Brookhaven National Laboratory; [3]University of California Santa Barbara; [4]Université Paris-Saclay, France

Relative to existing memristor materials, quantum materials (QM) present an exciting alternative materials platform for neuromorphic computing. At present, QM approaches are predominantly focused on electronic and magnetic phenomenology. Achieving and incorporating optical functionality may provide new opportunities for dynamically reconfiguring these neuromorphic elements or producing new QM-based optoelectronics for neuromorphic vision sensors. In this poster, we summarize multiple efforts within Q-MEEN-C to achieve neuromorphic optoelectronic phenomena in QM/semiconductor heterostructures. First, we demonstrate semiconductor/vanadate heterostructures wherein photoinduced carriers transfer from semiconductor to vanadate and drastically modify the resistive switching properties across vanadate metal-insulator transitions. Specifically, we show photoinduced order-of-magnitude variations in V_3O_5 resistivities with room temperature nonvolatile resistive switching that becomes volatile near the metal-insulator transition. Secondly, we demonstrate semiconductor/oxide heterostructures wherein photocarrier injection enables modification and photoinduced decoupling of structural and electronic transitions in VO_2 and V_2O_3. Lastly, we show how one can use extreme variations in VO_2 infrared optical properties across the metal-insulator transition to significantly modulate photocurrent in an adjacent low-bandgap semiconductor. Collectively, these investigations demonstrate intriguing optically-induced physical behaviors in QM/semiconductor heterostructures and portend new opportunities for achieving neuromorphic optoelectronic functionalities.

III-S1-10: AB INITIO MANY-BODY THEORY OF POLARONS

[CMS – EPW] Jon Lafuente-Bartolome[1,2], Chao Lian[1], Weng Hong Sio[1,3], Feliciano Giustino[1]

[1]The University of Texas at Austin, [2]University of the Basque Country at Bilbao, [3]University of Macau

AFFILIATED TALK – III-T1-3: Ab initio many-body theory of polarons

Polarons are fascinating realizations of emergent quasiparticles resulting from the interaction between fermions and bosons. In crystals, polarons form when electrons or holes become dressed

by phonons in the form of lattice distortions. In the presence of weak electron-phonon interactions, polarons behave like conventional Bloch waves with heavier effective masses. In the presence of strong interactions, on the other hand, polarons become localized wavepackets and profoundly alter the transport, electrical, and optical properties of the host material. In this poster we report on recent progress in *ab initio* calculations of polarons. In particular, (i) we review a methodology that enables the calculation of small and large polarons using density-functional perturbation theory and without resorting to cumbersome supercell calculations, as well as its implementation in the EPW code. (ii) We develop a generalization of this approach to a fully-fledged field-theoretic Green's function framework, and we show that for the prototypical Frohlich Hamiltonian our approach achieves an accuracy comparable to Feynman's celebrated path integral solution. (iii) We establish the link between polaron formation and the physics of phonon-induced band gap renormalization. We show how polaron formation and phonon-induced band structure renormalization, which traditionally have been considered as unrelated effects, are in fact complementary aspects of the same physical phenomenon and require a unified theoretical description. These developments bear significant implications on our current understanding of temperature-dependent band structures in semiconductors and insulators [Phys. Rev. Lett. 129, 076402 (2022); Phys. Rev. B B 106, 075119 (2022)].

III-S1-11: ENABLING HIGH-PERFORMANCE PHOTORESIST TECHNOLOGY THROUGH MATERIALS WITH MOLECULAR PRECISION

[EFRC – CHiPPS] Chenyun Yuan[1], Cameron Adams[2], Souvik Sarkar[3], Jacqueline Lewis[4], Ajay Ravi[4], Christopher Ober[1], Rachel Segalman[2], Brett A. Helms[3], Stacey Bent[4]
[1]Cornell University; [2]University of California, Santa Barbara; [3]Lawrence Berkeley National Laboratory; [4]Stanford University

Central to the manufacturing of smaller, more efficient devices is photolithography, the process by which transistors are patterned onto silicon wafers. The Center for High Precision Patterning Science (CHiPPS) is at the forefront of developing next-generation photoresists for EUV lithography, thus enabling ultra-precise feature etching at the sub-10 nm level.

This poster showcases our latest results towards novel materials chemistry platforms for photoresist technology, including sequence-defined peptoids, dry resists crafted using molecular layer deposition, and other hybrid materials. Peptoids, notable for their sequence-specificity and versatility, are potent components for EUV photoresists. When combined with metals, peptoids also exhibit high EUV absorption, thus directly addressing the prevalent challenges of resolution, roughness, and sensitivity. The application of molecular layer deposition enables the fabrication of metal-containing dry resists with exceptional precision and enhanced EUV absorption. Other hybrid materials boost the EUV absorption significantly and maintain high molecular precision, augmenting the effectiveness of our photoresists. These advances are interconnected, working synergistically to create photoresists that significantly improve the overall efficiency of EUV lithography.

Our work at CHiPPS explores the interactions of these advanced photoresists with low-energy secondary electrons, seeking to control the local chemical transformations that drive patterning outcomes. Through these approaches, we aim to minimize stochastic variations and deliver highly efficient, precise, and reliable EUV lithography. Join us as we delve into the cutting-edge science that underpins these achievements and discover how our research is pushing the boundaries of semiconductor manufacturing, setting the stage for the next generation of high-performance microelectronics.

III-S1-12: A PROGRAMMING MOIRÉ PATTERNS IN 2D MATERIALS BY BENDING

[EFRC – Pro-QM] M. Kapfer[1], B.S. Jessen[1], M.E. Eisele[1], M. Fu[1], D.R. Danielse[2], T.P. Darlington[3], S.L. Moore[1], N.R. Finney[3], A. Marchese[3], V. Hsieh[1], P. Majchrzak[4], Z. Jiang[4], D. Biswas[4], P. Dudin[5], J. Avila[5], K. Watanabe[6], T. Taniguchi[6], S. Ulstrup[4], P. Bøggild[2], P. J. Schuck[3], D. N. Basov[1], J. Hone[3], and C.R. Dean[1]
[1]Columbia University; [2]Technical University of Denmark, Denmark; *[3]Columbia University*; *[4]Aarhus University, Denmark*; *[5]Université Paris-Saclay, France*; *[6]National Institute for Materials Science, Japan*

A new method was demonstrated to manipulate moiré patterns in hetero- and homo-bilayers. By using the tip of an atomic force microscope to apply a lateral load, narrow ribbons of exfoliated monolayer 2D materials are made to bend in-plane. This was demonstrated on both monolayer graphene and monolayer TMD ribbon structures. It was shown that this technique achieves continuous variation of twist angles with improved twist-angle homogeneity and reduced random strain, compared with conventional assembly techniques. For the first time access to both angle and strain variation in single moire material was achieved. This effort also reported first evidence that moire disorder may be quenched by strain engineering.

III-S1-13: CENTER FOR 3 DIMENSIONAL FERROELECTRIC MICROELECTRONICS

[EFRC – 3DFeM] Susan Trolier-McKinstry[1], Nasim Alem[1], Thomas Beechem[2], Ismaila Dabo[1], Saptarshi Das[1], Suman Datta [3], Elizabeth Dickey[4], Giovanni Esteves[5], Venkatraman Gopalan[1], Michael David Henry[5], Jon Ihlefeld[6], Thomas N. Jackson[1], Sergei Kalinin[7], Kyle Kelley[8], Qi Li[1], Ying Liu[1], Yongtao Liu[8], Jon-Paul Maria[1], Vijay Narayanan[1], Kai Ni[9], Clive Randall[1], Andrew Rappe[10], Joan Redwing[1], Abhronil Sengupta[1], Nikhil Shukla[6]
[1]The Pennsylvania State University (lead institution); [2]Purdue University; [3]Georgia Institute of Technology; [4]Carnegie Mellon University, 5Sandia National Laboratories; *[6]University of Virginia; [7]University of Tennessee-Knoxville; [8]Oak Ridge National Laboratory; [9]Rochester Institute of Technology; [10]University of Pennsylvania*

MISSION: 3DFeM will exploit the 3rd dimension in microelectronics for functions beyond interconnects by incorporating low-power, non-volatile ferroelectric memory. Ferroelectric materials and new devices will be co-designed, integrated reliably, and densely interconnected with logic to enable low-power, 3D non-von Neumann computation. 3-dimensional ferroelectric microelectronics promise substantial reductions in the energy cost of computation. However, scaling has stalled with perovskite-type ferroelectric thin films, due to a combination of high processing temperature and strong thickness-dependence to the functional properties. To

overcome this challenge, our interdisciplinary research team has developed a series of wurtzite and fluorite ferroelectrics that are compatible with back-end-of-the-line processing temperatures, and are demonstrating device functionality in ferroelectric field effect transistors, ferroelectric random access memory, and ferroelectric tunnel junctions. This was done via a tight coupling of theory, modeling, and experimental work. This has enabled significant advances in our fundamental understanding of these new ferroelectrics, including development of new automated measurement techniques.

https://pennstateoffice365.sharepoint.com/sites/3DFeMSite

III-S1-14: EMERGENT HYDRODYNAMICS IN ENSEMBLES OF SOLID-STATE QUANTUM SENSORS

[EFRC – NPQC] C. Zu[1,2], F. Machado[1,2], B. Ye[1], S. Choi[1], B. Kobrin[1,2], T. Mittiga[1,2], S. Hsieh[1,2], P. Bhattacharyya[1,2], M. Markham[3], D. Twitchen[3] , A. Jarmola[1,4], D. Budker[1,5], C. R. Laumann[6], J. E. Moore[1,2], N.Y. Yao[7]
[1]University of California, Berkeley; [2]Lawrence Berkeley National Laboratory; [3]Element Six, UK; [4]US Army Research Laboratory; [5]Johannes Gutenberg Universitat Mainz, Germany; [6]Boston University; [7]Harvard University

This poster covers progress on collective behavior of quantum sensors made using the nitrogen-vacancy center in diamond. Conventional wisdom holds that macroscopic classical phenomena naturally emerge from microscopic quantum laws. However, despite this mantra, building direct connections between these two descriptions has remained an enduring scientific challenge. It is difficult to quantitatively predict the emergent 'classical' properties of a system (for example, diffusivity, viscosity and compressibility) from a generic microscopic quantum Hamiltonian. Here we introduce a hybrid solid-state spin platform, where the underlying disordered, dipolar quantum Hamiltonian gives rise to the emergence of unconventional spin diffusion at nanometre length scales. In particular, the combination of positional disorder and on-site random fields leads to diffusive dynamics that are Fickian yet non-Gaussian. Finally, by tuning the underlying parameters within the spin Hamiltonian via a combination of static and driven fields, we demonstrate direct control over the emergent spin diffusion coefficient. Our work enables the investigation of hydrodynamics in many-body quantum spin systems and is a step toward collective quantum sensing approaching the Heisenberg limit. Some additional information on aspects of collective behavior studied by NPQC research groups at Argonne National Laboratory and UCSB will also be presented in summary form.

III-S1-15: SPONTANEOUS SYMMETRY-BREAKING OF NONEQUILIBRIUM STEADY-STATES AND EMERGENCE OF ELECTRICALLY-INDUCED METAL-INSULATOR TRANSITIONS

[EFRC – reMIND] Fatima Jardali,[1] Adelaide Bradicich,[1] Timothy D. Brown,[2] R. Stanley Williams,[1] Suhas Kumar,[2] Patrick J. Shamberger[1]
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Spontaneous symmetry-breaking leading to electrical current density localization from a previously homogeneous distribution has been attributed to Negative Differential Resistance (NDR) in certain materials, which is postulated to occur because of the nonequilibrium thermodynamic force of entropy production minimization. However, this phenomenon has not been quantitatively predicted based on intrinsic material properties and an applied electrical stimulus. Here, we present an instability criterion for localization of current density and temperature from a thermal fluctuation in a parallel conductor model of a thin film that is subject to Newton's law of cooling. Electro-thermal localization accompanied by a decrease of entropy production is confirmed in a multiphysics simulation of current flow in a thin film. The instability criterion predicts conditions for spontaneous current density localization, relating symmetry breaking fundamentally to dynamical instability via Local Activity theory. Furthermore, we study the coexistence of electro-thermal localizations and metal insulator transitions (MITs) as device dimensions are varied in a 3D multiphysics model of a thin film device. We demonstrate that the localization of current density and temperature initiates even when the MIT precedes the emergence of steady-state electro-thermal localizations. Additionally, we find that there are critical device dimensions below which spatial inhomogeneities cease to appear. These results illustrate the key role localizations play in the onset of MITs, providing an explanation for electrically-induced behaviors and corresponding responses of thin films. Collectively, understanding this behavior points to a route to design desired electrical response in non-linear oscillator-type neuromorphic devices.

III-S1-16: MOLECULAR MAGNETIC QUANTUM MATERIALS

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AFFILIATED TALK – III-T1-11: Manipulating Molecular Entanglement Via Inelastic Scattering Of Itinerant Electrons

The Center for Molecular Magnetic Quantum Materials aims to discover, develop, and deliver the pivotal materials physics and chemistry knowledge of molecular magnetic quantum materials essential for quantum information technologies. Our goal is to transform molecular magnets from promising building blocks into viable *quantum materials* that are useful both for coherent quantum information systems and for quantum electron-spin devices. Our research activities cover magneto-electric couplings and magneto-striction in magnetic and electric field, spin-spin coupling, entanglement and decoherence, and spin coupling and entanglement at surfaces and in junctions due to molecule-substrate interactions. Starting with synthesizing a suite of molecules with desired properties, M^{2}QM experimentalists probe spin entanglement and decoherence using electron paramagnetic resonance at and away from the clock transition, measure magnetization at high magnetic field, electric polarization in a magnetic field and *vice versa* to study molecules

that demonstrate spatial-inversion-symmetry-breaking and/or spin-crossover behavior, and measure spin-dependent tunneling current across magnetic molecule vertical junctions. Our theory and computation team collaborates closely with experimental counterparts to advance understanding of control quantum behavior. As an example, we introduce a theoretical model of a molecular system hosting a few molecular spin qubits. These qubits can experience exchange interactions with itinerant electrons which allow inelastic scattering processes. In the context of quantum computing, such two-qubit interactions are necessary for implementing a universal set of quantum gates, but are difficult to control in molecular systems. We demonstrate that the entanglement between the qubits can be manipulated via the degrees of freedom of the itinerant electrons.

III-S1-17: FLOSIC FOR COMPLEX ANION-SOLVENT SOLUTIONS

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AFFILIATED TALK – III-T1-2: FLOSIC for Complex Anion-Solvent Solutions

Processes occurring in batteries, fuel cells, photovoltaics, and natural water-splitting complexes require computational capabilities that go beyond the most widely used density functional theory (DFT) methods and, specifically, that are able to treat ions in solution. The computational description of such processes must be able to correctly predict electron and ion transfer in solution or in the presence of dielectric media. However, due to unphysical self-interaction error (SIE), density functional approximations (DFAs) push electronic orbital energies well above experiment and may also predict wrong ordering of energy levels. The problem becomes especially severe in anionic systems, where positive DFA orbital energies incorrectly imply unbound electrons. In solution, electrons that should be tied to the anion can migrate, unphysically, onto neighboring solvent molecules Self-interaction corrected methods are needed. Recent developmental work aimed at improving the Fermi-Lowdin orbital self-interaction correction (FLOSIC) includes an implementation using complex orbitals (https://doi.org/10.1063/5.0091212), a quantum-learning method for automated determination of Fermi-Orbital Descriptors, (https://doi.org/10.1063/5.0135089) and significant new algorithms to enable simulations on a trianionic Cr complex, $[Cr(C2O4)]^{-3}$ embedded in a cluster of 117 water molecules. Our results in the latter calculation show that the HOMO of the trianion properly lies below the LUMO states of the water molecules. This poster presents a high-level view of why it is important to have automated methods for highly-charged ions in solution and introduces several new algorithms, encoded by the first author, that lead to a factor of 125 decrease in computer time required for FLOSIC calculations in the large-N limit.

III-S1-18: FIRST PRINCIPLES INVESTIGATION OF BULK SKYRMION FORMATION WITHIN THE 50% CO-DOPED Fe_5GeTe_2 LAYERED MAGNETIC METAL

[NPQC – EFRC] Jonathan T. Reichanadter[1,2], Jeff Neaton[1,2]
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The van der Waals-layered itinerant magnetic metal Fe_5GeTe_2 (F5GT) has recently garnered significant interest for its high-temperature and readily tunable magnetic ordering behavior. Moreover, its structural phase and interlayer stacking are highly sensitive to specific doping concentrations of Cobalt, leading to the formation of a polar structure at 50% doping that admits a zero-field neel-type skyrmion lattice at room temperature. Here we perform ab-initio density functional theory calculations across a variety of structural instances of Co-doped F5GT to elucidate the intricate coupling between atomic geometry, chemical composition, and magnetic order. Specifically, we examine the groundstates of different intra-layer structures as a function of total electron concentration to dissect the structural evolution of F5GT with Cobalt substitution. Next, bilayer formation calculations are performed that directly connect the Co-induced interlayer ordering to the AA' zigzag stacking phase. These structural findings are extended through magnetic moment and electronic structure calculations that provide new insight into how Co-substitution results in uncompensated in-plane Dzyaloshinskii-Moriya interactions that lead to skyrmion formation.

III-S1-19: EDGE OF CHAOS IN PHASE TRANSITION MATERIALS

[EFRC – reMIND] Suhas Kumar,[1] Timothy D. Brown,[1,2] R. Stanley Williams,[2] Brian Zutter,[1] Elliot J. Fuller,[1] Alec A. Talin,[1] Mahnaz Islam,[3] Eric Pop,[3] Alan Chiurun Zhang[1]
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AFFILIATED TALK – III-T1-5: Predictive Inverse Design of Neuronal Components

Nonlinear transport, such as in phase transition materials, has seen a surge of interest because of its utility in constructing neuronal components. However, designing the underlying material and the component structures for given requirements on component behavior is not trivial. This process requires a deep understanding of the fundamental relationships between the phase transition properties and neuronal behaviors. Such an understanding is presently a knowledge gap. In this work, we use the principle of local activity to build a model that connects neuronal behaviors (e.g., spiking, amplification of fluctuations, etc.) to phase transition properties (electrical, thermal, thermodynamic, etc.) and component size/structure. Crucially, the model can predict edge of chaos behavior, a previously hypothesized theoretical prediction of an operational region within locally active systems, wherein neuronal behaviors and biomimetic emergent computing is possible.

Our modeling framework, as a prototype, is capable of both forward design (i.e., prediction of component behaviors from material properties) and inverse design (i.e., predicting the material properties from desired component behavior). Using this model, on components built using a spin transition material ($LaCoO_3$), we demonstrate careful design of components capable of exhibiting local activity and edge of chaos. Further, we demonstrate neuron-like transistor-less and feedback-free amplification of dynamical signals from a single component, which is possible only because of isolation of local activity and edge of chaos.

III-S1-20: QUANTUM GEOMETRIC DETECTION AND MANIPULATION OF THE ANTIFERROMAGNETIC ORDER

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AFFILIATED TALK – III-T1-10: Harnessing quantum geometry for the detection and manipulation of antiferromagnetism

CATS has a goal to discover new transport and optical phenomena in magnetic topological materials. In particular, the interaction between polarized light and quantum topological materials is a highly intriguing topic in physics. In the magnetic topological insulator $MnBi_2Te_4$, CATS explored the light-matter-interaction in the antiferromagnetically coupled even-layers. Using circular polarized light, we report the surprising observation of helicity-dependent optical control of the fully compensated antiferromagnetic order for the first time. CATS has discovered that such optical control comes from the unique antiferromagnetic circular dichroism, which appears only in reflection but remains absent in transmission. As the antiferromagnetic spin texture breaks the inversion symmetry, it also leads to magnetic photocurrents that have been rarely studied before. CATS used linearly polarized light and found that it could generate an intrinsic photocurrent that was sensitive to external electric and magnetic fields. We explain these phenomena from the perspective of the unique quantum geometric properties in the material.

III-S1-21: EMISSION FREQUENCY CONTROLLED BY PRESSURE: A ROUTE TOWARDS OPTO-MECHANICAL TRANSDUCTION

[EFRC – CMQT] Eric A. Riesel[1], Rianna B. Greer[1], Michael K. Wojnar[1], Zhenxian Liu[2], Gregory D. Fuchs[3] Danna E. Freedman[1]
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Optomechanical transduction features theoretical transduction efficiencies nearly six orders of magnitude greater than that of electro-optic transduction. We envision a platform for optomechanical transduction in which paramagnetic molecules serve as electronic spin-based qubits with optical and phononic interfaces. Here molecules combine tunability with a high response to stress suggesting molecules featuring a spin/optical interface are the ideal optomechanical transduction agents. Performing optomechanical transduction within molecular samples requires strong coupling between mechanical stress and electronic structure. We set out to evaluate the sensitivity of a series of promising molecular qubit candidates to static stress by tracking the shifts in emission wavelength with pressure. These candidates are octahedral Cr(III) molecules known as “molecular rubies” due to their bright emission in the near-infrared region and narrow linewidths coupled to a S = 3/2 spin system. This series varies in ligand-based parameters like denticity, steric bulk, σ donator/π acceptor abilities, and symmetry. We find that complexes featuring ligands that possess significant π acceptor ability exhibit competitive charge-transfer-based emission under high hydrostatic stress conditions. Our results demonstrate that these molecules offer greater sensitivity to mechanical stress than that of solid-state rubies by more than an order of magnitude and that we can dramatically tune their electronic structure under moderate pressures – the first critical step towards optomechanical transduction.

III-S1-22: TOPOLOGICAL QUANTUM PHASE IN GROUP-IV ALLOY SYSTEM

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The discovery of topological quantum phases, such as topologically insulator, Dirac and Weyl semimetals, leads to renovated physics concepts. The exotic electronic and optical properties of those new quantum phases hold great potential to create a paradigm shift for device applications. Group-IV C, Si, and Ge with diamond cubic structure are band insulators/semiconductors with the conduction band bottom and valence band top originates from *s*- and *p*-orbitals, respectively. However, belonging to the same Group-IV in the periodic table, α-Sn is a zero-band gap semimetal and such natural band order is inverted, which places α-Sn in the vicinity of the topological phase boundary. Strain engineering can push α-Sn to topologically distinct phases such as Dirac semimetal and topologically insulator. Here we extend the tuning to alloying α-Sn with other group IV elements to realize various topological phases. Though the theoretical and experimental approaches, the highly collaborative efforts revealed possible topological phase in alloy systems, which shed light on the development of the novel topological quantum alloys for fundamental research and technology applications.

III-S1-23: AUGER-MEITNER RECOMBINATION IN SILICON FROM FIRST PRINCIPLES

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Auger-Meitner recombination is an intrinsic non-radiative carrier recombination process in semiconductors. In this process, an electron and a hole recombine across the band gap, transferring their energy via the Coulomb interaction to another electron or hole and exciting it to a high energy state. Auger-Meitner recombination is of broad interest as it has been shown to limit the maximum efficiency of solar cells, LEDs, bipolar transistors, and lasers. Despite its scientific and engineering importance, direct and phonon-assisted Auger-Meitner processes remain poorly understood in materials. In this poster we report on a recently-developed first-principles methodology to study both the direct and phonon-assisted Auger-Meitner recombination in indirect-gap semiconductors, and we demonstrate this new capability by investigating the microscopic origin of this effect in silicon. We show that our *ab initio* calculations are in excellent agreement with experimental measurements, and we demonstrate that phonon-assisted processes dominate the recombination rate in both n-type and p-type silicon. We also show how our methodology allows us to identify the contributions to Auger-Meither recombination from specific phonons and electronic valleys, and how this analysis tool offers new potential pathways to control Auger-Meitner rates via strain engineering [arXiv:2207.08028 and Phys. Rev. Lett. 2023, *in press*].

III-S1-24: FORMATION OF A SIMPLE CUBIC ANTIFERROMAGNET THROUGH CHARGE ORDERING IN A DOUBLE DIRAC MATERIAL

[EFRC – IQM] Vincent C. Morano[1], Tanya Berry[1], Thomas Halloran[1], Xin Zhang[1], Tyler J. Slade[2], Aashish Sapkota[2], Sergey L. Bud'ko[2], Weiwei Xie[3], Dominic H. Ryan[4], Zhijun Xu[2], Y. Zhao[5,6], Jeffrey W. Lynn[5], Tom Fennell[7], Paul C. Canfield[2], Collin L. Broholm[1], Tyrel M. McQueen[1]
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Double Dirac materials are a recently proposed class of topological materials in which nonsymmorphic symmetry protects a record 8-fold electronic degeneracy. Here we investigate the structural, magnetic, and electronic properties of $EuPd_3S_4$, a magnetic variant of the double Dirac candidate $LaPd_3S_4$ with 1:1 Eu^{2+}/Eu^{3+} mixed valency. We find a charge ordering transition at T_{CO}=340 K where J=7/2 Eu^{2+} and J=0 Eu^{3+} order on interpenetrating simple cubic sublattices. Density functional theory confirms that the loss of the nonsymmorphic symmetries at T_{CO} gaps out the 8-fold degenerate double Dirac state, giving two 4-fold degenerate Dirac points. We identify **k**=(πππ) antiferromagnetic order below the T_N=2.9 K transition, with the magnetic order living on the simple cubic Eu^{2+} sublattice. Depending on the moment direction, the magnetic order may gap the Dirac points to give 2-fold degenerate Weyl nodes. $EuPd_3S_4$ is perhaps the first example of a rare earth based simple cubic Heisenberg antiferromagnet. Application of a magnetic field at low temperature yields a spin flop at $\mu_0 H$=0.5 T, followed by the field-polarized paramagnetic state at $\mu_0 H$=3 T.

III-S1-25: INTERFACES AND HETEROSTRUCTURES OF UWBG MATERIALS

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The overarching goals of this topical area are to correlate interface structure, crystal polarity and chemistry across different UWBG materials systems and to understand the impacts on band offsets, interface states and charge transfer doping. Several growth techniques including MBE plasma CVD and MOCVD are providing samples that enable in-depth studies of a wide range of heterostructures including cubic-hexagonal crystal structures, IV/III-N interface chemistry and interface polarity. Characterization techniques including EPR, SEM, HRTEM, CL, electron holography, and SIMS, as well as *ab initio* simulations, are being used to deduce the alignment of band bending, to map electric fields near interfaces, and to develop an in-depth understanding of growth on different crystallographic surfaces. The preferential growth of cubic or hexagonal phases of boron nitride on diamond has been achieved by carefully controlling the hydrogen gas phase concentration. Thin AlF_3 films have been deposited on ultrawide bandgap diamond, AlN and BN using atomic layer deposition, and in-situ X-ray/UV photoelectron spectroscopy (XPS/UPS) was used to measure the electronic properties associated with the band alignment and interface

states, including work function, valence band maxima, NEA, and bandgap. The homoepitaxial growth of AlN on Al-polar AlN single crystals with a thin (~10nm) epitaxial GaN layer achieved the highest conductivity polarization-induced 2D hole gas yet reported. Python-based software has been developed for performing automated high-throughput first-principles calculations within the G_oW_o-BSE and GW_o-BSE framework to compute accurate optical gaps, fundamental gaps, band offsets, bandstructures, real-space wavefunctions, dielectric constants, and other excitonic properties.

III-S1-26: PHOTON-TO-MATTER CHIRAL QUANTUM STATE TRANSDUCTION USING MICROCAVITIES

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Photons are envisioned as ideal candidates for transporting quantum information. Their internal spin degree of freedom, which manifests as chiral optical polarization, can be coupled directly to matter-based excitations through chiroptical interactions. We will present our efforts aimed at controlling such interactions through the use of Fabry–Pérot (FP) microcavities. Importantly, cavity mirrors not only invert light propagation directions, but they also invert chiral optical polarization. This prompts the need for using materials that invert their optical response for counterpropagating light, which is an unusual material property. We have made significant progress in realizing multiple materials platforms that can accomplish this task, including organic thin films, inorganic crystals, monolayer transition-metal dichalcogenides, and plasmonic sheets. For some materials, the inverted chiroptical response emerges from topology, while for others it is due to an interference between linear birefringence and linear dichroism. For the latter, we introduced a theory based on which the chiroptical properties can be extracted from electronic structure calculations. This theory enabled us to design organic thin films that we embedded in FP microcavities, for which we experimentally and theoretically demonstrated a significant enhancement in the chiroptical interactions. We have further developed a quantum electrodynamical theory for chiral polaritons – hybrid light–matter excitations with high chiral selectivity – emerging when materials in FP microcavities reach the strong-coupling regime. We are working towards experimentally reaching this regime, which would open further opportunities to control photon-to-matter chiral quantum state transduction.

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Chemrxiv: 6480eb1ae64f843f4178ead5 (Under review at *Nat. Commun.*)

III-S1-27: SUPERFLUID DENSITY THROUGH A VAN HOVE SINGULARITY: Sr_2RuO_4 UNDER UNIAXIAL STRAIN

[EFRC – QSQM] Eli Mueller[1,2], Yusuke Iguchi[1], Fabian Jerzembeck[3], Marisa L. Romanelli[4], Jorge O. Rodriguez[4], Clifford W. Hicks[5], Yoshiteru Maeno[6], Vidya Madhaven[4], Kathryn A. Moler[1,2]

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AFFILIATED TALK – III-T1-4: Superfluid Density Through A Van Hove Singularity: Sr_2RuO_4 Under Uniaxial Strain

Strontium ruthenate (Sr_2RuO_4) is an archetype in the field of unconventional superconductivity. The metallic normal state from which superconductivity condenses is among the simplest and best understood among unconventional superconductors. Yet, after nearly three decades of strenuous effort, the pairing mechanism of the superconducting state remains unresolved. In recent years, uniaxial compression has emerged as a powerful new probe of the physics of Sr_2RuO_4. Uniaxial strain tunes the Fermi surface through a Van Hove singularity (VHS), resulting in a dramatic enhancement of the superconducting critical temperature, T_c, that peaks around 3.5K at the VHS. Here, we perform scanning SQUID microscopy on samples under uniaxial compression to study the low temperature behavior of the London penetration depth, $\lambda(T)$, as the system is strain tuned through the VHS. Our measurements show an approximately 15% enhancement in the zero-temperature superfluid density under strain with a maximum that coincides with the peak in T_c. When tuned near the VHS, we observe a T^2 dependence of $\lambda(T)$ below $0.5T_c$ instead of a T-linear dependence expected for line nodes in the gap. These results provide new input for the development of theories of unconventional superconductivity in Sr_2RuO_4.

III-S1-28: FRAGILE SUPERCONDUCTIVITY IN A DIRAC METAL

[EFRC – IQM] Chris J. Lygouras[1], Junyi Zhang[1], Jonah Gautreau[2], Mathew Pula[2], Sudarshan Sharma[2], Shiyuan Gao[1,3], Tanya Berry[1], Thomas Halloran[1], Peter Orban[1], Gael Grissonnanche[3], Juan R. Chamorro[1], Kagetora Mikuri[3], Dilip K. Bhoi[4], Maxime A. Siegler[1], Kenneth J.T. Livi[1], Yoshiya Uwatoko[4], Satoru Nakatsuji[1,4,5,6], B. J. Ramshaw[3,6], Yi Li[1], Graeme M. Luke[2,7], Collin L. Broholm[1,8], and Tyrel M. McQueen[1].
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AFFILIATED TALK – III-T1-9: Fragile Superconductivity in a Dirac Metal

Studying superconductivity in Dirac semimetals is an important step towards understanding quantum matter with topologically non-trivial order parameters. We report the properties of the superconducting phase in single crystals of the Dirac material $LaCuSb_2$ prepared by the self-flux method. Chemical and hydrostatic pressure drastically suppress the superconducting transition. Furthermore, due to large Fermi surface anisotropy, magnetization and muon spin relaxation measurements reveal Type-II superconductivity for applied magnetic fields along the **a**-axis, and Type-I superconductivity for fields along the **c**-axis. Specific heat confirms the bulk nature of the transition, and its deviation from single-gap *s*-wave BCS theory suggests multigap superconductivity. Our tight-binding model points to an anisotropic gap function arising from spin-orbital texture near the Dirac nodes, and provides an explanation for the appearance of an anomaly in specific heat well below T_C. Given the existence of superconductivity in a material harboring Dirac fermions, $LaCuSb_2$ proves an interesting material candidate in the search for topological superconductivity.

III-S1-29: MAGNETIC MOLECULE SYNTHESIS, ASSEMBLY INTO FUNCTIONAL MATERIALS, CHARACTERIZATION OF MAGNETIC AND QUANTUM PROPERTIES OF ASSEMBLED MATERIALS, SWITCHABILITY OF MAGNETIC/QUANTUM STATES, AND LONG COHERENCE OF DESIRABLE STATES

[EFRC – M^2QM] Garnet Chan[5], Hai-Ping Cheng[1,6], Shuang-Long Liu[1,6], Haechan Park[1], George Christou[1], Alexander Diodati[1], Ashlyn Hale[1], Stephen Hill[2,3], Mark Pederson[4], Michael Shatruk[2],
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Much effort is being concentrated in the M^2QM Center on using magnetic molecules (MM) as a platform for the generation, study, and control of magnetic/quantum properties relevant to next-generation technologies. This includes: quantum superposition and entanglement states in both solid and solution phases between metal ions within the same MM and within exchange-coupled $\{MM\}_n$ oligomers; the utility of such compounds as potential multi-qubit systems; understanding and control of quantum coherence through study of single MMs and their oligomers that exhibit quantum clock transitions (CTs) and thus are protected from magnetic decoherence sources; pulsed EPR spectroscopy of Gd qubits and qudits using specially designed Gd complexes with appropriate properties; and a number of additional initiatives. Inspired by the experimental progress in CT systems, theoretical studies have been carried out of model qubit systems at and away from CTs - decoherence caused by the proton bath, spin-orbit couplings, qubit-qubit couplings, and phonons have been assessed within the density matrix framework. In addition, model systems have been developed for the study of structures and properties of MMs, including single-molecule magnets (SMMs), on surfaces: this involves exchange-coupled mono-, di- or trinuclear MMs attached to the surfaces of large diamagnetic metal (M) oxide molecular clusters (M = Bi, Ce) as molecular analogues of MM qubits and SMMs on the surfaces of bulk metal oxides or their nanoparticles. All experimental studies are complemented by appropriate computations using DFT and associated methods.

III-S1-30: PROBING DYNAMIC AND MAGNETIC RESPONSES IN TOPOLOGICAL MATERIALS

[EFRC – CATS] Michael D. Smith[1], Victor L. Quito[2], Susanne Stemmer[3], Anton A. Burkov[4], Peter P. Orth[2,5], and Ivar Martin[1]
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Recent experimental progress in topological insulators and topological semimetals in the thin-film limit have provided intriguing experimental observations and posed a plethora of theoretical questions. CATS Thrust 2 has objectives to discover and understand these new phenomena and propose new ones that are enabled by thin films of topological materials. Here, we give two examples of these developments. First, we present a microscopic model for bilayer $MnBi_2Te_4$, a magnetic topological insulator, and derive the dynamical axion coupling due to the antiferromagnetic order as well as the axion dynamics. We will then discuss a more general theory of dynamical axions in the presence of counter-propagating electromagnetic waves - the Axion

Collider. We show that, for specific orientations of the counter-propagating electromagnetic waves, there is a large contribution to the power per unit volume deposited into the sample due to dynamical axions, which provides a promising avenue for condensed matter axion detection. We then discuss a microscopic theory for thin film Cd_3As_2 in the presence of a magnetic field, providing a theoretical framework for understanding recent experiments. We show that in the thin film limit Cd_3As_2 is a quantum spin hall insulator, and for sufficiently large in-plane magnetic fields can enter a 2D Weyl semimetal phase. We then investigate the effects of a tilted magnetic field by including an out of plane orbital field, explaining recent experimental data.

III-S1-31: DISORDER IN PROXIMITY COUPLED SUPERCONDUCTING NANO-ISLAND ARRAYS

[EFRC – QSQM] Emily N. Waite[1], Logan Bishop-Van Horn[2], Irene P. Zhang[2], Kathryn A. Moler[2], Nadya Mason[1]
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We study Josephson junction arrays comprised of many superconducting islands on the order of ~100 nm, where the composite system acts as a highly tunable superconductor. These arrays demonstrate a two-step transition to the superconducting regime, where the transition properties are modified by the spacing of the islands. In particular, by adding disorder to the positions of the islands during fabrication, the superconducting transition changes shape as the temperature is lowered. We describe transport of such disordered arrays, and also measurements using scanning superconducting quantum interference device (SQUID) susceptometry, which measures the local magnetic susceptibility. By comparing SQUID data to a Josephson junction network model, we observe that there are dissipation and nonlinearity in the response of the arrays that do not correspond to our model, demonstrating that the impact of disorder is more profound than our model is able to capture. Moving forward, we have several theoretical and experimental approaches to further investigate these results.

III-S1-32: SYNTHESIS AND CONTROL OF SHORT-RANGE ORDER IN SIGESN SEMICONDUCTOR

[EFRC – μ-ATOMS]: Dinesh Baral[1], Ezra Bussmann[2], Paul McIntyre[3], Andrew Minor[4], Shashan Misra[2], Gregory Salamo[1], Shui-Qing Yu[1], Yong-Hang Zeng[5], and Yuping Zeng[6]
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The goal of Thrust 2 is to demonstrate control over short range order (SRO) in the synthesis of SiGeSn with sufficient perfection, that the dependence of the intrinsic properties of SiGeSn on SRO can be measured, analyzed, and compared with modeling. This poster presents our progress toward this goal using two different synthesis approaches to achieve growth of different degrees of SRO and control over the spatial arrangement of SRO domains. The two approaches are: ***(1) Spontaneous,*** for which we utilized a strong background in synthesis using molecular beam epitaxy (MBE) by ***Y.H. Zhang*** with thermal sources and ***Zeng*** with e-beam sources, and chemical vapor deposition (CVD) by ***Yu*** with assisted plasma growth and ***McIntyre*** with nucleated low strain

wires. The poster will present the use of these methods by vary growth parameters, such as composition, strain, temperature, and deviation from thermal equilibrium, that have resulted in SiGeSn structures ready for characterization for SRO. ***(2) Stimulated:*** We have also investigated methods to stimulate SRO at the atomic scale using a new technique by ***Misra and Bussmann*** to precisely position atoms. In addition, ***Salamo*** has utilized MBE to digitally designed SRO while searching for SRO with scanning tunneling microscopy and ***Minor*** has developed a unique HRTEM/Raman system to form SRO domain patterns. The poster will present progress on the use of these techniques to produce SiGeSn samples with designed SRO. Based on year 1 results, the poster will present plans to reveal the correlation between growth and SRO in year 2.

III-S1-33: MANY-BODY EXCITED-STATE PHENOMENA IN MATERIALS: METHODS AND APPLICATIONS

[CMS – C2SEPEM] Steven G. Louie[1,2], James R. Chelikowsky[3], Jack Deslippe[2], Naomi Ginsberg[1,2], Felipe H. da Jornada[4], Jeffrey B. Neaton[1,2], Daniel Neuhauser[5], Diana Y. Qiu[6], Eran Rabani[1,2], Feng Wang[1,2], and Chao Yang[2]
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AFFILIATED TALK – III-T1-12: Diverse Nature of Excitonic States in Transition Metal Dichalcogenide Moiré Superlattices

Developing predictive, parameter-free methods and software tools to understand the science and applications of novel energy conversion and transfer processes in materials is a challenging quantum many-body problem, since in general excited-state phenomena are complex and accurate treatment of many-body interactions are essential. Here, we present some recent advances developed in our Center (C2SEPEM) using *ab initio* many-body field-theoretic techniques to address these challenges. We show recent progress in the development and validation of three open-source, production quality and highly scalable software packages – BerkeleyGW, StochasticGW and NanoGW – by combining novel theoretical concepts with advances in numerical methods and algorithms. For example, we demonstrate the capability of scaling unprecedented *GW* calculations to 10,000 electrons utilizing the entire Summit supercomputer at OLCF (more than 27,000 GPUs) achieving over 100 PFLOP/s of performance and time to solution to the order of minutes. Several breakthroughs in theory/method development and their applications are discussed. We developed a new *ab initio* time-dependent *GW* method to compute field-driven nonequilibrium and nonlinear excited-state phenomena including electron self-energy and excitonic effects. We showcase applications of this approach to understand novel Floquet-like band renormalization driven by excitonic field, and many-electron effects on second-harmonic generation. We developed new methods to describe exciton-phonon interactions and show that off-diagonal terms in the exciton-phonon coupling matrix elements are essential for predicting accurate exciton linewidths. Finally, we present a new pristine unit-cell matrix projection (PUMP) method to study excitons in large-area moiré superlattices. We predict moiré excitons that have a previously unidentified in-plane charge-transfer character.

III-S1-34: MODELING REACTIONS IN ORGANIC PHOTORESISTS EXPOSED TO EXTREME-ULTRAVIOLET LIGHT VIA A CHEMICAL REACTION NETWORK

[EFRC – CHiPPS] Jacob R. Milton,[1] Frances A. Houle,[1] Samuel M. Blau[1]
[1]*Lawrence Berkeley National Laboratory*

The most advanced semiconductor devices require extreme ultraviolet (EUV) light to create the patterns required for their manufacture by photolithography. Despite decades of research and development of EUV materials and processes, little is known about the chemistry these photons cause in photoresists due to the complexity of radical and ion reaction mechanisms in a condensed phase environment. Soft x-ray exposure is expected to generate a large number of different radicals and ions through both electron and photoionization processes, yielding too many possible species and reactions to investigate by hand. Thus, we use high-throughput workflows and filter-based reaction enumeration to generate a chemical reaction network that describes photoionization and electron ionization as well as downstream reactions. We are developing comprehensive reaction mechanisms for radiation-induced chemical and physical processes by populating multiscale stochastic kinetic simulations with first principles reaction properties. The model system under study is a random copolymer of poly(hydroxystyrene) and poly-(methylmethacrylate), triphenylsulfonium nonaflate, and triphenylsulfonium cyanobenzoate. This type of photoresist has been studied extensively for deep-uv photolithography, the main current patterning technology for semiconductors, and serves as a starting point for comparisons between the two exposure processes. This poster details the generation and refinement of the reaction network, interesting reactions and products predicted by the network, and current efforts to incorporate these reactions into kinetic models of radiation spurs generated after photon absorption.

III-S1-35: CHARACTERIZATION OF CHEMICAL AND PHYSICAL TRANSFORMATIONS IN MODEL RESISTS BY ELECTRON-GUN AND EUV EXPOSURES

[EFRC – CHiPPS] Maximillian W. Mueller[1], Qi Zhang[2], Terry McAfee[2], Patrick Naulleau[2], Dahyun Oh[1], Oleg Kostko[2], Cheng Wang[2]
[1]*San Jose State University;* [2]*Lawrence Berkeley National Laboratory*

State-of-the-art semiconductor lithography uses 13.5 nm, 92 eV extreme ultraviolet (EUV) light to expose photoresist materials and create chemical patterns on the nanometer scale. At these extremely low wavelengths light is not absorbed well by the photoresist, and when absorbed, the high photon energy leads to the emission of primary and secondary electrons with a wide range of energies. The formation of chemical patterns within the exposed photoresist is driven by these electrons, the mechanisms of which are not well defined. To characterize the physical structure of the chemical patterns in the film, we used Resonant Soft X-Ray Scattering (RSoXS), where soft x-rays tuned to an electron binding energy of carbon are diffracted through a photoresist patterned with a periodic structure similar to a diffraction grating. Using RSoXS data, the spacing, chemical contrast, and interfacial roughness are observed and compared with traditional microscopy data. To characterize electron-induced chemical transformations, we exposed photoresist films to a

broad electron beam ~8.5 mm in diameter with energies varied from 20 to 80 eV to study the effect of fast primary electrons as well as slower secondary electrons on photoresist materials. Chemical changes in the films were characterized in-situ during exposure using a quadrupole residual gas analyzer to identify the outgassed compounds from samples, and the time dependence of key chemical fragment masses was studied. The resulting thickness loss in the film was measured using ellipsometry, and relationships between energy, outgassing pressure, and thickness loss are shown.

III-S1-36: COMSUITE, A MODERN TOOL TO PREDICT PHYSICAL PROPERTIES OF CORRELATED MATERIALS COMBINING ELECTRONIC STRUCTURE METHODS WITH DYNAMICAL MEAN FIELD THEORY: APPLICATIONS TO THE TOPOLOGICAL SUPERCONDUCTOR, $FeSe_{0.5}Te_{0.5}$

[CMS – Comscope] Corey Melnick[1], Minjae Kim[2,3,4], Byungkyun Kang[1,5], Ran Adler[2], Walber Brito[2,6], Patrick Semon[1], Sangkook Choi[1,3], and Gabriel Kotliar[1,2]
[1]Brookhaven National Lab; [2]Rutgers University; [3]Korea Institute for Advanced Study; [4]Pohang University of Science and Technology; [5]University of Nevada, Las Vegas; [6]Universidade Federal de Minas Gerais
AFFILIATED TALK – III-T1-8: Theoretical RIXS Investigation of the Infinite Layers Nickelates

Strongly correlated systems are promising materials for energy applications and information technology. COMSCOPE, the center for material design and theoretical spectroscopy, has developed a new approach to combine electronic structure with dynamical mean field theory which is a) free from adjustable parameters; b) treats static and dynamic correlations on the same footing; c) uses a unique software engineering infrastructure enabling rapid software development on top of legacy codes; d) delivers correlation functions which can be directly measured experimentally; while e) offering multiple tradeoffs of speed and accuracy. We illustrate its power with an application to $FeSe_{1-x}Te_x$, a compound which realizes topological superconductivity, Majorana zero modes, time-reversal-symmetry breaking, a large s-wave superconducting gap, and strong spin orbit coupling, all in a single material. In this system both static and dynamic correlations are important. The theoretical photoemission spectra compare well with experimental observations. The electronic structure calculations provide new insights into the interplay of correlations and topology in this system. The proximity to an orbital selective Mott transition facilitates the appearance of the topological surface state by bringing the Dirac cone close to the chemical potential but destroys the Z_2 topological superconductivity when the system is too close to the orbital selective Mott phase.

III-S1-37: PHASES, STABILITY, AND PERFORMANCE OF FLUORITE-STRUCTURED OXIDES FOR NON-VOLATILE MEMORY

[EFRC – 3DFeM] Jon F. Ihlefeld,[1] Thomas E. Beechem,[2] Benjamin L. Aronson,[1] Samantha T. Jaszewski,[1] Fernando Vega,[2] Nikhat Khan,[1] Sebastian Calderon,[3] Elizabeth Dickey,[3] Kyle P. Kelley,[4] Leonard Jacques,[5] Songsong Zhou,[6] Jiahao Zhang,[6] Andrew Rappe,[6] Nikhil Shukla,[1] and Susan Trolier-McKinstry[5]
[1]University of Virginia; [2]Purdue University; [3]Carnegie Mellon University; [4]Oak Ridge National Laboratory; [5]The Pennsylvania State University; [6]University of Pennsylvania

Fluorite-structured ferroelectrics are attractive for non-volatile computer memory applications owing to their inherent compatibility with mainstream semiconductors, extreme thickness scalability, and relatively low processing temperatures. There are several outstanding challenges facing the material that prevent it from being implemented on a large scale. These include a lack of understanding of the mechanisms that stabilize the ferroelectric phase, polarization and leakage current instabilities related to endurance, and retention of data. In this poster, progress toward understanding phases present, phase stability, and performance of ferroelectric hafnia will be demonstrated. The ferroelectric phase is stable to ultra-thin thicknesses owing to an antipolar phonon mode that stabilizes the ferroelectric polar mode and this is driven by tensile strain. The presence of an antipolar orthorhombic phase in pure hafnium oxide films has been revealed by scanning transmission electron microscopy and optical characterization and found to exhibit true antiferroelectric behavior. The wake-up process arises from a phase transformation from this antipolar orthorhombic phase into the ferroelectric phase. Degradation of devices is driven by oxygen point defects that serve as trap sites and evolve with field cycling. Finally, oxygen vacancies that form due to oxygen scavenging by electrodes is shown to lead to memory retention loss due to imprint. Improvements via selection of electrode material, controlling oxygen point defect concentrations, and biaxial stress enhance performance and position the material to be a key contributor to low energy computer memory.

III-S1-38: SPIN-OSCILLATOR BASED ON QUANTUM MATERIALS FOR NEUROMORPHIC DEVICES AND NETWORKS

[EFRC – Q-MEEN-C] Padma Radhakrishnan[1], Robin Klause[2], Biswajit Sahoo[3], Haowen Ren[1,3], Jonathan Gibbons[2], Dayne Sasaki[4], Vivek Amin[6], Hanu Arava[7,8], Amanda Petford-Long[7,8], Mark D. Stiles[9], Julie Grollier[5], Yayoi Takamura[4], Axel Hoffmann[2], Eric E. Fullerton[3], and Andrew D. Kent[1]
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Spin Hall nano-oscillators (SHNOs) based on quantum materials are promising building blocks for complex oscillator networks that can emulate neural network functionality. We present SHNOs incorporating correlated materials and oxides that 1) create new types of spin-orbit torques, 2) have a fixed frequency, 3) enable larger excitation volumes and output signals, and 4) permit signal classification. Ordinary spin-orbit torques are limited to driving dynamics of in-plane magnetizations with highly anisotropic magnon dispersions, limiting efficient coupling in two-dimensional SHNO arrangements. This limitation can be overcome by using unconventional spin-orbit torques from materials that lack inversion symmetry due to their magnetic order. We investigated this possibility in FeRh, which reveals highly efficient non-conventional torques in its antiferromagnetic phase and Cr_3Pt, where the magnetic structure can be modulated via chemical ordering. In addition, IrO_2 was shown to produce a large damping-like torque associated with large spin-orbit coupling that allows the hybridization of the 5d electrons of the oxide with the itinerant electrons of a CoFeB layer. Oscillator-based neural networks operating through frequency multiplexing require SHNOs with a fixed frequency, which is not usually the case due to phase-amplitude coupling. We showed experimentally that the perpendicular anisotropy of SHNOs can

be tuned to give rise to fixed-frequency SHNOs. We further demonstrated a new type of hybrid SHNO based on a permalloy ferromagnetic-metal nanowire and low-damping ferrimagnetic insulator (lithium aluminum ferrite) with higher quality factors and output power than conventional SHNOs. Finally, we present demonstrations of reservoir computing for signal classification tasks using SHNOs.

III-S1-39: WHAT'S WRONG WITH DENSITY FUNCTIONAL THEORY CHEMICAL REACTION BARRIERS? A SUMMARY OF RECENT SELF-INTERACTION-CORRECTED STUDIES USING THE FLOSIC METHOD

[CCS – FLOSIC] Prakash Mishra[1], Priyanka Shukla[2], Aaron D. Kaplan[3], Chandra Shahi[3], John P. Perdew[3], Tunna Baruah[1], Rajendra R. Zope[1], J. Karl Johnson[2], Yashpul Singh[4], and Koblar A. Jackson[4]
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Computational predictions of chemical reaction barriers using density functional theory (DFT) methods typically underestimate reference or experimentally measured values of the barriers. In some cases the underestimates are so severe that the reactions are predicted to be barrierless. This poor performance is understood to reflect the effects of self-interaction errors in density functional approximations (DFAs). Recent studies[1-3] in the FLOSIC Center bring greater insight and understanding into the nature of these errors and establish the extent to which they can be overcome through self-interaction corrections. The studies use the BH76 benchmark set of reaction barriers and address a number of questions: How are errors in barrier height predictions affected by using more sophisticated DFAs? How successfully does the Fermi-Löwdin orbital self-interaction correction (FLOSIC) method improve DFA barrier heights and what do the calculations imply about the primary source of self-interaction error in the DFA calculations? And what is the role of density-driven errors in determining DFA barrier heights?

[1]Mishra et al. *Study of self-interaction-errors in barrier heights using locally scaled and Perdew-Zunger self-interaction methods*, Journal of Chemical Physics **156**, 014306 (2022)
[2]Shukla et al. *How do self-interaction errors associated with stretched bond affect barrier height predictions?*, J. Phys. Chem. A **127**, 1750 (2023).
[3]Kaplan et al. *Understanding density driven errors via reaction barrier heights,* J. Chem. Theor. Comput. **19**, 532 (2023).

III-S1-40: DESIGN OPTIMIZATION OF UWBG POWER DEVICES: A CO-DESIGN APPROACH

[EFRC – ULTRA] Robert Kaplar[1], Stephen Goodnick[2], Srabanti Chowdhury[3], Jack Flicker[1], Arunima Singh[2], H. Grace Xing[4], Marco Saraniti[2], Martin Kuball[5], Jonah Shoemaker[2], Harshad Surdi[2], Reza Vatan[2], Lee Gill[1], Mihai Negoita[1], Joseph Dill[2], Kelly Woo[3], Andrew Binder[1], Tathagata Biswas[2]
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AFFILIATED TALK – III-T1-6: Leveraging the resilience of diamond with its unique material properties towards Next Generation Grid innovation

The goal of co-design thrust within the ULTRA EFRC is to connect fundamental material properties of ULTRA materials to their impact on end-use application in power conversion systems, since the incorporation of UWBG power diodes will be driven by system-level benefits. A traditional approach is to compare materials systems using a standard Figure of Merit (FOM), however, this approach is by design agnostic to the nuances of different materials systems, including device types, device composition based on usage, and specific phenomena in materials systems. We must go beyond the FOM approach to compare the expected power and frequency performance of different ULTRA materials in specific device and circuit topologies. This allows us to understand not only what material properties are most important, but also the relative application space best suited for each material. To understand the full suite of potential device performance (in the absence of mature device technologies in ULTRA materials), we have developed an optimization tool that takes drift thickness and doping as input and minimizes system power dissipation for different materials systems and device types, incorporating effects that are important for UWBG semiconductors, such as Mott-Gurney conduction and incomplete dopant ionization, into the optimization. This optimized device design in then paired with technology computer aided design (TCAD) device to extract relevant device (diode, FET, superjunction, etc.) operational parameters that can be utilized in circuit simulation to give estimated power conversion system operational characteristics. This process allows for realistic material transport parameters based on measured and first principles simulation to directly impact expected behavior in end-use systems.

III-S1-41: ULTRAFAST WAVEFRONT SHAPING VIA SPACE-TIME REFRACTION

[EFRC – PTL] Q. Fan[1], A. M. Shaltout[1], J. van de Groep[2], M. L. Brongersma[1] and A. M. Lindenberg[1,3]
[1]Stanford University; [2]University of Amsterdam, Netherlands; [3]SLAC National Accelerator Laboratory

A myriad of metasurfaces have been demonstrated that manipulate light by spatially structuring thin optical layers. Manipulation of the optical properties of such layers in both space and time can unlock new physical phenomena and enable new optical devices. Examples include photon acceleration and frequency conversion, which modifies Snell's relation to a more general, nonreciprocal form. Here, we combine theory and experiment to realize wavefront shaping and frequency conversion on subpicosecond time-scales by inducing space-time refractive index gradients in epsilon-near-zero (ENZ) films with femtosecond light pulses. We experimentally tune wavefront steering by controlling the incident angle of the beams and the pump–probe delay without the need for nanostructure fabrication. As a demonstration of this approach, we leverage the ultrafast, high-bandwidth optical response of transparent oxides in their ENZ wavelength range to create large refractive index gradients and new types of nonreciprocal, ultrafast two-dimensional (2D) optics, including an ultrathin transient lens.

III-S1-42: LUMINESCENT CONCENTRATOR DESIGN FOR HIGH AMBIENT CONTRAST RATIO, HIGH EFFICIENCY DISPLAYS

[EFRC – PTL] O. Cifci[1], M. Yoder[1], L. Xu[1], H. Chen[1], C. Beck[1], J. He[1], B. Koscher[1], Z. Nett[2], J. Swabeck[2], A. Paul Alivisatos[2], R. Nuzzo[1], P. Braun[1]
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A key display characteristic is its efficiency (emitted light power divided by input power). While display efficiencies are being improved through emissive (e.g., quantum dot and organic light emitting display (OLED) designs, which remove the highly inefficient color filters found in traditional liquid crystal displays (LCDs), polarization filters, which block about 50% of the light, remain required to inhibit ambient light reflection. We introduce a luminescent cavity design to replace both the color and polarization filters. Narrow-band, large Stokes shift, CdSe/CdS quantum dot emitters are embedded in a reflective cavity pixel element with a small top aperture. The remainder of the top surface is coated black reducing ambient light reflection. A single pixel demonstrates an extraction efficiency of 40.9% from a cavity with an 11% aperture opening. A simple proof-of-concept multi-pixel array is demonstrated.

Poster Session 2

III-S2-01: UNDERSTANDING AND ENGINEERING FERROELECTRICITY IN WURTZITE FERROELECTRICS

[EFRC – 3DFeM] Joseph Casamento[1], John Hayden[1], Devin Goodling[1], Quyen Tran[1], Xiaojun Zheng[1], Leonard Jacques[1], Fan He[1], Albert Suceava[1], Rui Zu[1], Sebastian Calderon[2], Steven Baksa[1], Drew Behrendt[3], Yongtao Liu[4], Giovanni Esteves[5], Michael David Henry[5], Elizabeth Dickey[2], Kyle Kelley[4], Sergei Kalinin[6], Joseph Shepard[7], Andrew Rappe[3], Ismaila Dabo[1], Venkatraman Gopalan[1], Thomas Jackson[1], Susan Trolier-McKinstry[1], Jon-Paul Maria[1]
[1]Pennsylvania State University; [2]Carnegie Mellon University; [3]University of Pennsylvania; [4]Oak Ridge National Laboratory; [5]Sandia National Laboratories; [6]University of Tennessee, Knoxville; [7]Applied Materials Inc.

Detailed structural, chemical, electrical, and optical measurements have demonstrated the complex physics and structure-property relationships in wurtzite materials. Electron microscopy studies have shown the intermediate phase during polarization reversal is different than the nonpolar layered hexagonal phase for $Al_{1-x}Sc_xN$ alloys. These results provide the possibility to engineer different switching mechanisms in wurtzite ferroelectrics based on chemical and local bonding environment modifications. Scanning probe microscopy studies indicate the presence and ability to control surface electrochemical reactions during polarization reversal by modifying measurement conditions. Ferroelectricity was confirmed down to 10 nm thickness in $Al_{1-x}B_xN$ alloys on CMOS compatible metals, expanding the material system into new applications and toward integrated memory. $Zn_{1-x}Mg_xO$ alloys, with larger ionicity in the interatomic bonds and different solubility limits than AlN based compounds, show ~4x larger non-linear optical responses and very importantly, show ~2x lower coercive fields (~2.5 MV/cm) than $Al_{1-x}B_xN$ alloys (~5 MV/cm). The oxide and nitride wurtzites show large, temperature stable polarizations (>80 $\mu C/cm^2$), along with pronounced wake-up character. Both families of materials show outstanding data retention, but are currently limited in cycling endurance.

III-S2-02: STM INVESTIGATION OF ENGINEERED 1D CORRELATED ELECTRONIC STATES

[NPQC – EFRC] Tiancong Zhu[1,2], Canxun Zhang[1,2], Salman Kahn[1], Tomohiro Soejima[1], Wei Ruan[1], Yan-Qi Wang[1], Hsinzon Tsai[1,2], Shuopei Wang[3,4], Tianye Wang[1], Franklin Liou[1,2], Kenji Watanabe[5], Takashi

Taniguchi[5], Alex Zettl[1,2], Feng Wang[1,2], Michael P. Zaletel[1,2], Jeffrey B. Neaton[1,2], Alex. Weber-Bargioni[2], Z. Q. Qiu[1,2], Guangyu Zhang[3,4], Joel E. Moore[1,2], Michael F. Crommie[1,2]
[1]University of California at Berkeley, Berkeley; [2]Lawrence Berkeley National Laboratory; [3]Chinese Academy of Sciences, China; [4]Songshan Lake Materials Laboratory, Dongguan; [5]National Institute for Materials Science, Japan

We provide two examples and demonstrate the capability of scanning tunneling microscopy (STM) and scanning tunneling spectroscopy (STS) as powerful tools for comprehending and manipulating diverse correlated electronic states in 1D electronic systems (1DES). In engineered atomic-sharp mirror twin boundaries (MTB) of 1H-$MoSe_2$, we show direct characterization of the Coulomb interaction strength through gate-tuned STS. We also show that such repulsive Coulomb interaction can lead to the formation of Tomonaga-Luttinger liquid (TLL), and demonstrate the unique spin-charge separation, a Hall-mark of the TLL behavior, through spectroscopic imaging. In twisted monolayer-bilayer graphene (tMBLG), we show the capability to directly visualize the 1D chiral interface states that leads to the quantized Hall conductance in this quantum anomalous Hall (QAH) system. Through the combination of global electrostatic gating and local tip-induced quantum dots, we also demonstrate for the first time the full control of the spatial location and chirality of these correlation-driven chiral interface states, which opens door to electrical programmable QAH chiral edge states for novel electronic devices and advancements in information science.

III-S2-03: STRONG PHOTON-MAGNON COUPLING USING A LITHOGRAPHICALLY DEFINED ORGANIC FERRIMAGNET

[EFRC – CMQT] Qin Xu[1], Hil Fung Harry Cheung[1], Donley S. Cormode[2], Tharnier O. Puel[3], Huma Yusuf[2], Iqbal B. Utama[4], Dmitry Lebedev[4], Srishti Pal[1], Michael Chilcote[1], Mark C. Hersam[4], Michael E. Flatté[3], Ezekiel Johnston-Halperin[2], and Gregory D. Fuchs[1]
[1]Cornell University; [2]The Ohio State University; [3]University of Iowa; [4]Northwestern University

We demonstrate a cavity-magnonic system composed of a superconducting microwave resonator coupled to a magnon mode hosted by the organic-based ferrimagnet vanadium tetracyanoethylene ($V[TCNE]_x$). Our work is motivated by the challenge of scalably integrating a low-damping magnetic system with planar superconducting circuits. We take advantage of the properties of $V[TCNE]_x$, which has ultra-low intrinsic damping, can be grown at low processing temperatures on arbitrary substrates, and can be patterned via electron beam lithography. Our devices operate in the strong coupling regime, with a cooperativity exceeding 10^3 at T~0.4 K, suitable for scalable quantum circuit integration. This work paves the way for high-cooperativity hybrid quantum devices in which magnonic circuits can be designed and fabricated as easily as electrical wires.

III-S2-04: OPTICAL AND TRANSPORT MEASUREMENTS OF 2D MAGNETIC MOLECULE FILMS

[EFRC – M^2QM] J. Koptur-Palenchar[1], X. Jiang[1], C. Bunker[1], Shuang-Long Liu[1], Duy Le[3], XX Zhang, M. Shatruk[2], A. Hebard[1], Talat Rahman[3], HP Cheng[1,4], XG Zhang[1]
[1]University of Florida; [2]Florida State University; [3]University of central Florida; [4]Northeastern University

We study a new type of 2D material composed of discrete magnetic molecules, bound by anisotropic van-der-Waals interactions into a 2D packing. For an exfoliated [Fe(tBu2qsal)2] (FTBQS) film, optical spectroscopy suggests the few-layered molecules preserve the temperature-induced spin-crossover switching observed in the bulk form but show a drastic increase in thermal hysteresis unique to these thin 2D molecule assemblies. In a second study, tunnel heterojunctions are formed by sandwiching 1 nm-thick MnPc thin films between ferrimagnetic NiCoO conducting substrates and eutectic (EGaIn) top electrodes. Differential conductance (dI/dV) measurements reveal a combination of magnetic impurity scattering induced zero-bias anomalies, surface magnon scattering, and strong oscillations in dI/dV due to Coulomb blockade, suggesting the formation of 2D molecular islands.

III-S2-05: MICCoM: Recent Progress and New Directions

[CMS- MICCoM] Giulia Galli[1,2], Maria Chan[1], Juan de Pablo[1,2], Andrew Ferguson[2], Marco Govoni[3], Francois Gygi[4], Joseph Heremans[1], Jonathan Whitmer[5], Jie Xu[1]
[1]Argonne National Laboratory; [2]University of Chicago; [3]University of Modena and Reggio Emilia, Italy; [4] University of California Davis; [5]Notre Dame University

AFFILIATED TALK – III-T2-8: Engineering the formation of spin-defects from first principles

The Midwest Integrated Center for Computational Materials (MICCoM) develops and disseminates interoperable computational tools – open-source software, data, simulation methods, and validation procedures – enabling the community to simulate and predict the properties of functional materials. Our focus is on two areas: solid-state materials for quantum technology applications and materials on low power electronics. The former is a class of systems with potential impact in designing qubits, quantum sensors, and quantum communication's devices. The latter class of materials is related to the field of microelectronics, with potential, long term impact on semiconductor manufacturing.

The Center's scientific strategy is built under the premise that the functionality of materials depends critically on the integration of dissimilar, often defective components and on the interfaces that arise between them. Hence our emphasis is placed on understanding and characterizing defects and interfaces, and on predicting finite-temperature spectroscopic and coherence properties.

The description of dissimilar and defective components requires the development of first-principles electronic-structure methods, coupled to appropriate dynamical descriptions of matter and advanced sampling techniques, in order to predict multiple properties of complex systems and to capture the relevant length and time scales of importance to materials design. A key hallmark of MICCoM is the coupling of classical and quantum codes, together with their use on several high-performance and quantum computing architectures.

The Center's has been engaged since its inception in verification, validation and benchmarking activities for multiple properties of materials and is fostering close collaborations between theory and experiments.The 250-word abstract of the poster may not contain figures. All abstracts will be

compiled into a single electronic abstract book using the font, font size, margins, and line spacing in this document.

III-S2-06: MULTISCALE CHARACTERIZATION TECHNIQUES FOR NEUROMORPHIC MATERIALS

[EFRC – Q-MEEN-C] Alexandre Pofelski[1], Elliot Kisiel[2], Henry Navarro[2], Tianxing Wang[2], Erbin Qiu[2], Zahir Islam[3], Oleg Shpyrko[2],Shriram Ramanathan[4], Ivan K. Schuller[2], Alex Frañó[2], and Yimei Zhu[1]
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Quantum materials demonstrated great potential to execute energy-efficient computing tasks when interconnected in a neural network setting. Knowledge gaps remain regarding the micro/mesoscale connectivity and tunability to maximize the energy efficiency, pushing the development of novel characterization techniques. The neuromorphic functionalities are challenging to characterize because of their non-linear dependence on external stimuli, their stochastic character, and their high degree of variability (natural or engineered). In-situ and/or in-operando quantitative methods are therefore required to capture the mechanisms of interest at the appropriate length scale. Understanding of both local and global impacts of the studied phenomena is fundamental to designing energy efficient neuromorphic applications.

We present here our recent instrumental and methods development contributing to a better understanding of the prototypical vanadium dioxide (VO_2) metal-insulator transition (MIT) at different length scales. Starting from the mesoscale, Dark-Field X-ray Microscopy (DFXM) utilizes an x-ray objective lens in the diffracted beam to spatially resolve large areas (50x50 μm^2) at submicron resolutions. We studied the filament formation and nucleation within VO_2 neuromorphic devices and probed the underlying substrate indicating strong interactions on the substrate as the result of filament formation. Pursuing further, to the nanometer length scale, we observed in-situ the VO_2 MIT under radio frequency excitation inside a Transmission Electron Microscope (TEM) and obtained preliminary results regarding the MIT dynamics at picoseconds timescale using the laser-free pulsed TEM. Finally reaching the sub-nanometer resolution, we utilized electron energy loss spectroscopy to measure quantitatively the selective doping of VO_2 with hydrogen modulating the MIT.

III-S2-07: DEVELOPING LOCAL PROBES TO UNDERSTAND POLARIZATION PHENOMENA IN WURTZITE AND FLUORITE FERROELECTRICS

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AFFILIATED TALK – III-T2-1: Atomic Scale Polarization Switching in Wurtzite Ferroelectrics

Domain wall dynamics, including nucleation, motion, and pinning on structural defects define fundamental behaviors of ferroelectrics such as coercive bias, time dependent responses, nonlinearities, enhanced electromechanical and dielectric responses, amongst many others. Understanding the underlying mechanisms responsible for these fundamental behaviors is vital for the development of back-end-of-the-line compatible ferroelectric materials including $Hf_{1-x}Zr_xO_2$, $Al_{1-x}B_xN$, and $Zn_{1-x}Mg_xO$. Moreover, understanding the polarization dynamics in these materials requires probing these phenomena on the local level. Here, we apply a multimodal approach by implementing and cross correlating atomic force microscopy, scanning transmission electron microscopy, and various local optical techniques including nano-Fourier transform infrared spectroscopy, second harmonic generation, and photoluminescence. This allows us to leverage a variety of probe sizes ranging from 0.1 to 100 nm, to better understand how the functional properties are correlated with local intrinsic and extrinsic defects, ultimately enabling the further development of relevant materials. Furthermore, we develop and implement machine learning based scanning probe microscopy to investigate the correlation between local polarization hysteresis, nonlinearities with domain structures, and domain growth mechanisms, allowing for high-throughput characterization and understanding of local polarization phenomena. The combination of these advanced characterization techniques enables us to gain fundamental insight into the factors that affect ferroelectric switching and how ferroelectric domains nucleate and grow in $Hf_{1-x}Zr_xO_2$, $Al_{1-x}B_xN$, and $Zn_{1-x}Mg_xO$ material systems.

III-S2-08: AVOIDING DECOHERENCE IN MOLECULAR MAGNETIC QUANTUM SYSTEMS

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Understanding complex molecular qubits requires model Hamiltonians derived from electronic quantum calculations. Interactions necessary to describe the ground- and low- energy excitations, include spin-spin and/or spin-orbit effects and field-, charge-, or phonon- induced coupling between interesting states. In a recent extension of the center's interest in frustrated triangular molecular magnets, where lack of inversion symmetry allows an external electric field to couple directly to the chiral spin-coupled ground state, Pederson et al reported computations of spin-electric coupling in a {V3} triangular spin-coupled magnetic molecule. This coupling provides efficient means for manipulating spin states for quantum information processing. Shatruk et al are working toward synthesis. Alternatives for charge-induced switching exist (Rahman et al). For qubits governed by spin-orbit coupling, the effective Hamiltonian depends on Stevens Operators with coefficients derived from constrained DFT. Cheng and Chan, extended this methodology via a generalized spin-orbital Kohn-Sham picture, and created a series of low-energy Kohn-Sham determinants that correspond to different linear combinations of |JM> states. Resulting expectation values and a set of linear equations determine spectral parameters. Initial applications to an Er complex are encouraging and the focus is now on the Ho clock qubit. A third application,

focuses on low-energy excitons or spin-crossover (Trickey et al) for realization of two-state magnetic qubits. The full suite of M^{2}QM computational and machine-learning methods are deployed to determine when ligands (Hennig & Zhang et al) and inter- and intra- molecular qubit coupling (Cheng & Pederson et al) allow for qubits that are devoid of decohering mechanisms.

III-S2-09: CHEMOMECHANICAL MODIFICATION OF QUANTUM EMISSION IN MONOLAYER WSe_2

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AFFILIATED TALK – III-T2-10: Chemomechanical Modification of Quantum Emission in Monolayer WSe_2

Two-dimensional (2D) materials have attracted attention for quantum information science due to their ability to host single-photon emitters (SPEs). Although the properties of atomically thin materials are highly sensitive to surface modification, chemical functionalization remains unexplored in the design and control of 2D material SPEs. Here, we report a chemomechanical approach to modify SPEs in monolayer WSe_2 through the synergistic combination of localized mechanical strain and noncovalent surface functionalization with aryl diazonium chemistry. Following the deposition of an aryl oligomer adlayer, the spectrally complex defect-related emission of strained monolayer WSe_2 is simplified into spectrally isolated SPEs with high single-photon purity. Density functional theory calculations reveal energetic alignment between WSe_2 defect states and adsorbed aryl oligomer energy levels, thus providing insight into the observed chemomechanically modified quantum emission. By revealing conditions under which chemical functionalization tunes SPEs, this work broadens the parameter space for controlling quantum emission in 2D materials.

III-S2-10: A HOLISTIC APPROACH TO HIGH PRECISION PATTERNING SCIENCE

[EFRC – CHiPPS] Emma Vargo[1], Stacey F. Bent[2], Samuel M. Blau[1], Weilun Chao[1], Brett A. Helms[1], Frances A. Houle[1], Oleg Kostko[1], Patrick P. Naulleau[1], Paul F. Nealey[3,4], Christopher K. Ober[5], Dahyun Oh[6], Rachel A. Segalman[7], Cheng Wang[1], Ricardo Ruiz[1]
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Despite continuous advancements in patterning technology and the introduction of EUV lithography, achieving high-precision patterning with EUV photon energy (at 91.6 eV) remains a significant challenge for enabling large-scale semiconductor manufacturing. To tackle these grand challenges in patterning science, the Center for High Precision Patterning Science (CHiPPS), a DOE-funded Energy Frontier Research Center, is dedicated to designing materials and processes that can efficiently harness high-energy photons for selective chemical reactions, enabling atomically precise patterning at the nanoscale. Additionally, CHiPPS aims to mitigate stochastic effects arising

from variations at the photon, atom, and molecular scales, which currently limit sub-nanometer level precision.

CHiPPS adopts a holistic approach to patterning science by exploring the fundamental interactions between light and matter. It proposes co-designed materials and processes for precision patterning, including sequence-defined and structured hybrid photoresists, molecular-level control of solvation steps, self-assembling materials for minimizing stochastic impacts, and molecularly precise and selective pattern transfer. To support its research activities, CHiPPS utilizes a world-class EUV patterning research facility at LBNL and benefits from a unique X-ray characterization setup at the Advanced Light Source (ALS).

In this poster, we summarize CHiPPS' holistic approach to advance patterning science and to revolutionize semiconductor patterning, pushing the boundaries of nanoscale precision manufacturing and paving the way for future advancements in the field.

III-S2-11: ELECTRICAL TRANSPORT STUDY FOR GESN (GE RICH) AND SNGE (SN RICH) ALLOYS

[EFRC – μ-ATOMS] Priyanka Petluru[1], Shang Liu[2], Jifeng Liu[2], Tyler McCarthy[3], Yong-Hang Zhang[3], Dinesh Baral[4], Shui-Qing Yu[4], Jin Hu[4], Izak Baranowski[3], Dragica Vasileska[3], Haochen Zhao[5], Yuping Zeng[5], Ezra Bussmann[1], Michael Lilly[1], Tzu-Ming Lu[1]
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As short-range order of Ge and Sn atoms is expected to impact electrical properties such as the band gap, effective mass, and mobility, the goal of this research is to investigate these characteristics through electrical transport measurements. In order to successfully undertake all aspects of this project, a collaboration between Sandia National Laboratories and the University of Delaware, Dartmouth College, Arizona State University, and the University of Arkansas was necessary. As part of this joint effort, Sandia was primarily responsible for the fabrication of devices and electrical characterization measurements, including low-temperature current and Hall measurements. Additionally, the university partners' growth capabilities were utilized to provide the materials, with the theory and modeling also provided by Arizona. Furthermore, quantum transport measurements were also performed by Arkansas, while Delaware provided SIMS data. A set of thin GeSn films on Si substrates provided by Dartmouth were fabricated into transistors, with preliminary electrical measurements indicating the ability to modulate the drain-source current as a function of gate voltage. As these GeSn films were not grown epitaxially, these results demonstrate the potential of this material to be grown on substrates other than silicon. In addition, the fabrication of devices on Sn-rich SnGe alloys grown by Arizona proved to be challenging, as a result of the low temperatures necessary to prevent the transformation of α-Sn to β-Sn, though leveraging alternative processes such as vacuum curing has proven to be effective. The overall outcome of this research will have a significant impact on the synthesis of semiconductors for microelectronics.

III-S2-12: NEUROMORPHIC NETWORKS WITH QUANTUM MATERIALS

[EFRC – Q-MEEN-C] Ravindra S. Bisht[1], Jaeseoung Park[2], Yuhan Shi[2], Sangheon Oh[2], Haoming Yu[3], Chen Wu[2], Nikhil Tilak[1], Sylvie Rangan[1], Tae J. Park[3], Yifan Yuan[1], Sarmistha Das[2], Uday Goteti[2], Lexi Velas[6], Hee Taek Yi[1], Hussein Hijazi[1], Abdullah Al-Mahboob[4], Jerzy T. Sadowski[4], Hua Zhou[5], Seongshik Oh[1], Eva Y. Andrei[1], Monica T. Allen[2], Pavel Salev[2], Javier del Valle[2], Marcelo Rosenberg[2], Ivan K. Schuller[2], Duygu Kuzum[2], Alex Frañó[2], Robert C. Dynes[2], Shriram Ramanathan[1], and Catherine Schuman[6]
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AFFILIATED TALK – III-T2-5: Non-Local Interactions in Hydrogenated Perovskite Nickelate Synaptic Networks

There is a tremendous opportunity to leverage inherent properties of quantum materials to capture key behaviors of synapses, such as plasticity, and neurons, in an integrated energy efficient way. We showcase three examples of synapses and neurons based on quantum materials presenting their behavior when integrated into larger networks composed of these devices. In our first example, we demonstrate plasticity, a mechanism essential to learning, in hydrogenated perovskite nickelate synaptic networks. The type of plasticity exhibited in these networks is both local and non-local (i.e., impacting synapses not directly connected). Non-local plasticity mechanisms have been largely unexplored algorithmically because of lack of ability to implement them. With this demonstration, these mechanisms are now feasible and can be investigated at the algorithmic level. In our second example, we demonstrate the ability of several nickelate devices to be connected showcasing their ability to perform signal integration efficiently and in future can be implemented in neural nets in hardware. In our third example, we show the integration of Mott neurons with Ag CBRAM crossbars, acting as synaptic devices. In this case, we showcase performance on a real-world application and demonstrate extreme energy efficiency with near ideal software accuracy. These examples demonstrate that there are a wide variety of quantum materials each with unique advantages that can be used to compose neuromorphic systems. In the future, we will develop benchmarks and metrics to further understand and compare the performance of these systems, both with each other and with conventional CMOS implementations.

III-S2-13: LONG-RANGE, NON-LOCAL SWITCHING OF SPIN TEXTURES IN A FRUSTRATED ANTIFERROMAGNET

[EFRC – NPQC] S. Haley[1,2]; V. Rosa Rocha[1,2], et al.
[1]University of California, Berkeley; [2]Lawrence Berkeley National Laboratory
AFFILIATED TALK – III-T2-3: Long-range, Non-local Switching of Spin Textures in a Frustrated Antiferromagnet

Antiferromagnetic spintronics is an emerging area of quantum technologies that leverage the coupling between spin and orbital degrees of freedom in exotic materials. Spin-orbit interactions allow spin or angular momentum to be injected via electrical stimuli to manipulate the spin texture of a material, enabling the storage of information and energy. In general, the physical process is intrinsically local: spin is carried by an electrical current, imparted into the magnetic system, and the spin texture will then rotate in the region of current flow. In this study, we show that spin information can be transported and stored ``non-locally" in the material Fe$_{x}$NbS$_2$. We

propose that collective modes can manipulate the spin texture away from the flowing current, an effect amplified by strong magnetoelastic coupling of the ordered state. This suggests a novel way to store and transport spin information in strongly spin-orbit coupled magnetic systems.

III-S2-14: MAGNETISM AND BANDS TOPOLOGY IN $Nd_2Ir_2O_7$ PROBED BY RAMAN SCATTERING SPECTROSCOPY

[EFRC – IQM] Yuanuan Xu[1], Yang Yang[2], Predrag Nikolic[3], Jeremie Teyssier[4], Takumi Ohtsuki[5], Yang Qiu[5], Satoru Nakatsuji[1,5], D. van der Marel[4], Natalia Perkins[2], Natalia Drichko[1]
[1]Johns Hopkins University; [2]University of Minnesota; [3]George Mason University, [4]University of Geneva; [5]University of Tokyo.

Pyrochlore iridates present a unique interplay of magnetic frustration, electron correlations, and spin orbit coupling. A Weyl semimetal state was predicted in these materials when the quadratic band touching splits into Weyl nodes as a result of time reversal symmetry breaking by the all-in-all-out (AIAO) ordering of the Ir moments. We show that not only is $Nd_2Ir_2O_7$ the best candidate to realize these theoretical expectations, but because both the A (Nd) and B (Ir) sites of the pyrochlore lattice of this material are magnetic, there is an unique enhancement of the magnetic interactions in the Nd pyrochlore lattice. Using polarized Raman scattering spectroscopy we can separate electronic and magnetic contributions to the response, and follow their temperature dependence down to 7 K through the ordering of Ir moments at T_N(Ir)= 33 K and Nd moments ordering at about 14 K. We detect Gamma-point magnon excitations of the AIAO order of Ir moments. A step-like decrease of the electronic scattering at T_N(Ir) is interpreted as a signature of the splitting of quadratic band touching into Weyl nodes. We show that the presence of Ir results in the renormalization of magnetic interactions between Nd moments: Below T_N(Ir) spin ice fluctuations of Nd magnetic moments are detected through a collective mode at 15 meV, which disappears when Nd moments order in AIAO for temperatures below 14 K.

III-S2-15: ELECTRIC CONTROL AND SENSING OF MAGNETIC STATES IN MOLECULAR SYSTEMS

[EFRC – M²QM] Johnny Adams[1], James Wampler[2], Marc Lewkowitz[1], Ping Wang[3], Shubham Bisht,[3] Dibya Jyoti Mondal,[3] Michael Shatruk[3], Minseong Lee[2], Vivien Zapf[2], Ali Sirusi Arvij[4], Shuang-Long Liu[1], Hai-Ping Cheng[1,6], M. Fhokrul Islam[5], Mark Pederson[5], Neil S. Sullivan[1]
[1]University of Florida; [2]Los Alamos National Laboratory; [3]Florida State University; [4]San Juan College; [5]University of Texas El Paso; [6]Northeastern University

We are investigating how to couple magnetic spin states to electric fields in molecular systems. Electric fields are a traditional route for manipulating and sensing information that can be scaled to the 10s of nm. Thus establishing electric control of quantum information in spin systems can be an important ingredient of future quantum technologies. We explore two routes for electrically controlling spin states in molecules containing 3d transition metal spins: (1) frustrated clusters of 3d spins that naturally form a spatial-inversion and/or polar spins structures and therefore can match the symmetry of an electric field in zero or applied magnetic fields and (2) spin crossover complexes of 3d transition metals where a change in the orbital distribution of electrons has

drastic effects on the molecular volume and lattice symmetry, thus changing the response of molecules to electric fields.

We present results for the direct observation of electrically-induced modification of the magnetic susceptibility of the molecular nano-magnet $[Fe_3O(O_2CPh)_6(py)_3]ClO_4 \cdot py$, an Fe_3 oxo-centered carboxylate trimer. This magnetoelectric effect is a result of simultaneously breaking spatial inversion symmetry and time-reversal symmetry due to the spin configurations of the antiferromagnetic trimer. Changes in the magnetic susceptibility in response to applied electric fields were measured using a novel tunnel diode oscillator for sensing magnetic susceptibiltiy. We also use pulsed magnetic fields to explore how the electric polarization of a lattice changes in spin-crossover and valence-tautomer complexes. We show magnetic field-induced spin crossovers that toggle the electric polarization of the lattice. We combine experimental, analytical and first-principle analyses to achieve the fundamental understanding of the nature of magnetoelectric coupling in these systems.

III-S2-16: THE ROLE OF KITAEV EXCHANGES IN 1D AND 2D COBALT MAGNETS

[EFRC – IQM] C.M. Morris[1], Xinshu Zhang[1], N. Deshai[2], Yuanyuan Xu[1], T. Halloran[1], Ruidan Zhong[3], T. McQueen[1], C. Broholm[1,4], R. J. Cava[3], N. Drichko[1], R. Kaul[2,5], N. P. Armitage[1,6]
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Kitaev quantum spin liquids (QSLs) are exotic states of matter that are predicted to host Majorana fermions and gauge flux excitations. However, so far, all known Kitaev QSL candidates are known to have appreciable non-Kitaev interactions that push these systems far from the QSL regime. Co based magnets have been proposed to be perhaps a more ideal platform for realizing Kitaev QSLs. In this talk I will show evidence for a Kitaev interactions in the quasi-one-dimensional ferromagnet $CoNb_2O_6$. Although it is usually believed to be the best material realization of a 1D Ising chain, by combining terahertz spectroscopy and calculations we have shown that $CoNb_2O_6$ is well described by a model with bond-dependent interactions. We call this model the "twisted Kitaev chain", as these interactions are similar to those of the honeycomb Kitaev spin liquid. The ferromagnetic ground state of $CoNb_2O_6$ arises from the compromise between two axes. Owing to this frustration, even at zero field domain walls have quantum motion, which is described by the celebrated Su–Schriefer–Heeger model of polyacetylene and shows rich behavior as a function of field. Most recently, we have also investigated the honeycomb cobalt-based magnet, $BaCo_2(AsO_4)_2$, which was also proposed to have Kitaev interactions. The physics of this system and evidence for bond directional exchanges will be discussed.

III-S2-17: BRIDGING MACROSCOPIC AND MICROSCOPIC NONLINEAR OPTICS

[EFRC – Pro-QM] Chiara Trovatello[1], C. Dean[1], J. Hone[1], D.N. Basov[1], X.-Y. Zhu[1], M. Delor[1], P. James Schuck[1]
[1]Columbia University

AFFILIATED TALK – III-T2-2: Layered semiconductors are changing the game in quantum information

Nonlinear optics lies at the heart of classical and quantum sources of radiation which are essential for both fundamental spectroscopy and optical information processing. For example, one photon at frequency ω can annihilate into two lower energy photons, resulting in an entangled photon pair: the basic building block of a quantum computer. The maximum efficiency of a nonlinear process is achieved by minimizing the wave vector mismatch, at the so-called phase matching condition *(Δk*=0). Typical phase-matched nonlinear crystals have moderate nonlinearities (1-20 pm/V), but can achieve high conversion efficiencies (10^{-2}-10^{-1}) due to their large thickness (millimeter/centimeter). However, such macroscopic thickness does not easily lend itself to on-chip integration. Here we aim to miniaturize nonlinear crystals, achieving phase matching in engineered stacks of layered semiconductors such as non-centrosymmetric transition metal dichalcogenides, which possess huge nonlinear susceptibilities of 100-1000 pm/V and promise the same efficiencies of bulk crystals within micron-thicknesses. Bridging macroscopic and microscopic nonlinear optics will enable new on-chip technologies including nonlinear waveguides, nano-lasers, and entangled photon sources. More generally, miniaturized quantum light sources promise to impact the future of secure quantum information, creating entirely new digital protocols and technologies, and enabling significant advances in computing speed and energy efficiency.

III-S2-18: UWBG NITRIDE PN JUNCTION DIODES OF NEAR UNITY IDEALITY FACTOR USING DISTRIBUTED POLARIZATION DOPING

[EFRC – ULTRA] Debdeep Jena[1], Shivali Agrawal[1], Len van Deurzen[1], H. Grace Xing[1], Joseph Dill[1], David J. Smith[2], Saurabh Viswakarma[2], Mary Allen Zvanut[3], Subash Paudel[3]
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A key hurdle towards high-power electronic switches using ultra-wide bandgap semiconductors is the realization of pn junction diodes. This goal has been hampered by the lack of efficient conductivity control of both n and p-type regions of UBWG semiconductors such as diamond, Ga_2O_3, and Al(Ga)N. We report the ULTRA team's first realization of near unity ideality factor UWBG AlGaN pn junction diodes. This was achieved by a cross-cutting collaborative effort within ULTRA that addressed the co-design problems of growth (Jena), donor doping (Zvanut) and polarization-induced doping (Jena), ohmic contact formation (Xing) enabled by analysis of interface atomic structure (Smith), and the measurement, characterization, and modeling of the UWBG diodes (Jena).

Epitaxial growth on single-crystal Aluminum Nitride (AlN) substrates by homoepitaxy was enabled by the atomic surface clean (ASC) process, a method developed by ULTRA team members. The entire PN junction heterostructure using Silicon doped AlGaN n-type layers of 70-80% Aluminum, and distributed polarization doped p-type graded AlGaN layers with 100-60% Aluminum remained coherently strained to the AlN substrate as proved by X-ray diffraction and electron microscopy. Some of the lowest contact resistances for UWBG nitride semiconductors were enabled by efficient doping. Through capacitance-voltage measurements, the mobile hole concentration and their spatial distribution in graded AlGaN layers were measured at various temperatures. The pn

junction diode exhibited ultralow leakage in its off state, near unity ideality factor during turn on, and interband electroluminescence with emission corresponding to radiative recombination across the large energy bandgap of the depletion region of the junction.

III-S2-19: CONVERTING NON-EQUILIBRIUM CHARGE DENSITY INTO SPIN CURRENT

[EFRC – NPQC] Marc Vila[1,2], Joel E. Moore[1,2]
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The interconversion between charge and spin degrees of freedom is of both fundamental and technological relevance in spintronics. While a non-equilibrium spin density and a charge current are related by the well known Rashba-Edelstein effect, here we theoretically report on the generation of spin current by means of a time-dependent modulation of the charge density. By using the Boltzmann transport equation, we show that when the chemical potential is varied, a spin current is generated in the time scale it takes for system to re-equilibrate in the new chemical potential. The effect is ubiquitous in many systems with spin-orbit coupling, and its symmetry requirements are the same as those from the Rashba-Edelstein effect. We apply our theory to three paradigmatic Rashba models corresponding to two-dimensional electron gases, graphene and the surface state of topological insulators, and to a realistic model of chiral tellurium nanowires displaying parallel spin-momentum locking stemming from Kramers-Weyl fermions. We propose a simple device scheme to optically resolve the spin accumualted at the sample boundaries and discuss the extension of our results to non-spin-orbit coupled systems. Our findings show fundamental insights between charge-to-spin conversion and puts forward an all-electrical way to generate spin currents without the need for charge currents, magnetic materials or optical methods.

III-S2-20: EPITAXIAL THIN FILMS OF KAGOME METALS

[EFRC – CATS] Caolan John[1], Qianheng Du[2], Anand Bhattacharya[2], Joseph Checkelsky[1]
[1]Massachusetts Institute of Technology; [2]Argonne National Laboratory

The Kagome metals are a fascinating playground for the interplay between magnetism and band topology, where flat bands, Dirac crossings, magnetic interactions and geometric frustration can give rise to a wide range of ground states. These include massive Dirac semimetals, antiferromagnetic Weyl semimetals, and putative 2D Chern insulators. While many of these states have been explored in bulk samples, high quality epitaxial thin films have been challenging to realize due to the metastable nature of some of these phases and their propensity to form island like structures due to weak bonding to substrates. CATS has a major effort to grow and characterize thin films of magnetic topological materials, including Kagome metals. CATS address these challenges in a number of Kagome metals, including attempts to investigate the ultrathin limit, and point to the new research directions that these films will enable.

III-S2-21: THERMODYNAMICS OF NON-LINEAR OPTICAL RESPONSES OF FERROELECTRICS

[CMS – COMMS] Aiden Ross[1], Rui Zu[1], Anna Morozovska[2], Venkatraman Gopalan1, Long-Qing Chen[1]
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AFFILIATED TALK – III-T2-4: Thermodynamics of Non-linear Optical Responses of Ferroelectrics

Ferroelectric materials are prime candidates for non-linear photonic devices such as high-speed photonic modulators and quantum photonic integrated circuits owing to their excellent non-linear optical properties. However, there is a lack of a general theoretical framework to predict and understand the non-linear optical properties of ferroelectrics and their associated couplings to polarization, stress, and strain that are critical to their integration into photonic devices. We are developing a thermodynamic formulation to extend the widely used Landau-Ginzburg-Devonshire theory to accurately predict and optimize the optical properties of ferroelectrics. We separate the contributions of the ferroelectric soft mode and bound electrons to the total polarization and incorporate electro- and elasto-optical couplings. Our preliminary results on BaTiO3 demonstrate the capability of a newly developed thermodynamic energy function to accurately describe the experimentally measured temperature-dependent birefringence and electrooptic (Pockels) effect. The constructed thermodynamic model provides a new powerful tool to understand, predict, and engineer optical phenomena in ferroelectrics. In particular, the proposed theoretical framework will form the thermodynamic foundation for the phase-field model of non-linear optical properties of mesoscale ferroelectrics under development by our collaborating team with respective expertise in the phase-field method, advanced numerical algorithms, and non-linear optical properties of crystals.

III-S2-22: A NEW GENERATION OF RARE-EARTH PSEUDOPOTENTIALS AND APPLICATIONS TO QUANTUM MATERIALS

[CMS – CPSFM] Gani Annaberdiyev[1], Haihan Zhou[2], Benjamin Kincaid[2], Guangming Wang[2], Subhasish Mandal[3], Jaron T. Krogel[1], Lubos Mitas[2], Panchapakesan Ganesh[1]
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AFFILIATED TALK – III-T2-9: A New Generation of Rare-Earth Pseudopotentials and Applications to Quantum Materials

We develop rare-earth element (R) correlation-consistent effective core potentials (ccECPs) for many-body methods such as quantum Monte Carlo (QMC) and post-Hartree-Fock methods. The core-valence partitioning includes the f-electrons in the valence space with {4f, 5s, 5p, 5d, 6s} orbitals, allowing for high-fidelity simulations of different effective charges and magnetic configurations in quantum materials. The many-body accuracy of such ECPs is probed for the first time with accounts of accurate electron correlations in the atomic spectrum and RH_3, RO molecules. The proof-of-concept results are shown for mid-lanthanide Gd and Tb elements, which possess significant magnetic characters and thus are expected to be challenging. A further DFT+U application is demonstrated for Tb on the putative Chern magnet $TbMn_6Sn_6$, which agrees well with scanning tunneling microscopy results. The Gd and Tb ccECP accuracy tests, as well as application in quantum materials such as $TbMn_6Sn_6$, clearly demonstrate a pathway for a new

generation of lanthanide and actinide effective core potentials and opens a new avenue for QMC calculations of rare-earth materials.

III-S2-23: NATURE OF SHORT-RANGE ORDER IN GROUP IV ALLOYS

[EFRC – μ-ATOMS]: Xiaochen Jin[1], Shunda Chen[1], Yunfan Liang[2], Damien West[2], Dragica Vasileska[3], Shengbai Zhang[2], and Tianshu Li[1]
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AFFILIATED TALK – III-T2-11: Impacts of Short-Range Order on Properties of Group IV Alloys

Short-range order (SRO) has been recently demonstrated to play a crucial role in modulating a wide range of physical properties in medium-entropy alloys (MEAs) and high-entropy alloys (HEAs). However, there is a lack of general understanding of SROs in their physical origin, structural complexity, and impact of properties in complex concentrated alloys. Using group IV alloys as a platform, we carry out an in-depth investigation to gain a fundamental understanding of these questions through a concerted theoretical effort. We show local lattice distortion plays a decisive role in driving SRO and substantially controlling the electronic, topological and transport properties of group IV alloys. Importantly, the distribution of SRO parameter, which depicts the fraction of atoms adopting a specific local structural configuration, is found to carry crucial structural information that is missing in the commonly adopted average SRO parameter. To extend the spatiotemporal scale of atomistic modeling to enable a side-by-side comparison with advanced characterization methods such as atom probe tomography and 4D-TEM, we further develop machine-learning interatomic potentials for the alloys based on neuroevolution potential. We show that the machine-learning interatomic potentials not only can accurately reproduce the results based on DFT calculations, but also enable a discovery of new, interesting SRO structural properties that are not easily accessible by DFT calculations.

III-S2-24: ENGINEERING SYNTHETIC FERROELECTRICS IN MOIRÉ VAN DER WAALS STRUCTURES

[EFRC – CATS] Zhiren Zheng[1], Xueqiao Wang[1], Xirui Wang[1], Kenji Yasuda[1], Suyang Xu[2], Qiong Ma[3], Pablo Jarillo-Herrero[1]
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In recent years, the research development in van der Waals (vdW) materials has introduced new degrees of freedom and flexibility in engineering the symmetry of lattice structures. Through the control of stacking order and rotational alignment, a new class of vdW synthetic ferroelectrics can be engineered on-demand. CATS Thrust 3 has an objective to discover these novel ferroelectrics and potentially combine them with topological materials to generate new phenomena and field-control methods. In this poster, we present two classes of synthetic ferroelectrics that are being studied in our group, namely interfacial ferroelectricity and electronic ferroelectricity. In the parallel-stacked boron nitride (BN) bilayer or transition metal dichalcogenide (TMD) bilayer systems, the relative stacking order of the two layers can generate a vertical polarization that can be switched by an external electric field. The switching is achieved by a relative in-plane shift that

is less than a unit cell size. The polarization and domain movement are further probed by a graphene sensor layer and piezoelectric force microscopy. On the other hand, electronic ferroelectricity is found in BN-bialyer graphene (BLG)-BN moiré structure, with a potential extension to pure multilayer graphene system. Our measurement reveals that the layer-contrasting moiré structure leads to dichotomy of localized and itinerant subsystems, where the coupling between the two can lead to a novel electronic ratchet effect and switchable electric polarization. Altogether, CATS research has led to a new class of vdw synthetic ferroelectrics where its constituents are not ferroelectric in nature.

III-S2-25: EXPLORING CHARGE-TRANSPORT IN MOLECULAR AND POLYMER COORDINATION COMPOUNDS FOR NEUROMORPHIC COMPUTING

[EFRC – reMIND] Donald A. Robinson,[1] Manuel Quiroz Rodriguez,[2] Mohana Shivanna,[1] Nova Wu,[1] Vitalie Stavila,[1] Kim Dunbar,[2] Gaurav Vats,[3] Andrew J. Ferguson,[3] Jeffrey L. Blackburn,[3] Marcetta Y. Darensbourg,[2] Alec A. Talin[1]
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Redox active coordination complexes are attractive for multi-level memristive devices with properties that enable highly complex logic functions for a wide range of algorithms. Here we focus on the redox chemistry and transport in two classes: (1) crystalline compounds hexaammineruthenium (III), $[Ru(NH_3)_6]^{3+}$ and hexacyanometalate (III), $[M(CN)_6]^{3-}$ (M = Fe^{3+} or Ru^{3+}), and (2) molecular transition metal-organic coordination complexes.

$[Ru(NH_3)_6]^{3+}$ and $[M(CN)_6]^{3-}$ are known to undergo rapid electron transfer during electron exchange reactions in solution or reversible one-electron reduction at electrode/solution interfaces. Recently, we combined these complexes to produce insoluble crystals of $Ru(NH_3)_6M(CN)_6$ with linear current-voltage characteristics. Thermal treatment of the hexaammineruthenium hexacyanometallate crystals causes desorption of the NH_3 ligands and transforms the crystals into cyanide-bridged Ru-Fe and Ru-Ru Prussian blue analogs with high defect densities while preserving the initial macroscale geometry of the single-crystal precursors. These monocrystalline redox-tunable semiconductors represent a unique system for understanding the link between electronic conductivity of a bulk crystal and the rate of electron transfer between constituent molecular complex ions, as elucidated with in-situ spectroscopic methods and single-crystal electrical measurements.

We have developed heterocyclic amine or metal dithiolene ligand systems that form transition metal complexes that exhibit redox cascades with transitions amenable to spectroscopic interrogation. Using synthetic control, we can manipulate the redox state of the complex and alter the counterions required for charge compensation in the solid-state. These tailored ligands offer control over ligand and metal redox properties and the solid-state packing, to elucidate their roles in thin-film conductance switching in various device geometries/structures.

III-S2-26: 3D COMPATIBLE FERROELECTRIC MEMORY FOR EMERGING FERROELECTRIC MATERIALS AND THEIR NOVEL COMPUTING APPLICATIONS

[EFRC – 3DFeM] Yi Xiao[1], Shan Deng[2], Akif Aabrar[3], Arnob Saha[1], Nafiul Islam[1], Joseph Casamento[1], Jon-Paul Maria[1], Abhronil Sengupta[1], Suman Datta[3], Vijaykrishnan Narayanan[1], Kai Ni[2]
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With the discovery of CMOS-compatible ferroelectric materials like HfO_2, $Al_{1-x}Sc_xN$, $Al_{1-x}B_xN$, and $Zn_{1-x}Mg_xO$, there is a strong need to develop appropriate ferroelectric memory cells for corresponding ferroelectric materials. Considering the diverse properties of these ferroelectric materials, a universal memory cell structure empowering 3D compatible and scalable array does not exist. For instance, wurtzite ferroelectrics excel in polarization charge but have a large coercive field, making them suitable for capacitor based ferroelectric random access memory (FeRAM) rather than ferroelectric field-effect transistors (FeFETs). Conversely, fluorite HfO_2 shows promise in enabling scalable FeFETs. This poster highlights 3DFeM's efforts to develop 3D compatible and scalable memory using both wurtzite and fluorite ferroelectric materials and explore their applications in novel computing paradigms. The 1T-1C FeRAM cell employing ferroelectrics, together with monolithic 3D integration, can enable a non-volatile memory technology matching DRAM density and near-DRAM performance. Like DRAM, this cell will use destructive read. To address this, adoption of a 2T-nC FeRAM cell is proposed for wurtzite ferroelectrics, where the cell write is like the 1T-1C FeRAM and a non-destructive read is performed like the FeFET with the assistance of a read transistor, thus exploiting the strength while avoiding the major issues of both types of memories. This approach demonstrates superior scaling capability and is 3D compatible. For fluorite HfO_2, stacking of 3D compatible metal oxide thin film channel-based FeFETs was demonstrated multiple tiers. Finally, the applications of the 2T-nC cell in enabling complex logic functions and the use of FeFETs for brain-inspired computing will be presented.

III-S2-27: PHONON AND THERMAL PROPERTIES OF UWBG MATERIALS AND INTERFACES

[EFRC – ULTRA] Martin Kuball[1], Richard Wilson[2], Alexander Balandin[2,3], Srabanti Chowdhury[4], Debdeep Jena[5], H. Grace Xing[5], David J. Smith[6], Marco Saraniti[6], Yuji Zhao[6], Timothy Grotjohn[7]
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Before high-power ultrawide bandgap semiconductors reach their potential, key gaps in the understanding of phonon transport need to be filled. These gaps include: (i) understanding how bulk vs. interfacial properties govern heat flow, (ii) developing metrologies that can distinguish bulk properties, sub-continuum transport, and interfacial resistance, and (iii) identifying ultra-material combinations and synthesis processes that lead to thermally conductive interfaces.

We report our efforts to address these issues. We investigated bulk and surface acoustic phonons in boron-doped single-crystal diamond films using Brillouin-Mandelstam light scattering spectroscopy. It was found that the frequency and the group velocity of acoustic phonons decrease non-monotonically with increasing boron doping concentration, revealing pronounced

phonon softening. The results have important implications for thermal transport in heavily doped diamond films. In evaluating the thermal conductivity of doped diamond films, one should take into consideration not only the concentration of dopants acting as scattering centers but also the changes in the acoustic phonon velocities. Time-domain thermoreflectance measurements reveal that doping causes a factor of up to 5 reductions in the thermal conductivity of diamond, and leads to a non-monotonic temperature dependence. We also have developed a new thermal metrology tool based on magneto-optic thermometry. This allows us to simultaneously measure the thermal conductivity of sub-micron thin films and the thermal resistance of buried semiconductor/semiconductor interfaces. Finally, another key ULTRA EFRC goal is to discover methods for integrating high thermal conductivity heat spreading layers, to aid heat extraction from electronics materials such as Ga_2O_3 which have low thermal conductivity.

III-S2-28: MECHANISTIC UNDERPINNINGS OF ELECTRONIC TRANSITIONS AND SITE-SELECTIVE MODIFICATION OF TRANSITION METAL OXIDES FOR OSCILLATOR-BASED COMPUTING

[EFRC – reMIND] John Ponis,[1] George Agbeworvi,[1] Michelle A. Smeaton,[2] Joseph Handy,[1] Saul Perez-Beltran,[1] Kenna Ashen,[1] Matt Pharr,[1] Fatima Jardali,[1] Patrick J. Shamberger,[1] Katherine L. Jungjohann,[2] Xiaofeng Qian,[1] Jinghua Guo,[3] Jeffrey L. Blackburn,[2] Andrew J. Ferguson,[2] Lance Wheeler,[2] and Sarbajit Banerjee[1]
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Development of energy-efficient neuromorphic and oscillator-based computing architectures is predicated upon the design of materials exhibiting electronic instabilities, such as electric-field-mediated metal-to-insulator transitions. The integration of these computing elements into analog circuits requires strategies for modifying the properties of electronic transitions—onset criteria, conductance differentials, and hysteresis widths—which further requires mechanistic understanding at the level of atoms and electrons.

We have developed a foundry of single-crystals of $M_xV_2O_5$ compounds with varying connectivity of the V—O framework and substantial diversity of up to three distinct s-, p-, and d-block cations positioned in specific interstitial sites. These single crystals have enabled precise elucidation of the coupling of spin, charge, orbital, lattice, and atomic degrees of freedom that underpin sharply discontinuous metal—insulator transitions. Some examples of newly discovered mechanisms include a superlattice order/disorder transition of interstitial Cu-ions between 2D V_2O_5 layers in ε-$Cu_xV_2O_5$, lattice anharmonicity mediated by repulsions between stereochemically active lone pairs in Pb- and Cu-co-intercalated tunnel-structured $M_xM'_yV_2O_5$ compounds, and polaron oscillation mediated by ion-shuttling in 1D β'-$Cu_xV_2O_5$. We have further demonstrated extreme modulation of the defect-induced charge carrier density in mesoporous films of nanocrystalline α-V_2O_5 and α-MoO_3, via solution-phase chemical treatment with $SnCl_2$ (and other transition metal salts). These changes in the carrier density manifest huge modifications of the electrical conductivity and optical properties of the thin films through control of redox states and defect dynamics. These studies highlight the versatility of the structural frameworks and the ability to precisely modulate electronic structure through ion intercalation and diffusion.

III-S2-29: LONG LIVED ELECTRONIC SPIN QUBITS IN SINGLE-WALLED CARBON NANOTUBES

[EFRC – CMQT] Jia-Shiang Chen[1,2], Kasidet Jing Trerayapiwat[3], Lei Sun[1], Matthew D. Krzyaniak[2], Michael R. Wasielewski[1,2], Tijana Rajh[1,4], Sahar Sharifzadeh[3], Xuedan Ma[1,2,5]
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Electron spins in solid-state systems offer the promise of spin-based information processing devices. Single-walled carbon nanotubes (SWCNTs), an all-carbon one-dimensional material whose spin-free environment and weak spin-orbit coupling promise long spin coherence times, offer a diverse degree of freedom for extended range of functionality not available to bulk systems. A key requirement limiting spin qubit implementation in SWCNTs is disciplined confinement of isolated spins. Here, we report the creation of highly confined electron spins in SWCNTs via a bottom-up approach. The record long coherence time of 8.2 µs and spin-lattice relaxation time of 13 ms of these electronic spin qubits allow demonstration of quantum control operation manifested as Rabi oscillation. Investigation of the decoherence mechanism reveals an intrinsic coherence time of tens of milliseconds. These findings are evident that combining molecular approaches with inorganic crystalline systems provides a powerful route for reproducible and scalable quantum materials suitable for qubit applications.

III-S2-30: OBSERVATION OF A MASSIVE PHASON IN A CHARGE-DENSITY-WAVE INSULATOR

[EFRC – QSQM] Soyeun Kim[1], Yinchuan Lu[1], Xiao-Qi Sun[1], Chengxi Zhao[1], Nina Bielinski[1], Azel Murzabekova[1], Kejian Qu[1], Ryan A. Duncan[2], Quynh L. D. Nguyen[2], Mariano Trigo[2], Daniel P. Shoemaker[1], Barry Bradlyn[1], and Fahad Mahmood[1]
[1]University of Illinois at Urbana-Champaign; [2]SLAC National Accelerator Laboratory

The lowest-lying fundamental excitation of an incommensurate charge-density-wave material is believed to be a massless phason—a collective modulation of the phase of the charge-density-wave order parameter. However, long-range Coulomb interactions should push the phason energy up to the plasma energy of the charge-density-wave condensate, resulting in a massive phason and fully gapped spectrum. Using time-domain terahertz emission spectroscopy, we investigate this issue in (TaSe4)2I, a quasi-one-dimensional charge-density-wave insulator. On transient photoexcitation at low temperatures, we find the material strikingly emits coherent, narrowband terahertz radiation. The frequency, polarization and temperature dependences of the emitted radiation imply the existence of a phason that acquires mass by coupling to long-range Coulomb interactions. Our observations underscore the role of long-range interactions in determining the nature of collective excitations in materials with modulated charge or spin order.

III-S2-31: OBSERVATION OF FRACTIONAL QUANTUM ANOMALOUS HALL EFFECT

[EFRC – Pro-QM] Jiaqi Cai[1], Eric Anderson[1], Heonjoon Park[1], Yinong Zhang[1], Xiaoyu Liu[1], Chong Wang[1], Xiaowei Zhang[1], Fengren Fai[2], William Holtzmann[1], Chaowei Hu[1], Zhaoyu Liu[1], Takashi Taniguchi[3], Kenji

Watanabe[3], Ying Ran[4], Jiun-haw Chu[1], Ting Cao[1], Liang Fu[5], Wang Yao[2], Cui-Zu Chang[6], David Cobden[1], Di Xiao[1], Xiaodong Xu[1]
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The interplay between spontaneous symmetry breaking and topology can result in exotic quantum states of matter. A celebrated example is the quantum anomalous Hall (QAH) state, which exhibits an integer quantum Hall effect at zero magnetic field due to topologically nontrivial bands and intrinsic magnetism. In the presence of strong electron-electron interactions, fractional-QAH (FQAH) states at zero magnetic field can emerge. These states could host fractional excitations which obey anyonic statistics. In this poster, we report experimental observation of FQAH states in twisted $MoTe_2$ bilayer. Magnetic circular dichroism measurements reveal robust ferromagnetic states at fractionally hole filled moiré minibands. Using trion photoluminescence as a sensor, we obtain a fan diagram showing linear shifts in carrier densities corresponding to the ν = -2/3 and -3/5 ferromagnetic states with applied magnetic field. These shifts match the Streda formula dispersion of FQAH states with fractionally quantized Hall conductance of σ_{xy}=-2/3 e^2/h and -3/5 e^2/h, respectively. The assignment of the FQAH states is further confirmed by electrical transport measurements. Exact diagonalization calculation using realistic parameters finds degenerate ground states at ν=-2/3 and -3/5 with many-body Chern number -2/3 and -3/5, respectively. Our findings demonstrate the long-sought FQAH states.

III-S2-32: DOUBLE PHOTOEMISSION SPECTROSCOPY IN TOPOLOGICAL SUPERCONDUCTORS

[EFRC – QSQM] Ka Ho Wong[1], Ameya Patwardhan[2], Peter Abbamonte[2], Fahad Mahmood[2], and Dirk K. Morr[1]
[1]University of Illinois at Chicago; [2]University of Illinois at Urbana-Champaign

We demonstrate that the double photoemission rate measured in two electron coincidence spectroscopy (2e-ARPES) experiments, provides unprecedented insight into the nature of topological superconductivity. We show that the spin dependence of double photoemission rate allows one to detect superconducting spin-triplet correlations that are induced in a topological superconductor even in the absence of an associated triplet superconducting order parameter. This ability to detect spin-triplet correlations allows one to distinguish between two recently proposed scenarios for the microscopic origin of topological superconductivity in FeSe0.45Te0.55. Finally, we show that the double photoemission rate exhibits a characteristic intensity maximum that can be employed to detect topological phase transitions.

III-S2-33: CENTER FOR PREDICTIVE SIMULATION OF FUNCTIONAL MATERIALS

[CMS – CPSFM] Paul Kent[1], Anouar Benali[2], Anand Bhattacharya[2], Raymond Clay[3], Panchapakesan Ganesh[1], Jaron Krogel[1], Ho Nyung Lee[1], Ye Luo[2], Cody Melton[3], Lubos MItas[4], Brenda Rubenstein[5], Hyeondeok Shin[2], Luke Shulenburger[3], Joshua Townsend[3]

[1]*Oak Ridge National Laboratory;*[2]*Argonne National Laboratory;* [3]*Sandia National Laboratories;* [4]*North Carolina State University;* [5]*Brown University*

In this poster we highlight recent progress in many-body quantum mechanical calculations for correlated and quantum materials including for $TbMn_6Sn_6$, a proposed quantum limit Chern magnet, the antiferromagnetic topological insulator, $MnBi_2Te_4$, and the 2D magnetic monolayer CrI_3. The electronic correlations, magnetism, van der Waals, and spin-orbit interactions in these materials challenge first principles methods. We therefore have developed and utilize new first-principles Quantum Monte Carlo (QMC) techniques including for obtaining fully relaxed geometries in QMC, for including spin-orbital effects, and make use of our newly developed correlation-consistent effective core potentials (ccECPs), including for the rare-earths. These developments are released for wider application in the open-source QMCPACK code (https://qmcpack.org, https://github.com/QMCPACK/qmcpack) and website https://pseudopotentiallibrary.org. These activities are part of the Center for Predictive Simulation of Functional Materials (https://cpsfm.ornl.gov) which is focused on the development, validation, and distribution of external-parameter-free methods and open-source codes to predict and understand the properties of functional materials, emphasizing those with strong electronic correlations, van der Waals, and spin-orbit interactions.

III-S2-34: CIRCULAR DICHORISM OF CRYSTALS FROM FIRST PRINCIPLES

[CCS – ADEPTS] Christian Multunas[1], Andrew Grieder[2], Junqing Xu[2], Yuan Ping[2,3], and Ravishankar Sundararaman[1]

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AFFILIATED TALK – III-S2-35: Circular Dichorism of Crystals from First Principles

Chiral crystals show promise for spintronic technologies on account of their high spin selectivity, which has led to significant recent interest in quantitative characterization and first-principles prediction of their spin-optoelectronics properties. Here, we develop a computational framework for efficient ab-initio calculations of circular dichroism (CD) in crystalline materials. We leverage direct calculations of orbital angular momentum and quadrupole matrix elements in density-functional theory (DFT) and Wannier interpolation to calculate CD in complex materials, removing the need for band convergence and accelerating Brillouin-zone convergence compared to prior approaches. We find strong agreement with measured CD in molecules and crystals, ranging in complexity from small bulk unit cells to 2D hybrid perovskites, and show the importance of the quadrupole contribution to the anisotropic CD in crystals. We showcase the capability to predict CD for complex structures on a 2D hybrid perovskite, finding strong orientation dependence and identifying the eigen-directions of the unit cell with the strongest CD. We additionally decompose CD into separate contributions from inorganic, organic, and mixed organic-inorganic transitions, and find that the chiral molecules dominate the CD, with the inorganic lattice predictions in crystals will facilitate experimental development of complex chiral crystals for spin selectivity, and lays the groundwork for first-principles simulation of spin transport and dynamics in these materials within our CCS collaboration targeting spin-selective chemistry.

III-S2-35: SPIN DYNAMICS AND TRANSPORT USING AB INITIO DENSITY-MATRIX DYNAMICS

[CCS– ADEPTS] Rafi Ullah[1], Mani Chandra[2], Josh Quinton[2], Andrew Grieder[1], Junqing Xu[3], Christian Multunas[2], Mayada Fadel[2], and Ravishankar Sundararaman[2], and Yuan Ping[1,3]
[1]University of Wisconsin-Madison; [2]Rensselaer Polytechnic Institute; [3]University of California, Santa Cruz

Ab initio spin dynamics and transport simulations are critical for realizing the potential of spintronics and spin-selective photo-chemistry. In particular, simulations would be invaluable to predict key physical parameters including spin lifetime, spin diffusion and coherence length, magneto-optical spectra, and (spin)-photocurrent.

We are developing a computational framework and an open-source implementation targeting exascale GPU-based computing resources for simulating spatio-temporal quantum dynamics and transport accounting for a range of quantum degrees of freedom (e.g., charge, spin, orbital, lattice) in arbitrary device geometries. This framework accounts for scattering processes using an *ab initio* density matrix formalism for electron-phonon, electron-electron, and electron-impurity interactions with self-consistent spin-orbit coupling, and accounting for optical illumination, electric and magnetic fields. We will leverage exascale computing capabilities to pioneer the simulation of spin and charge dynamics and transport, from DC to terahertz, in disparate materials with arbitrary geometry up to micrometer length scales, which is essential to study complex chemical systems. We will present initial results on novel spin dephasing that manifests in spatially-resolved transport. Further, we show that materials with a unique symmetry and spin-orbit coupling, in which a Persistent Spin Helix (PSH) occurs, are immune to this dephasing. We will also present the generation and steady-state of photocurrents including excitation, scattering and recombination processes. Finally, we will show first-principles simulations of spin dephasing in external magnetic fields due to fluctuation of *g* factors.

III-S2-36: OVERCOMING STOCHASTICS IN EUV LITHOGRAPHY BY DIRECTED SELF-ASSEMBLY AND AREA-SELECTIVE ATOMIC LAYER DEPOSITION

[EFRC – CHiPPS] Kyunghyeon Lee[1,2], Emma Vargo[3], Christopher J. Eom[1,2], Areza Sumitro[3], Beihang Yu[3], Yujin Lee[4], Maggy Harake[4], Rachel Segalman[5], Stacey Bent[4], Ricardo Ruiz[3], Paul F. Nealey[1,2]
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AFFILIATED TALK – III-T2-6: Pushing the Precision Limits in EUV Lithography: Overcoming Stochastics with Directed Self-Assembly and Area-Selective Atomic Layer Deposition

The introduction of EUV lithography has provided a pathway for continued scaling of semiconductor manufacturing by enabling smaller features thanks to the much shorter wavelength of EUV photons. However, the use of this high energy radiation has also led to stochastic variations due to both low photon counts and random variations within the patterning materials that limit the quality of the lithographic patterns at high resolution and throughput. To mitigate stochastic effects, we've turned to two bottom-up approaches: First, we demonstrate

directed self-assembly (DSA) of block copolymers to rectify imperfections in EUV patterns that leverages smooth interface between two immiscible blocks. Our approach starts with a new family of A-b-(B-r-C) copolymers where the surface energy and the interaction parameter χ between the polymer blocks can be tuned separately, enabling self-assembling structures that are compatible with lithographic processes at EUV-relevant dimensions. This material provides improved roughness control within the high χ region as well as insights into the impact of χ on pattern quality. Second, recognizing the challenges in pattern transfer from thinner resist films at smaller dimensions, we introduce the use of sequence-define polypeptoid brushes as preferential nucleation sites for a new type of area-selective deposition by vapor phase infiltration. By grafting these brushes in targeted areas alongside blocking agents, we successfully create an inorganic hardmask after a minimal number of atomic layer deposition cycles, facilitating a fast and precise pattern transfer. Through these comprehensive strategies, we address the stochastic challenges in EUV lithography, enabling high-precision patterning for next-generation lithography.

III-S2-37: ULTRAFAST X-RAY SCATTERING REVEALS COMPOSITE AMPLITUDE COLLECTIVE MODE IN WEYL CHARGE DENSITY WAVE MATERIAL $(TaSe_4)_2I$

[EFRC – QSQM] Ryan A. Duncan[1,2] Quynh L. Nguyen[1,2], Gal Orenstein[1,2], Gilberto A. de la Pena[1,2], Viktor Krapivin[1,2], Yijing Huang[1,2], Chance Ornelas-Skarin[1,2], Soyeun Kim[3], Kejian Qu[3], Daniel P. Shoemaker[3], Samuel W. Teitelbaum[4], Fahad Mahmood[3], David A. Reis[1,2], Mariano Trigo[2]
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$(TaSe_4)_2I$ is a quasi-1D Weyl semimetal that hosts a low-temperature charge density wave state with a complex lattice distortion along multiple phonon coordinates. It has lately attracted much research interest as a putative dynamical axion insulator due to recent magnetotransport measurements in the CDW phase. We report ultrafast x-ray scattering experiments of $(TaSe_4)_2I$ following photoexcitation with femtosecond infrared laser pulses, carried out at the LCLS and SACLA hard x-ray free-electron laser facilities. Time-resolved diffraction signals were obtained at the first-order (q_{CDW}) and second-order ($2q_{CDW}$) CDW sidebands surrounding the (2 2 4) crystal Bragg peak. Several sub-THz frequency components are observed, one of which we identify an amplitude mode derived primarily from the transverse acoustic component of the CDW static distortion. This mode does not exhibit any pump-induced softening, even up to fluences that entirely quench the CDW order, and the excitation of this mode appears to be displacive in nature. We explain these features with a model of an indirect excitation of this mode mediated through a coupling to the optical phonon component associated with a tetramerization of the Ta chains, which is predicted to be involved in structural instabilities of the high-symmetry phase.

III-S2-38: COMPUTATIONAL MESOSCALE MATERIALS SCIENCE

[CMS – COMMS] Long-Qing Chen[1], Ismaila Dabo[1], Eugene. A. Eliseev[2], Venkatraman Gopalan[1], Wenrui Hao[1], Jiamian Hu[1], Anna N. Morozovska[2]
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The central goal of COMMS is to develop mesoscale computational models, efficient numerical algorithms for exascale computation, and software validated for quantum and functional materials. Built upon the accomplishments of the prior award period, the specific efforts of the renewal are to: (1) Further extend our dynamic phase-field model (DPFM) of coupled structural and electronic carrier dynamics to photon dynamics through the study of the formation and responses of mesoscale structures to external mechanical and electromagnetic fields such as light; (2) Construct a set of novel phase-field models of coupled phase transitions such as metal-insulator transitions, magnetic phase transitions, and superconducting phase transitions to study mesoscale electronic and structural pattern formation and evolution under the influence of lattice strain and chemical doping; (3) Develop and deploy the corresponding software modules as well as a number of powerful input/output (I/O), data-generation, and mesostructure characterization tools; and (4) Experimentally validate and refine the theory and computational tools through extensive collaborations with experts outside the core team on crystal growth, and experimental characterization of mesoscale structures of quantum materials. An outcome is an experimentally validated software package, Q-POP, parallelized to enable petascale and exascale computing for understanding the mesostructures of quantum and functional materials and their responses to external stimuli towards designing device architectures for harnessing these functionalities.

III-S2-39: CHARACTERIZATION OF ATOMIC SHORT RANGE ORDER IN SIGESN ALLOYS

[EFRC – μ-ATOMS] Shang Liu[1], J. Zach Lentz[2], Xiaoxin Wang[1], Lilian Vogl,[3] Haochen Zhao[4], Hiro Nakamura[5], Qinglong Jiang[6], Mansour Mortazavi[6], Yuping Zeng[4], Shashank Misra[7], Ezra Bussmann[7], Tzu-Ming Lu[7], Jin Hu[5], Shu-Qing Yu[5], Andrew Minor[3], Paul McIntyre[2], Jifeng Liu[1]
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Characterization of atomic short range order (SRO) in SiGeSn closes the feedback loop between theoretical predictions and materials growth to understand and engineer the SRO towards novel and potentially reconfigurable optoelectronic properties. We are developing a set of multiscale, complimentary approaches to characterize not only the average SRO but also the nanoscale statistical distribution of SRO, since both are theoretically predicted to drastically impact the optoelectronic and transport properties. Extended X-ray absorption fine structures (EXAFS) provided average SRO and verified the theoretically predicted unfavorable Sn-Sn 1st nearest neighbor (1NN) in GeSn from two independent experiments on relax thin films and nanowires, respectively. Furthermore, atom probe tomography analyses map the SRO distribution in 3D down to 5x5x5 nm^3 scale, leading to two major discoveries (1) We identified clear differences in the SRO between MBE and CVD growth methods. (2) We found that SRO can be drastically modified by

using different CVD precursors, revealing a facile potential approach to control and engineer the SRO to our advantage, e.g. lattice-matched SRO heterojuncitons and quantum wells. To achieve even better accuracy at even smaller scale for verifying co-existing types of SRO, 4D-STEM approach was used to analyze SiGeSn/GeSn QW, where the SRO has been confirmed by diffuse diffraction rings. In addition to SRO in 3D structures, we also started investigation of 2D SRO for monolayers of Sn on Si and Ge to understand the evolution of SRO during layer-to-layer growth. These results highlight preliminary success of our multiscale approach.

III-S2-40: PIEZOMAGNETIC SWITCHING OF THE ANOMALOUS HALL CONDUCTIVITY IN AN ANTIFERROMAGNET AT ROOM TEMPERATURE

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Piezomagnetism is a linear coupling between strain and magnetization in a ferromagnet that enables mechanical control of the magnetic moment. We have recently observed its analog for the Hall vector, the dual form of the Hall conductivity tensor, in the metallic antiferromagnet Mn_3Sn. Our experiments show that the Hall vector can be efficiently controlled, both in magnitude and direction, by the application of uniaxial strain of the order of 0.1%. The experimental data are well described by a Landau theory with the Hall vector as the order parameter.

III-S2-41: CONTROLLING LIGHT EMISSION FROM MONOLAYER MoS_2 WITH DIELECTRIC METASURFACES

[EFRC – PTL] S. C. Lau[1], Y. Liu[1], W. S. Cheng[2], A. Johnson[1], Q. Li[1], E. Simmerman[1], O. Karni[1,3], J. Hu[1], F. Liu[1], M. Brongersma[1], T. F. Heinz[1,3], and J. A. Dionne[1]
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AFFILIATED TALK – III-T2-12: Controlling Light Emission from Monolayer MoS_2 with Dielectric Metasurfaces

We investigate the modulation of excitonic properties in monolayer molybdenum disulfide (MoS_2), a semiconducting transition metal dichalcogenide (TMDC), through the use of dielectric metasurfaces comprised of silicon nano-disks. MoS_2 monolayers possess robust excitons with a valley degree of freedom, which is accessible through circularly polarized light. By strategically coupling MoS_2 with metasurfaces, we achieve precise manipulation of valley excitonic emission, impacting intensity, wavelength, and polarization.

By tailoring the dimensions of silicon nano-disks, we tune the disks' Mie scattering modes to match the frequency of MoS_2 exciton emission. The design yields an enhancement of MoS_2 photoluminescence (PL) intensity exceeding 30 times that of monolayers on flat substrates. The enhancement results from both excitation and emission amplification by metasurface modes.

We also observe notable modifications in MoS_2 emission spectral distribution due to interactions between neutral excitons, trions, and defect-bound excitonic states with metasurface resonances. The correlation between circular polarization of PL emission and metasurface modes is attributed to the Purcell effect, which is supported by photoluminescence lifetime measurements.

Beyond the experimental findings, our study employs comprehensive electromagnetic simulations to elucidate the metasurface response, advancing our comprehension of nanoscale light-matter interactions. The research highlights the potential of dielectric metasurfaces for shaping and exploiting excitonic behavior in semiconducting monolayers like MoS_2, which support tailored nanophotonic applications of such material systems.

III-S2-42: THERMALLY RESPONSIVE HYDROGELS FOR PASSIVE TEMPERATURE REGULATION UNDER DIRECT SUNLIGHT

[EFRC – PTL] D. Xie[1], W. Li[2], C. A. Richards[1], H. Gao[1], C. Chen[1], N. Miljkovic[1], S. Fan[3], J. Lee[4], S. N. Joshi[4], and P. V. Braun[1]
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By spontaneously emitting midinfrared radiation to outer space through the atmospheric window and reflecting sunlight, daytime radiative coolers achieve notable passive cooling performance. However, existing daytime radiative cooling systems generally lack the ability to adaptively switch between heating and cooling states based on ambient conditions. Herein a passive thermal regulation system that features a temperature-dependent switchable solar reflectance from 0.05 (low temperature) to 0.8 (high temperature) is presented. This, along with a ≈0.95 midinfrared emittance, it enables automatic switching between radiative cooling and solar heating. Switchablity is enabled using a poly(*N*-isopropylacrylamide) (PNIPAM) hydrogel which exhibits high solar scattering above its tunable lower critical solution temperature (LCST) and transparency below its LCST. The lower part of the hydrogel is loaded with graphite to absorb solar energy in the heating state. In testing under sunny and partly cloudy outside conditions, this system maintains a temperature close to the set LCST.

III-S2-43: MODELING NUCLEAR SPIN MEMORY RESILIENCE FOR QUANTUM NETWORKS

[EFRC – PTL] C. J. Ciccarino[1], F. H. da Jornada[1], P. Narang[2]
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Quantum networks based on point defects in insulating systems have been a subject of extensive recent research. Building a quantum network requires entanglement of quantum nodes over large distances. Efficient entanglement can be greatly enhanced by introducing quantum repeater nodes; however the use of repeaters also requires memory nodes, typically nuclear spins in the nearby lattice, to store intermediate states. The quantum coherence of these memory qubits is often limited by the stochastic events associated with optical manipulation of the nearby defect spin, due to the ever-present electron-nuclear (hyperfine) coupling. Understanding the resilience of these memories – in other words, how many entanglement attempts they can maintain

coherence over – is crucial for bracketing the limitations and potential of the quantum network. Theoretical studies of nuclear spin memory resilience are currently lacking. In this work we capture the spin dynamics of a ^{13}C quantum memory interacting with a nearby NV center and a bath of nuclear spins using a generalized cluster-correlation expansion (gCCE) technique. We investigate the coherence and resilience of the nuclear spin memory due to both stochastic resets of the NV center's spin and interactions with the nuclear spin bath. Our work captures the underlying quantum mechanical processes involved in nuclear spin dynamics and opens the door for studying more complicated multi-memory systems.

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