2019 EFRC PI MEETING STUDENT AND POSTDOC TEAM SCIENCE CONTEST

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INTRODUCTION TO THE GRADUATE STUDENT AND POSTDOC TEAM SCIENCE CONTEST AT THE 2019 EFRC PRINCIPAL INVESTIGATORS' MEETING

There are more than 1,400 graduate students postdoctoral researchers involved in the Energy Frontier Research Center (EFRC) program. To highlight their accomplishments and further the development of the future scientific energy workforce, the Department of Energy's Office of Basic Energy Sciences (BES) sponsored a Student and Postdoc Team Science Contest as part of the 2019 EFRC Principal Investigators' Meeting in Washington, D.C. on July 29-30, 2019. Each Director was invited to nominate a team of two or more graduate student and/or postdoctoral researchers to present a joint talk about their center research. The DOE EFRC management team selected 14 finalists. At the meeting, teams of DOE program managers selected the top six teams based on how well the research exemplified the opportunities provided by the center funding modality, scientific excellence, topical diversity, and quality of the presentation. The winners received an award certificate from Harriet Kung, Associate Director of the DOE Office of Basic Energy Sciences, during a ceremony at the end of the meeting.
For more information, visit the EFRC program website: http://science.osti.gov/bes/efrc].

The talk abstracts are listed below in alphabetical order by EFRC acronym. Team members are highlighted in orange; presenters at the meeting are underlined.

TEAM SCIENCE WINNERS

(Standing, from left) Xin Gao, Bryan Kudisch, Andrew Miechan, and Daniel Oblinsky. (Sitting, from left) Simon Cooper, Kyle Biegasiewicz, and Michael Black.

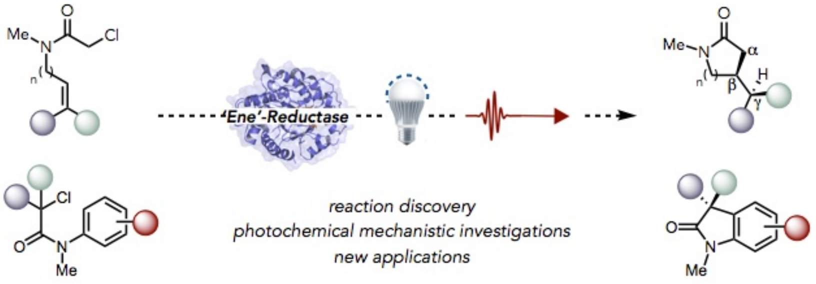
DISCOVERY OF A NEW PHOTOBIOCATALYST PLATFORM: NON-NATURAL RADICAL PHOTOCHEMISTRY ENABLED BY FLAVOPROTEINS

[BioLEC] Kyle F. Biegasiewicz[1], Bryan Kudisch[1], Simon J. Cooper`, Xin Gao[1], Michael Black[1], JiHye Kim[1], Daniel Oblinsky[1], Braddock A. Sandoval[1], Andrew Meichan[1], Samuel E. Garfinkle[1], Gregory D. Scholes[1], and Todd K. Hyster[1]
[1]*Princeton University*

Photobiocatalysis is a field that attempts to mimic the utility and efficiency of natural photosynthesis but with the goal of driving non-natural chemical reactions. The grand challenge associated with this task is that enzymes have naturally evolved to catalyze their own specific set of natural reactions, and as a result, the versatility of their inherent mechanistic machinery has largely been underexplored. Further, biological photochemistry is already a rare occurrence, oftentimes requiring whole "photosystems" worth of unique proteins (ie photosynthesis), such that the use of existing photochemical architectures in biology for new catalysis is a Herculean effort.

Surmounting these challenges, we discovered a new class of radical-mediated photobiochemical transformations using visible light, where our key shift in thinking was in the use of flavin-dependent 'ene'-reductases, which are enzymes without any natural photochemical activity. By surveying of a library of structurally homologous flavoproteins and their respective mutants, we have demonstrated a plethora of novel enantioselective transformations on a wide-variety of non-natural substrates. Critical to the success of these studies was the identification of the photochemical mechanisms of the various oxidation states of flavin using ultrafast spectroscopy, taking optical snapshots of various chemical intermediate species in the catalytic cycle and uncovering the disparate photophysics present in these 'ene'-reducatases as compared to all previously studied flavoproteins.

With the knowledge that we've gained regarding the synthetic utility and photochemical workings of these systems, we are poised to move forward towards traditionally difficult bond activations for diverse applications.



Contributions: T.K.H., K.F.B., S.J.C., X.G., J.-H.K. designed the experiments. K.F.B., S.J.C., X.G., J.-H.K. performed and analyzed results. B.A.S. cloned the improved variant used in the study, S.E.G. obtained x-ray quality crystals and solved the crystal structures. L.A.J. determined the absolute configuration. B.K. and D.G.O. conducted the photophysical and photochemical mechanistic investigation, which B.K., D.G.O., and G.D.S. analyzed and interpreted. T.K.H. and G.D.S. supervised the project.

(From left) Daniel Martin and Samantha Johnson

THE EFFECT OF ELECTROSTATICS ON SMALL MOLECULE BINDING AND CATALYSIS USING A POLYCATIONIC IRON PORPHYRIN

[CME] Daniel J. Martin[1], Samantha I. Johnson[2], James M. Mayer[1], Simone Raugei[2]

[1]Yale University; [2]Pacific Northwest National Laboratory (PNNL)

The Center for Molecular Electrocatalysis (CME) aims to store and harvest chemical energy using small, abundant molecules (e.g. O_2, NH_3 and N_2). However, these small molecules are often quite stable and difficult to activate. The oxygen reduction reaction (ORR) is one such quintessential chemical-to-electrical energy conversion reaction and is common to most fuel cells. The reaction is kinetically challenging and typically requires expensive metals (e.g. high-surface area platinum) or high overpotentials. Iron porphyrins are well-established molecular analogues for studying the ORR, as they are easily functionalized, use an earth-abundant metal, and are known for their ability to bind and activate O_2.[1]

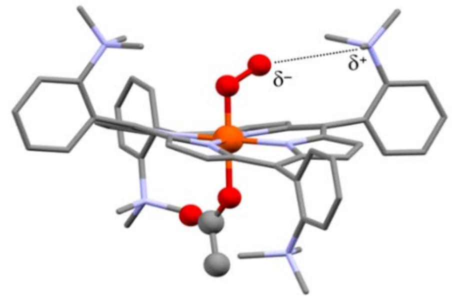


Fig 1. A computed model of $Fe^{III}(O_2^{\bullet-})(OAc)$, a probable intermediate during catalytic turnover, highlighting the subtle electrostatic interactions between the substrate and the charged ligand.

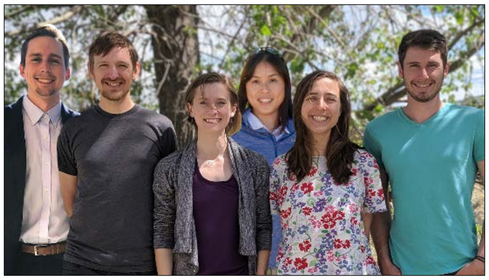
Iron αβαβ-*tetra*(*o*-*N*,*N*′,*N*′′-trimethylanilinium)porphyrin (Fe-*o*-TMA), which features cationic trimethylaminium groups, has been reported as an exceptional catalyst for electrochemical CO_2 reduction. The cationic groups in the ligand were proposed to electrostatically stabilize a high-energy CO_2 adduct, $Fe^{I}(CO_2^{\bullet-})$.[2] Current CME studies have shown that Fe-o-TMA with buffered acetic acid is an ORR catalyst. However, in this case, O_2 binding is not significantly enhanced via through-space coulombic interactions. Rather, the interactions between Fe-*o*-TMA and carboxylate axial ligands are more important.

This work seeks to understand the molecular nature of small molecule binding and activation to Fe-*o*-TMA. Both experimental studies and density functional theory calculations were used cooperatively to understand the electrostatic interactions between the positively charged trimethyaminium groups and bound O_2, CO_2, and carboxylate adducts. With a focus on Fe-*o*-TMA catalyzed ORR, we show that the $Fe^{III/II}$ reduction potential is sensitive to coordinating anions in solution and that the O_2 binding energies for this catalyst are similar to those for porphyrin systems lacking the cationic moieties. This counterintuitive result sheds light on the difference between electrostatic effects on O_2 vs. CO_2 binding and highlights how secondary sphere interactions and metal-center electronics affect small molecule binding and activation. These results have broad applications, from energy storage in small molecules to understanding how biological structures use their environments to control reactivity.

Contributions: As a continuation of ongoing collaborations between the authors, DJM initiated this new direction and executed the experimental work, with advice from JMM. SIJ and SR designed the computational research, and SIJ executed and interpreted the calculations.

[1] a) B. D. Matson, et al., *Chem. Commun.* **2012**, *48*, 11100-11102; b) M. L. Pegis, et al., *ACS Cent. Sci.* **2016**, *2*, 850-856; c) M. L. Pegis, et al., *Chem. Rev.* **2018**, *118*, 2340-2391.

[2] I. Azcarate, et al., *J. Am. Chem. Soc.* **2016**, *138*, 16639-16644.



(From left) Chris Bartel, Sage Bauers, Karen Heinselman, Bor-Rong Chen, Rachel Woods-Robinson, John Mangum, and Elisabetta Arca (not shown).

DESIGNING NEW NITRIDE SEMICONDUCTORS: FROM COMPUTATIONAL DISCOVERY TO EXPERIMENTAL REALIZATION

[CNGMD] S.R. Bauers[1], C.J. Bartel[2], R. Woods-Robinson[3], J.S. Mangum[4], B.R. Chen[5], K. Heinselman[1], E. Arca[1], W. Sun[6], A.M. Holder[2], A. Zakutayev[1], S. Lany[1], G. Ceder[3, 6], L. Schelhas[5], M. Toney[5]
[1]National Renewable Energy Laboratory; [2]University of Colorado Boulder; [3]University of California, Berkeley; [4]Colorado School of Mines; [5]SLAC National Laboratory; [6]Lawrence Berkeley National Laboratory

To accelerate materials discovery, the Center for Next Generation of Materials Design (CNGMD) couples first-principles theory with high-throughput and directed synthesis as well as advanced characterization to understand and predict structure, properties, and phenomena. This approach is exemplified by our successful and on-going quest to discover new metal nitride semiconductors.

Despite nitrogen being approximately four times more prevalent than oxygen in Earth's atmosphere, there are ten times fewer known nitrides than oxides, a consequence of the stability of molecular nitrogen.[1] However, the same chemistry in nitrogen that leads to its highly stable diatomic form imparts unique chemical and physical traits when successfully incorporated in the solid state. In this work, we rationally targeted new spaces for nitride discovery, realized these materials in the lab, and identified new chemical mechanisms that determine the stability and optical properties of solid-state nitrides.

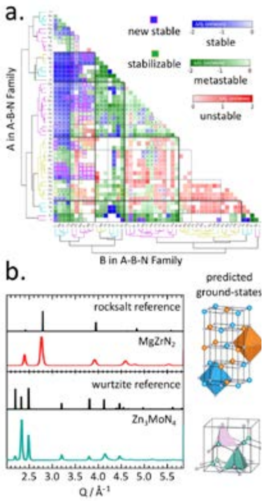


Fig 1: (a) Stability map of the ternary metal nitrides led to (b) experimental discovery of several new ternary nitrides.

As a core component of this work, we created a stability map of inorganic ternary nitrides using an ionic substitution algorithm and high-throughput density functional theory calculations (Fig 1a).[2] From this map, we 1) revealed the space of stable ternary nitrides to be twice as large as was previously known, with 203 new predicted stable compounds, and 2) extracted insights into the chemical origin of these new materials. Leveraging these predictions, we synthesized several compelling materials as thin-films using elevated nitrogen chemical potentials and confirmed their structures through a combination of synchrotron X-ray diffraction (Fig 1b) and high-resolution transmission electron microscopy. These discoveries—$ZnMoN_2$, Zn_3MoN_4, Zn_3WN_4, Zn_2SbN_3, $MgTiN_2$, $MgZrN_2$, $MgHfN_2$, Mg_2NbN_3, and Mg_2SbN_3—span a wide range of structures and chemistries and exhibit a diverse set of useful properties including tunable band gaps, redox-mediated stabilization, large dielectric constants, defect tolerance, small effective masses, and structural compatibility with known nitrides.[3,4,5] The full map of materials (Fig. 1a) was also assessed with a novel set of chemical bonding descriptors parsed from the computed electronic structure. In doing so, we partitioned the nitrides into those stabilized by the classical inductive effect and those stabilized by a newly proposed chemical mechanism, where nitrogen *donates* electron density, reducing the metals, which we term the *reductive* effect.

This work directly demonstrates and expands the materials development pipeline, integrating theory, computation, synthesis, and characterization to not only predict and realize new functional materials, but also to probe and understand the chemical mechanisms underlying their stability and properties. Looking beyond nitrides, this integrative materials-design approach will enable future efforts to explore under-developed chemical spaces for discovery of new functional materials for a range of applications.

References: **[1]**Sun et al. *Chem. Mater.* 29, 6936 (2017); **[2]**Sun et al. *Nat. Mater.* in press; **[3]**Arca et al. *J. Am. Chem. Soc.* 140, 4293 (2018); **[4]**Bauers et al. *arXiv*: 1810.05668; **[5]**Bauers et al. *Jpn. J. Appl. Phys.* in press.

Contributions: SB, KH and EA synthesized and characterized new nitrides; CB performed the chemical bonding analysis; RWR contributed experimentally and computationally; JM performed TEM characterization; BRC performed synchrotron characterization.

(From left) Tyler Mathis, Xuehang Wang, Nicolette Sanders, Ray Matsumoto, Lukas Vlcek, and Matt Thompson

DYNAMICS OF ELECTROLYTES UNDER CONFINEMENT IN NEXT GENERATION (PSEUDO)CAPACITIVE MATERIALS

[FIRST] X. Wang[1], L. Vlcek[2], M.W. Thompson[3], T.S. Mathis[1], R. Matsumoto[3], N.C. Sanders[4]

[1]Drexel University; [2]ORNL/UTK; [3]Vanderbilt University; [4]Oak Ridge National Laboratory

The key challenges impeding the predictive design of novel electrode materials and electrolytes for faster, lighter, thinner electrochemical energy storage devices include 1.) lack of understanding of the electrochemical processes occurring at electrode-electrolyte interfaces, and 2.) lack of knowledge about the transport of charge-storing ions and solvents in electrolyte systems, both in the bulk and under confinement. The FIRST Center has brought together a team of researchers from various institutions with expertise in advanced characterization techniques, materials synthesis, and computational modeling for probing in-depth the fundamental science of electrochemical fluid-solid interfaces and transport in electrolyte systems. Of particular interest are two-dimensional (2D) electrode materials with nano-confined fluids, which show rapid ion transport and surface-redox reaction rates. One such group of materials are 2D transition metal carbides and nitrides referred to as MXenes, which are metallically conductive, ionophilic materials with highly reactive surfaces capable of high-rate, pseudocapacitive charge storage. Recently we demonstrated how changing the organic solvent of lithium-ion-containing electrolytes can double the charge stored by the Ti_3C_2 MXene.[1] The fundamental science behind this unconventional finding was investigated by a combination of *in situ* electrochemical characterization, molecular dynamics (MD) simulations, and quasi-elastic neutron scattering (QENS) to reveal that when a carbonate-based solvent is used, the lithium ions will intercalate into the Ti_3C_2 layers in a de-solvated state. The opposite is true when a nitrile- or sulfoxide-based solvent is used, where solvent molecules will co-intercalate with the lithium ions, lowering the overall charge storage capability of Ti_3C_2, as shown by the MD simulation in **Figure 1** of a charged Ti_3C_2 electrode with the different electrolytes used in this study. To better understand and make use of this observation, we have conducted computational and experimental studies to screen optimal combinations of electrolyte ions and solvents for maximizing ion transport in room-temperature ionic liquids (RTILs), which are notorious for their slow transport properties. By surveying a diverse set of organic solvents using a Molecular Simulation Design Framework (MoSDeF) suite of software tools and MD simulations, we found that pure solvent diffusivity dominates the conductivity of RTIL-solvent mixtures.[2] This builds on our previous studies showing how solvent polarity impacts the transport properties in these types of electrolyte mixtures.[3] Altogether, our work shows how rigorous study of the interplay between charge-storing ions, organic solvents, and novel electrode materials can be used in the design of high-power and high-energy (pseudo)capacitive systems.

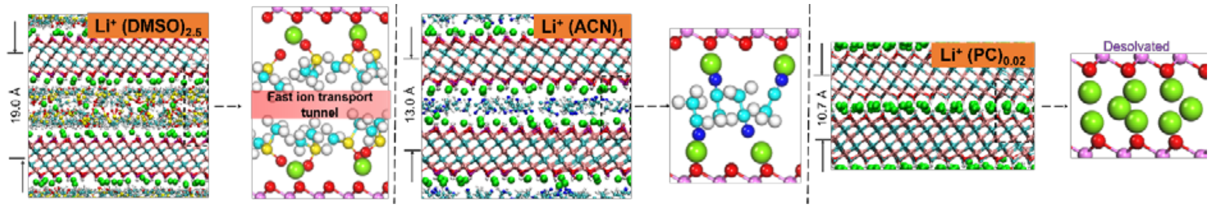
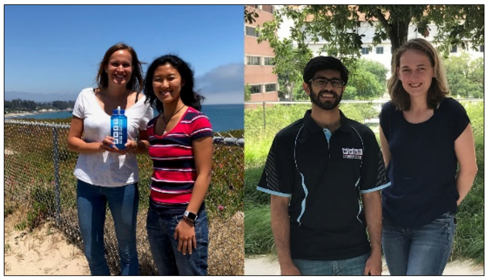


Figure 1. Molecular dynamics simulations showing the differing degrees of Li^+ ion confinement for charged Ti_3C_2 electrodes for $[Li^+][TFSI^-]$ dissolved in different electrolyte solvents[1].

References: [1]X. Wang et al., *Nature Energy* **2019,** *4* (3), 241-248; [2]M.W. Thompson et al., *J. Phys. Chem. B* **2019,** *123* (6), 1340-1347; [3]N.C. Osti et al., *J. Phys. Chem. Lett.* **2017,** *8* (1), 167-171.

Contributions: X.W. and T.M. conducted electrochemical experiments; N.C.S. made electrolyte conductivity measurements; M.W.T. and R.M. conducted computational screening within the MoSDeF framework; L.V. conducted MD simulations integrated with quasielastic neutron scattering results.



(From left) Segolene Antoine, Sally Jiao, Rahul Sujanani, and Malgorzata Chwatko

UNDERSTANDING THE IMPACT OF MESOSCALE MEMBRANE ARCHITECTURE ON WATER TRANSPORT

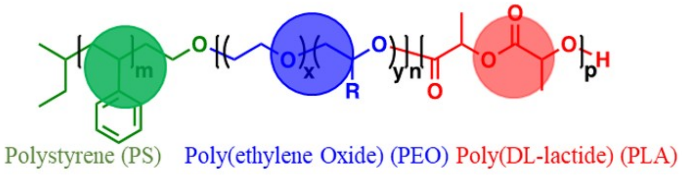
[M-WET] Segolene Antoine[1], Malgorzata Chwatko[2], Dipak Aryal[2], Rahul Sujanani[2], Sally Jiao[1], Venkat Ganesan[2], Nathaniel Lynd[2], Rachel Segalman[1], Lynn Katz[2], Benny Freeman[2]
[1]University of California, Santa Barbara; [2]The University of Texas at Austin

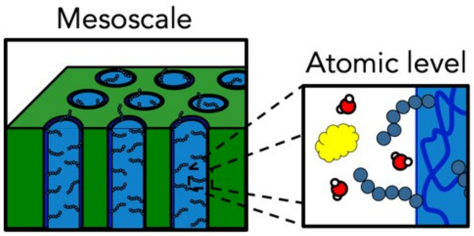
Water and energy are crucial resources for humanity but are interconnected as it takes copious amounts of energy to produce clean water. Synthetic membranes are widely used for purifying relatively clean water (e.g., seawater and brackish water desalination etc.) due to low energy requirements of membranes relative to alternatives (e.g., thermally-based separations).

However, current membranes were not designed to treat highly impaired water, such as produced water, due to extensive fouling and poor separation properties. Furthermore, there is a lack of fundamental and systematic studies probing the impact of polymer structure and membrane morphology on transport properties. Block copolymers (BCPs) self-assembly offers a highly tunable platform to achieve novel water filtration membranes with uniform pore sizes, well-defined pore size distributions (PSDs) and varied morphologies.

To study the impact of pore size on the water diffusion, both experimental and simulation approaches were utilized. The BCPs were synthesized *via* anionic polymerization and controlled ring-opening polymerization. BCPs were composed of polystyrene (PS), poly(ethylene oxide) (PEO) and polylactide (PLA) (PS-*b*-PEO-*b*-PLA). Membrane morphology was controlled via polymer composition such that the hydrophilic PEO block coats the pores. We propose that tuning the length of the hydrophilic block (PEO) will change both the size and hydrophilicity of the pores and consequently water diffusion through them. To achieve this, we varied the PEO block volume fraction from 0 to 20% while adjusting the PLA block volume fraction. Simulation results show that with increasing PEO block length the diffusion of water seems to decrease. Macroscopic water permeation measurements, which are used to characterize commercial materials, are being performed.

These results validated the simulation models that will be used in an inverse design strategy to determine the best morphologies exhibiting high water flux and subsequently target them experimentally. A key goal of this study is to understand how mesoscale architecture (i.e., pore geometry and chemistry) affects transport. This supports the broad goals of M-WET by providing optimized geometrical parameters used in future M-WET studies to design new membranes that can provide fit for purpose water and recover valuable solutes with less energy. This effort will bridge the polymer chemistry, membrane science, modelling, and water chemistry communities together.





Contributions: SA, MC synthesized the polymers used in this work. SA, RS tested macroscopic membrane performance. DA and SJ performed the simulations. VG, NL, RS, LK, BF helped to design the experiments and analyze data, supervised the work.

(From left) Nicholas H. Bashian, Andrew Dawson, Rebecca Kubena, and Josh Zak

INVESTIGATING THE REDOX ACTIVITY AND LITHIATION OF ICOSAHEDRAL BORON CLUSTERS IN THE SOLID STATE

[SCALAR] Rebecca M. Kubena[1], Dahee Jung[1], Zeeshan Parvez[1], Jonathan C. Axtell[1], Nicholas H. Bashian[2], Andrew Dawson[1], Josh Zak[3], Anton Van der Ven[4]*, Brent C. Melot[2]*, Kimberly A. See[3]*, Sarah H. Tolbert[1]* & Alexander M. Spokoyny[1]*

[1]UC Los Angeles; [2]University of Southern California; [3]Caltech; [4]UC Santa Barbara

Molecular borane clusters are well-known to exhibit reversible redox activity in solution. Specifically, icosahedral dodecaborate (B_{12}) clusters exhibit two sequential one-electron redox processes that can occur at different potentials depending on the nature of the organic substituents decorating the boron. This tunability, along with multiple accessible redox states, make these clusters appealing targets for developing new materials for rechargeable batteries. Within SCALAR, the Spokoyny group has been preparing several new insoluble redox-active B_{12} derivatives for use as novel cathode materials. They work closely with the Tolbert and Melot groups to study the fundamental electrochemical performance of these materials using potentio- and galvanostatic techniques. Cyclic voltammetry indicates a single distinct reversible Faradaic feature in several forms of the cluster that have been precipitated by derivatizing with Zn(II) ions, styrene, and carboxylic acid (Fig. 1a), which supports the idea that Li-ions can be inserted into the network of clusters. Further galvanostatic studies for the styrene cluster have showed promising reversibility on extended cycling (Fig. 1b). The Raman expertise of the See group is being leveraged to understand the stability of the organic functional groups decorating the surface of the clusters (Fig. 1c). The ability directly to monitor the vibrational mode during *operando* cycling experiments allows us to directly understand the impact of redox processes on the local structure of the clusters and quickly identify parasitic attacks on the organic groups. In parallel, the Melot group is performing *operando* X-ray diffraction measurements to monitor global changes in the bulk crystal structure. This complementary approach using extremely sensitive techniques leads to a more holistic understanding of the entire material system and provides deeper mechanistic insight. Supporting these efforts, the Van der Ven group is using computational modelling to determine stabile phases and stability limits. The complex and multi-faceted nature of these unique boron based materials necessitates the range of methods made available through multiple research groups. Utilizing the combined expertise of this multi-university effort allows for a fully comprehensive study of the synthetic, structural, and electrochemical dynamics of this new class of boron clusters based electrodes.

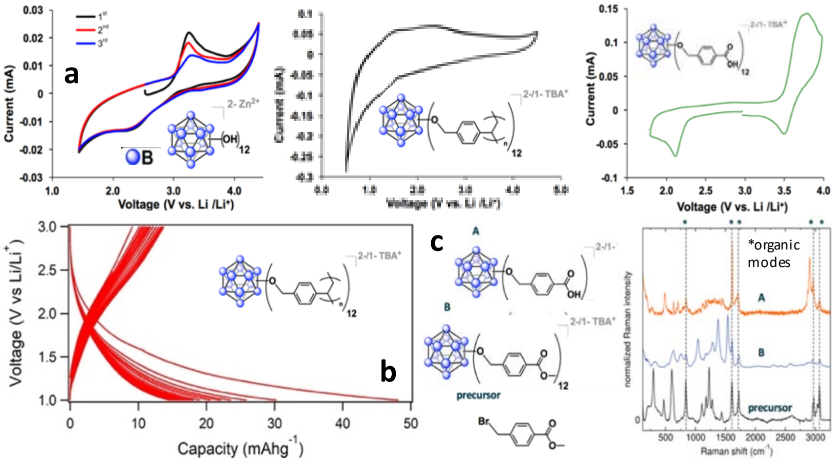


Figure 1. Preliminary data consisting of **(a)** cyclic voltammetry, **(b)** galvanostatic voltammetry, and **(c)** Raman spectroscopy of several B_{12} derivatives including zinc, polystyrene and carboxylic acid varieties

Contributions: R.M.K, D.J, Z.P, and J.C.A synthesized and characterized the boron cluster based materials. N.H.B and A.D performed electrochemical experiments, N.H.B. conducted operando XRD measurements. J.K performed Raman measurements. A.V. and colleagues did all theoretical modeling.

TEAM SCIENCE FINALISTS

(From left) Rachel Bangle and Jenny Schneider

TRANSPARENT CONDUCTING OXIDES AS HIGHLY VERSATILE DYE-SENSITIZED PHOTOELECTRODES

[AMPED] Rachel E. Bangle[1], Jenny Schneider[1], Renato N. Sampaio[2], Ludovic Troian-Gautier[1] and Gerald J. Meyer[1]
[1]*UNC Chapel Hill;* [2]*Brookhaven National Laboratory*

Transparent conductive oxides (TCOs) are commercially available materials used for a variety of opto-electronic applications. In recent AMPED research we have found that these materials, when cast as mesoporous thin films of TCO nanocrystallites, are versatile photoelectrode materials with some distinct advantages over semi-conducting oxides. The high doping level of TCOs such as In_2O_3:Sn (ITO) ($N_D > 10^{20}$ cm^{-3}) exhibit metallic properties that include high electron mobility and conductivity while retaining high transparency in the visible region for dye-sensitized catalysis applications.

We have recently shown that mesoporous ITO electrodes can support long-lived charge separation after dye-sensitized electron transfer. Remarkably the states live for almost a second, and recombination occurs with first-order kinetics (Fig. 1a). The key to success was to spatially position the molecular sensitizer (*S*) distant from the ITO nanocrystalline with an intervening electron acceptor. In unpublished work, we have found that closely related long-lived states with a molecular catalyst are indeed capable of driving multi-electron transfer water oxidation for water splitting applications.

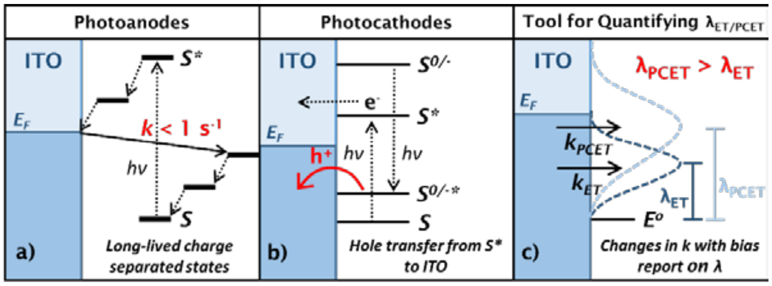
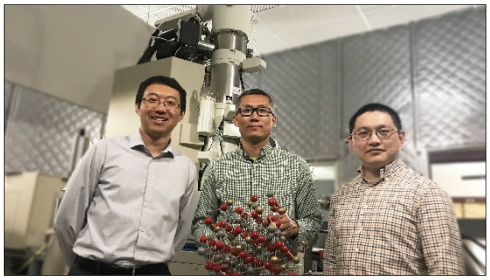


Figure 1: TCOs serve as a (a) photoanode sensitized with a molecular assembly built for sequential electron transfer, (b) photocathode undergoing hole transfer with a sensitizer, and (c) tool for quantifying λ by monitoring changes in rate with applied bias.

Furthermore, owing to the high concentration of TCO electrons, reductive quenching of sensitizer excited states (*S**), also called hole transfer, has been shown to be operative (Fig. 1b). The acceptor states of ITO overlap with the *S** acceptor levels ($S^{0/-}$*), allowing hole transfer from the sensitizer to ITO. In sharp contrast, the direction for electron transfer was reversed in a semiconducting material such as TiO_2, which exclusively quenches by oxidative electron transfer from *S** to the oxide. This novel photocathodic reactivity of TCOs is discussed in terms of tandem dye-sensitized solar cell applications.

In addition, dye-sensitized TCOs have been successfully applied as a tool to experimentally quantify the reorganization energy for electron transfer λ_{ET} and proton-coupled electron transfer λ_{PCET} (Fig. 1c). The approach required only a TCO, a means to photo-initiate the ET/PCET reaction, and a method to monitor the kinetic rate constant as a function of applied potential. Herewith, the metallic character of ITO allowed the potentiostatic control of the Fermi level (E_F) and thus of the reaction free energy change over a 1 eV range. The reduction of a ruthenium-based water oxidation catalyst from Ru^{III}-OH to Ru^{II}-OH_2 required 0.4 eV higher reorganization energy than did electron transfer without proton involvement, Ru^{III}-OH_2 to Ru^{II}-OH_2. Hence, this study provides quantitative data for parameters controlling interfacial charge transfer processes, a key variable in photoelectrosynthetic cells.

Contributions: REB quantified the kinetics and yields of light-driven hole transfer reactions at dye-ITO interfaces. JS applied Marcus-Gerischer theory to bias dependent kinetic data to extract reorganization energies for PCET reactions that occur with water oxidation catalysts. RNS and LT-G realized long-lived charge separation at ITO interfaces that are competent for water oxidation. GJM directed this research.



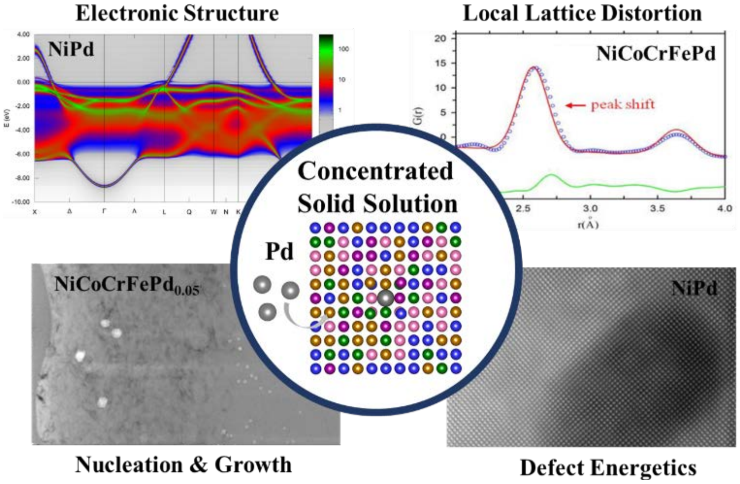
(From left) Xing Wang, Zhe Fan, and Yang Tong

TUNING LOCAL ATOMIC ENVIRONMENTS TO CONTROL RADIATION DAMAGE

[EDDE] Yang Tong[1], Zhe Fan[1], Xing Wang[1], Sai Mu[1], Shijun Zhao[1], Chenyang Lu[2], Li Jiang[2], Dilpuneet Aidhy[3], Gihan Velisa[1], Lumin Wang[2], Fuxiang Zhang[1], Karren L. More[1], Yanwen Zhang[1]
[1]Oak Ridge National Laboratory; [2]University of Michigan; [3]University of Wyoming

Modifying an alloy's compositional complexity provides a promising pathway for the future implementation of advanced structural materials that intrinsically resist severe radiation damage in nuclear energy applications. The wide selection of alloying elements available for modifying and tuning the chemical landscape of concentrated solid-solution alloys (CSAs) presents us with many opportunities to design novel alloys but also poses a new challenge: how can we efficiently and effectively optimize elements/compositions to create an alloy with the desired, targeted properties? Therefore, understanding and revealing the intricate correlations between elemental composition and radiation damage formation and suppression is timely and of great interest to accelerate the design of radiation-tolerant CSAs.

3*d* transition metal-based CSAs (e.g., Ni, Co, Fe, Cr) have demonstrated superior radiation-tolerance. The EDDE team investigated the effect of adding Pd (a 4*d* transition element) into 3*d* CSAs to further modify a CSA's local atomic environments. In the cases discussed here, we found that their radiation-resistance was enhanced by the addition of Pd. Experimental characterization and theoretical modeling at different length scales revealed the underlying complex mechanisms (see Figure). Transmission electron microcopy studies were conducted to statistically analyze defects in irradiated CSAs. We found that under irradiation, fewer, smaller imperfections and abnormal faceted bubbles or voids formed in the Pd-containing CSAs.[1] Synchrotron X-ray total scattering results showed that alloying with Pd induced both local and long-range lattice distortion.[2] *Ab initio* calculations further revealed that the lattice distortions in Pd-containing-CSAs reduced both the electron conductivity and lattice-mediated thermal conductivity through smearing of both the electron and phonon bands, which served to significantly slow the dissipation of heat and affected defect production and evolution during irradiation. Molecular dynamics simulations demonstrated that radiation-induced defects are preferentially isolated to inhibit their growth. These results provide valuable insights toward the design and deployment of compositionally complex CSAs for nuclear environment applications.



References: [1] Z. Fan, S. Zhao, K. Jin, D. Chen, Y.N. Osetskiy, Y. Wang, H. Bei, K.L. More, Y. Zhang, Acta Mater. 164 (2019) 283-292. [2] Y. Tong, G. Velisa, S. Zhao, W. Guo, T. Yang, K. Jin, C. Lu, H. Bei, J.Y.P. Ko, D.C. Pagan, Y. Zhang, L. Wang, F.X. Zhang, Materialia 2 (2018) 73-81.

Contributions: X.W. and Z.F. performed the transmission electron microscopy characterization, Y.T. conducted the synchrotron X-ray characterization, S.M. conducted the *ab initio* calculations, and D.A. performed the molecular dynamics simulations.

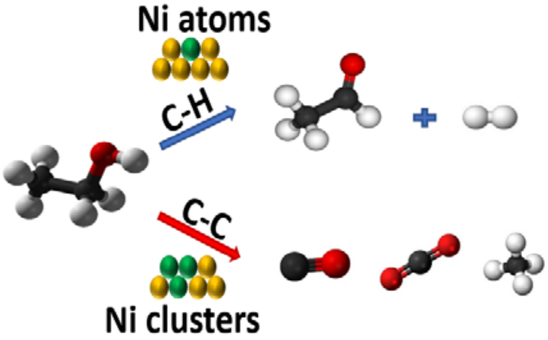
(From left) Kaining Duanmu, Georgios Giannakakis, Paul Kress, and Zhen Qi

MECHANISTIC STUDIES OF NON-OXIDATIVE ETHANOL DEHYDROGENATION ON NIAU SINGLE ATOM ALLOYS

[IMASC] Georgios Giannakakis[1]; Kaining Duanmu[2]; Paul Kress[1]; Zhen Qi[4]; Jurgen Biener[3]; Simon R. Bare[4]; Charles Sykes[1]; Philippe Sautet[2]; Maria Flytzani-Stephanopoulos[1]
[1]Tufts University; [2]University of California, Los Angeles; [3]Lawrence Livermore National Laboratory; [4]SLAC National Laboratory

Non-oxidative dehydrogenation of ethanol to acetaldehyde is of much practical interest since the main byproduct is hydrogen, which does not require additional separation steps unlike water, the byproduct under oxidative conditions. Mechanistically, ethanol dehydrogenation is also of interest as the first step in both ethanol steam reforming and ethanol oxidation. The commercial copper-based catalysts suffer from sintering, leading to deactivation. Gold (Au) catalysts are an alternative, as Au provides enhanced stability and exhibits 100% selectivity, albeit at the cost of low conversion. Here, we report the beneficial effect of alloying the Au surface with nickel (Ni) atoms, and the catalytic behavior of the resulting single atom alloy (SAA).

We have successfully deposited single atoms of Ni in Au surfaces[1], forming NiAu SAAs either supported on silica or in unsupported nanoporous form. The alloying of isolated Ni atoms with Au effectively suppressed the sintering of Au in both cases, based on SEM and TEM. It also lowered the activation energy of the ethanol dehydrogenation reaction significantly (from 96±3 to 59±5 kJ/mol), while the high selectivity of Au was maintained even at high temperatures (280 °C), at which point Ni forms clusters that catalyze the ethanol decomposition reaction (see scheme). The evolution of the catalytic structure was followed by CO-DRIFTS, allowing for structure-activity correlations. The Ni structure before reaction, after reduction, and during reaction was determined in-situ by EXAFS. The formation of Ni ensembles affected selectivity, as confirmed by TPD experiments performed under UHV conditions on single Au crystals doped with Ni. Ethanol drives Ni to the Au surface from the sub-surface where it exists after reduction, thereby activating the catalyst, as shown by XPS and confirmed by DFT calculations. *In-operando* mechanistic studies were performed on the NiAu SAAs via ethanol DRIFTS, high energy resolution fluorescence detection (HERFD) XAS, and Kinetic isotope effects (KIE) studies, which showed that both O-H and C-H bond activation are kinetically relevant steps. This was corroborated by density functional theory (DFT) calculations of the reaction mechanisms on NiAu SAA and Au surfaces, which also showed that the overall barrier on NiAu SAA is much lower than on Au surfaces, in agreement with experiments. Last, PdAu SAAs, which have been reported as promising selective hydrogenation catalysts[2], were also tested under similar reaction conditions but did not improve the catalytic activity to the same extent as Ni, as shown by kinetic measurements, ethanol DRIFTS, and verified by DFT. This difference, identified first in our EFRC work, will be further probed in other reaction systems of interest to the EFRC.

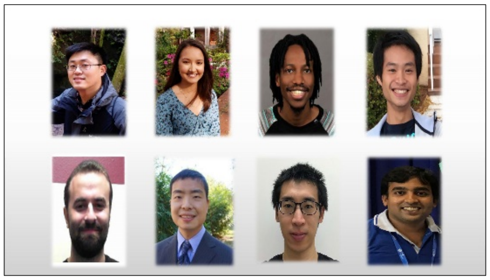


References:

[1]Giannakakis, G. *et al.* ,*Top. Catal.* **2018,** 61, 475
[2]Liu, J. *et al.* , *Catal. Sci. Technol.* **2017,** 7, 4276

Contributions:

G.G. performed kinetic, isotopic and spectroscopic studies, conducted XAS, TEM and XPS measurements. K.D. performed DFT calculations. P.K. conducted surface science studies. Z.Q. synthesized nanoporous materials and took SEM images.



(Top row from left) Jie-Xiang Yu, Ashlyn Hale, Rainier Berkley, and Dian-Teng Chen
(Bottom row from left) Jonathan Marbey, Haoming Jin, Xiaochen Zhu, and Tuhin Ghosh

SYNTHESIS, CHARACTERIZATION AND PREDICTIVE FIRST-PRINCIPLES CALCULATIONS

[M^{2}QM] Jie-Xiang Yu[1], Jonathan Marbey[2], Tuhin Ghosh[1], Ashlyn Hale[1], Dian-Teng Chen[1], Rainier Berkley[3], Hoaming Jin[1], Xiaochen Zhu[1], George Christou[1], Arthur F. Hebard[1], Talat Rahman[3], Stephen Hill[2], and Hai-Ping Cheng
[1]University of Florida; [2]Florida State University; [3]University of Central Florida

We report recent progresses on Mn-based single molecular magnets (SMMs). In particular, we investigated Mn_3 dimers and Mn_{84} molecules. High-frequency EPR measurements demonstrate coherent superposition of the quantum/spin states associated with a pair of covalently linked Mn_3 molecules. Via modifications, we can turn small SMMs (Mn_3, Mn_4) into robust supermolecular oligomers that can have FM or AFM couplings, and which may have applications in mutli-qubit devices. First-principles calculations confirmed the signs of exchange interactions. Furthermore, our calculations predict changes in the spin coupling as a function of applied pressure. For large SMMs (Mn_{70}, Mn_{84}), our goal is to study how large SMMs dope the graphene nano-structure and change its transport characteristics. Studies of these two limits, qubits and novel junctions for spintronic applications, are in line with the center mission: To deepen understanding and optimize control of electron-level physical processes to turn molecular magnets into quantum materials. We tune inter-molecule communication via magnetic interactions in clusters and solids and we design and perfect the underlying materials science for future computers and electronics.

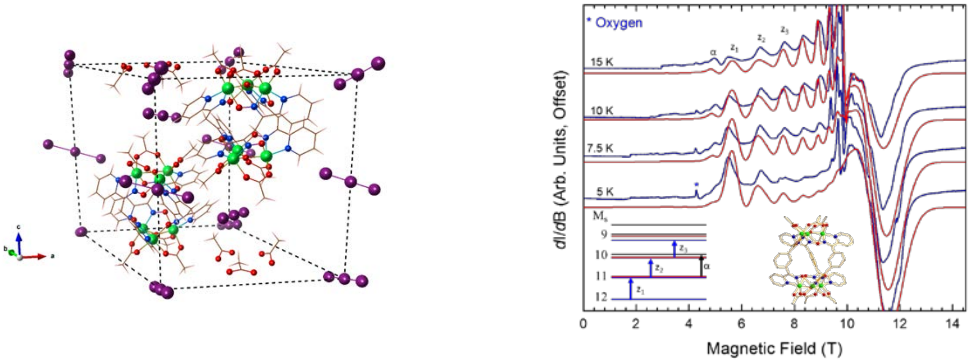
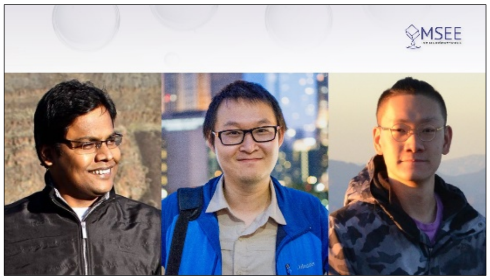


Figure 1. Left pannel: FM Mn_3-dimer in crystalline form; Right panel: EPR measurements.

Author Contributions: J.-X. Yu and H.-P. Cheng, Performed first-principles calculations and analysis of Mn3-dimers in gas phase and in bulk form; T. Ghosh and G. Christou, synthesized Mn_3 dimers; A. Hale and G. Christou synthesize Mn_n (n=70,84), D.-T. Chen and H.-P. Cheng performed first-principles calculations and analysis of Mn_{84}; R. Berkley and T. Rahman performed first-principles calculations of Mn_3-dimer; X.-C. Zhu H.-M. Jin and A. F. Hebard fabricated graphene nano-junction and transport measurements; J. Marbey and S. Hill performed EPR measurements.



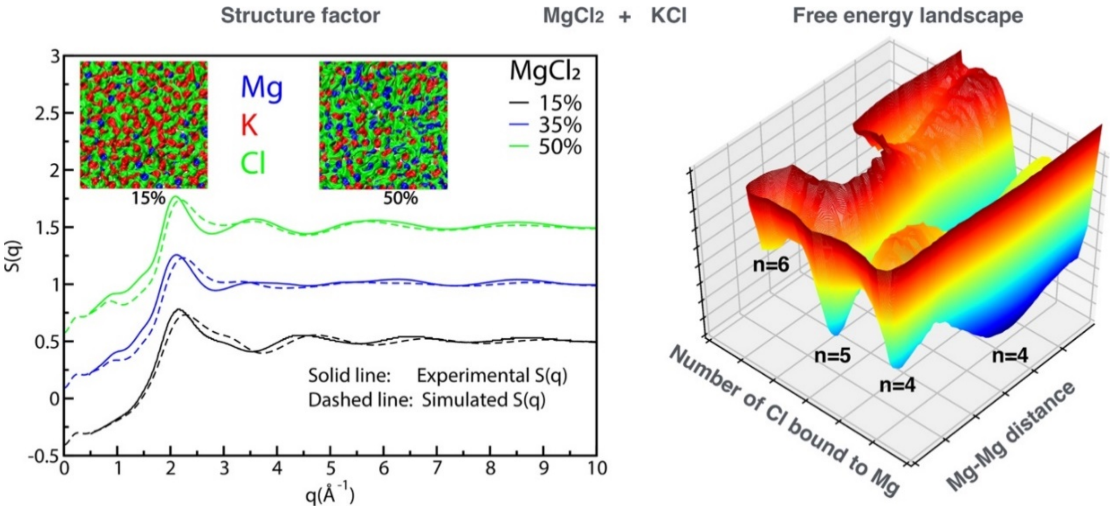
(From left) Santanu Roy, Fei Wu and Haimeng Wang

BRIDGING THE GAP BETWEEN THEORY AND EXPERIMENTS ON THE STRUCTURE, DYNAMICS, AND THERMODYNAMICS OF MOLTEN SALTS

[MSEE] Santanu Roy[1], Fei Wu[2], Haimeng Wang[3], Shobha Sharma[2], Yong Zhang[3], Matthew S. Emerson[2], Vyacheslav S. Bryantsev[1], Edward J. Maginn[3], Claudio J. Margulis[2], Alexander S. Ivanov,[1] Shannon M. Mahurin,[1] Phillip Halstenberg,[1] Simerjeet Gill,[4] Mehmet Topsakal,[4] Bobby Layne,[4] Kotaro Sasaki[4]

[1]Oak Ridge National Laboratory; [2]University of Iowa; [3]University of Notre Dame; [4]Brookhaven National Laboratory

A fundamental and predictive understanding of the structure, dynamics, and reactivity of molten salts in the bulk and at interfaces under extreme conditions of temperature and radiation is crucial for the design of a new generation of molten salt nuclear reactors, ensuring their operating efficiency and safety. Achieving the necessary understanding requires significant advances in computational and experimental methods. In our new *Molten Salts in Extreme Environments (MSEE)* EFRC, we apply theory and molecular dynamics (MD) simulation methods at the electronic and classical levels to provide novel atomistic insights into the structure and dynamics of molten salts. These insights permit us to interpret and derive more information from experimental measurements of structure by high-energy X-ray and neutron scattering techniques at high temperature regimes. We focus on a series of molten chloride salts with monovalent, divalent, and trivalent cations, and their mixtures, and we model structural, thermodynamic, and transport properties as functions of temperature. We are breaking new ground in molten salt MD simulations, which requires thorough and rigorous comparison between our experiments and our *ab initio* and classical polarizable and nonpolarizable force field molecular dynamics results. This enables us to assess the quality of our parameterizations, and lays a strong foundation for modeling more complex mixtures including fuel salts, corrosion, and fission products. In this talk, we will discuss our advances so far in understanding properties of molten salts such as structure factors, coordination structure, self-diffusivities, viscosities, ionic conductivities and thermal conductivities, as well as the mechanisms and kinetics of ion-pairing and ion-exchange processes in molten salts.



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Contributions: S.R. analyzed free energy landscapes and rate processes, F.W. analyzed structure factors, and H.W. analyzed dynamical properties such as self-diffusivities, viscosities, and conductivities.

(From left) Hyeyoung Cho, Jiaoyan Li, Jiaqi Jin and Hassnain Asgar

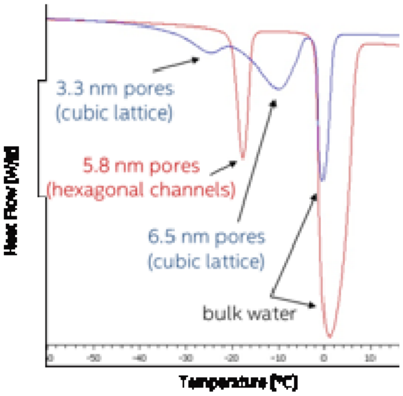
PROPERTY CHANGES UNDER CONFINEMENT IN ARCHITECTED MATERIALS

[MUSE] Pranay Asai[1], Hassnain Asgar[2], Michael Bartl[1], Darryl Butt[1], Hyeyoung Cho[1], Milind Deo[1], Greeshma Gadikota[2], Jan Goral[1], Hai Huang[3], Jiaqi Jin[1], Jiaoyan Li[3], Jan Miller[1], Subhash Risbud[4], Viktoriya Semekina[1], Yiping Xia[4], Ilya Zharov[1]

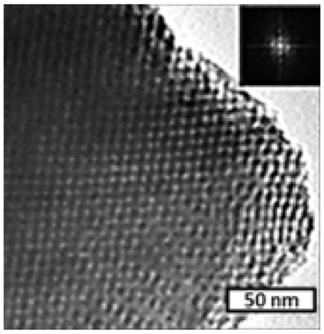
[1]University of Utah; [2]University of Wisconsin; [3]Idaho National Laboratory; [4]University of California, Davis

The mission of MUSE is to synthesize geomaterials with repeatable hierarchical heterogeneity and develop an understanding of transport and interfacial properties of fluids confined within these materials. There is considerable evidence that the known laws of phase transitions, and flow are affected by the presence of fluids confined in porous materials with nanometer-sized pores. Specially created nanoporous silica powders were architected into discs by using spark plasma sintering. The samples were imaged and characterized for a complete description of porosity using X-ray tomography, scanning electron microscopy and small and wide-angle neutron scattering. Phase transitions (melting and boiling points) and fluid permeabilities were measured in the powders and architected samples using high-pressure differential scanning calorimetry. Phase transition points were significantly different in the nanopores of the architected samples. The entire vapor pressure curve for pure hydrocarbons was below the bulk vapor pressure curve. Gibbs Ensemble Monte Carlo simulations were used to reproduce experimental trends. Permeabilities of polar and non-polar fluids in the architected discs were different indicating a breakdown in Darcy's Law in nanopores. Different permeabilities for the different fluids used showed importance of fluid-solid interactions. Flow in the nanopores of the siliceous matrix was modeled using molecular dynamics. Dissipative particle dynamics was used to molecular dynamics and explore flows in the multiple silica nanopore arrays, considering their packing and length. The models confirmed experimental findings. This paper illustrates the central mission of MUSE of synthesizing and characterizing architected materials, and of measuring and understanding fluid properties inside these materials.

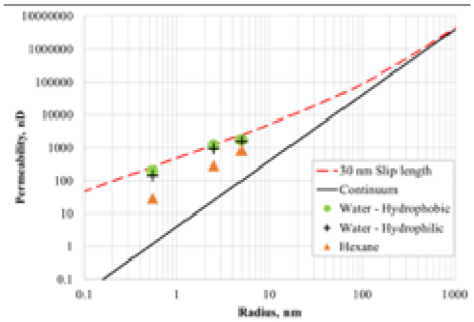
Changes in Phase Transitions



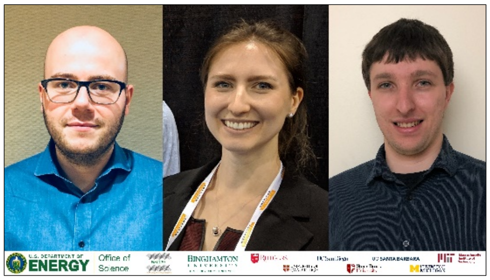
Synthesis and Characterization



Deviations from Darcy's Law



Contributions: Synthesis and Characterization – Asgar, Bartl, Butt, Cho, Gadikota, Goral, Risbud, Semekina, Xia and Zharov; Measurements – Cho, Deo, Jin, Miller and Xia; Modeling – Asai, Jin and Li

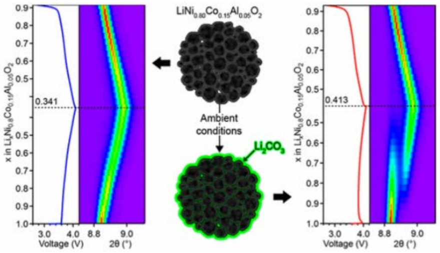


(From left) Antonin Grenier, Julija Vinckeviciute, and Zachary Lebens-Higgins

FROM CATION TO ANION REDOX: PUSHING THE ULTIMATE LIMIT OF LAYERED OXIDES

[NECCES] Zachary W. Lebens-Higgins[1], Antonin Grenier[2], Julija Vinckeviciute[3], Anton Van der Ven[3], Karena Chapman[2], Louis F. J. Piper[1]
[1]Binghamton University; [2]Stony Brook University; [3]University of California, Santa Barbara

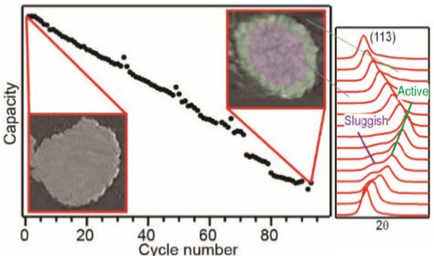
Narrowing the gap between theoretical and practical reversible capacities of layered oxide cathodes remains a critical challenge for next generation Li-ion batteries.[1] NECCES identified $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ (NCA) as a model system for understanding the chemical reactions at various length scales that govern cycling performance of layered oxides. The solid solution behavior of the NCA ternary system is effectively modeled by an O3 phase ($R\bar{3}m$) up to 90 % Li-extraction with aluminum inhibiting phase transitions from O3 to O1.[2]



Li_2CO_3 overlayer [3]

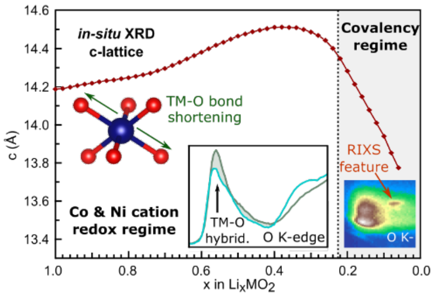
The electrochemistry of Ni-rich cathodes is strongly influenced by their sensitivity to air-exposure. In the first charge of NCA, high impedance from surface Li_2CO_3 gives rise to reaction heterogeneity during delithiation.[3] Without this overlayer the heterogeneity is eliminated resulting in the intrinsic solid-solution behavior.

Suppressing Li_2CO_3 and related overlayer species is key for long-term cycling performance,[4] yet challenges remain in retaining high capacities when operating above 4.3 V vs. Li+/Li0. Among the high voltage operating challenges, operando x-ray diffraction revealed intergranular fracturing to be a dominant capacity fading mechanism between 2.7-4.5V, accounting for up to 20% capacity loss [5]. Primary particles lose electrical contact and become "sluggish" because of fracturing due to large mechanical stress associated with lattice breathing.



Intergranular fracturing fade mechanism [5]

The c-lattice collapse at high voltages above 4.3 V vs. Li+/Li0 is considered to arise from covalency-driven oxygen redox and plays a key role in the mechanical induced fracturing. A combination of resonant inelastic x-ray scattering (RIXS) with an array of structural and electronic probes were used to provide direct insight into the charge compensation process. Nickel and cobalt redox were found to occur in tandem below 4.25 V resolving a long-standing issue. Oxidized oxygen signatures in O K-edge RIXS maps were observed to emerge concurrently with the c-lattice collapse. The RIXS feature's evolution with delithiation presents evidence of depopulating O 2p states,[6] and suggests that covalency may be utilized elsewhere for rational design of anionic redox.



Cation and anion charge compensation considered in delithiation of NCA

NECCES references: [1.] Adv. Energy Mater. (2017) 160288; [2] *J. Mater. Chem. A* (2018) **6**, 4189-4198; [3] *Chem. Mater.* (2017) **29**, 7345-7352; [4] J. Electrochem. Soc. (2017) A3727-A3741; [5] *Nano Lett.* (2017) **17**, 3452–3457;

Contributions: Z. W. L.-H. & L. F. J. Piper conducted x-ray spectroscopy experiments regarding charge compensation. A. G. & K. C. conducted operando synchrotron x-ray diffraction and structural analysis. J. V & A. V. V. performed supporting density functional theory calculations.

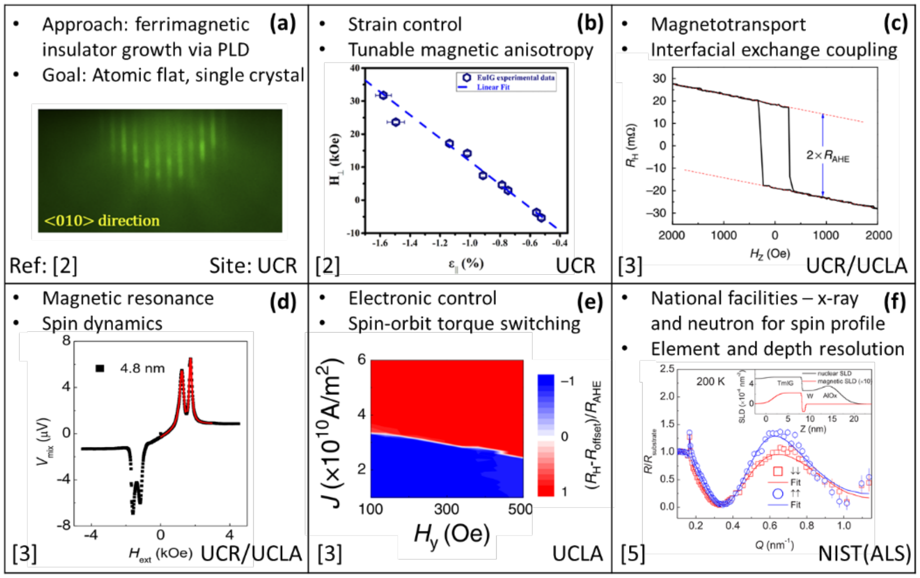
(From left) Qiming Shao and Víctor H. Ortiz

FERRIMAGNETIC INSULATOR FOR ULTRAFAST AND ULTRALOW-POWER SPINTRONIC DEVICES

[SHINES] Victor H. Ortiz[1], Qiming Shao[2], Mohammed Aldosary[1], Alexander Grutter[3], Junxue Li[1], Guoqiang Yu[2], Yawen Liu[1], Chi Tang[1], Kang L. Wang[2], and Jing Shi[1]

[1]University of California, Riverside; [2]University of California, Los Angeles; [3]NIST

We aim to study the mutual effects of ferrimagnetic insulator and heavy metal with strong spin-orbit coupling by combining the material growth and characterization strength at UCR and spin-orbit torque measurement strength at UCLA. We achieved high-quality rare earth iron garnet film growth and control of the perpendicular magnetic anisotropy (a desirable attribute for memory technology) by tuning the strain in the films (a)(b) [1][2]. We investigated interfacial exchange coupling by performing magnetotransport measurements (b) [1-5] and spin dynamics by using magnetic resonance (c) [3-4]. Extensive spin-orbit torque switching experiments reveal highly efficient switching of the ferrimagnetic garnet (e) in both ferromagnetic and antiferromagnetic regimes [3-4]. We also leveraged external collaborations with NIST and Advanced Light Source (ALS) to perform XMCD and neutron reflectometry experiments to resolve element- and depth-dependent spin profiles [5]. The close collaboration between UCR and UCLA allows us to gain rapid and deep understanding of the interplay between spin, magnon and electron at the atomic scale in the thin film systems, which is an objective of SHINES.



References: [1] C. Tang, et al., Phys. Rev. B, 94, 140403(R) (2016); [2] V. H. Ortiz, et al., APL Mater., 6, 121113 (2018); [3] Q. Shao, et al., Nat. Commun., 9, 3612 (2018); [4] J. Li, et al., Phys. Rev. B, 95, 241305(R) (2017); [5] Q. Shao, et al., Phys. Rev. B, 99, 104401 (2019).

Contributions: Víctor H. Ortiz and the UCR group grew and characterized magnetic garnet thin films. Qiming Shao and the UCLA group performed the current-induced switching measurements. Both groups contributed to the device fabrication and deposition of heavy metal layer, and to magnetotransport and magnetic resonance measurements.

2019 EFRC PI MEETING – EFRC ACRONYMS

ENERGY FRONTIER RESEARCH CENTERS (TEAM SCIENCE FINALISTS ONLY)

[AMPED] Alliance for Molecular PhotoElectrode Design for Solar Fuels
Gerald Meyer, University of North Carolina
Class: 2009 – 2020

[BioLEC] Bioinspired Light-Escalated Chemistry
Gregory Scholes, Princeton University
Class: 2018 – 2022

[CME] Center for Molecular Electrocatalysis
R. Morris Bullock, Pacific Northwest National Laboratory
Class: 2009 – 2022

[CNGMD] Center for Next Generation of Materials by Design: Incorporating Metastability
William Tumas, National Renewable Energy Laboratory
Class: 2014 – 2020

[EDDE] Energy Dissipation to Defect Evolution
Yanwen Zhang, Oak Ridge National Laboratory
Class: 2014 – 2020

[FIRST] Fluid Interface Reactions, Structures and Transport Center
Sheng Dai, Oak Ridge National Laboratory
Class: 2009 – 2022

[IMASC] Integrated Mesoscale Architectures for Sustainable Catalysis
Cynthia Friend, Harvard University
Class: 2014 – 2022

[M^{2}QM] Center for Molecular Magnetic Quantum Materials
Hai-Ping Cheng, University of Florida
Class: 2018 – 2022

[MSEE] Molten Salts in Extreme Environments
James Wishart, Brookhaven National Laboratory
Class: 2018 – 2022

[MUSE] Multi-Scale Fluid-Solid Interactions in Architected and Natural Materials
Darryl Butt, University of Utah
Class: 2018 – 2022

[M-WET] Center for Materials for Water and Energy Systems
Benny Freeman, University of Texas at Austin
Class: 2018 – 2022

[NECCES] NorthEast Center for Chemical Energy Storage
M. Stanley Whittingham, Binghamton University
Class: 2009 – 2020

[SCALAR] Center for Synthetic Control Across Length-scales for Advancing Rechargeables
Sarah Tolbert, University of California, Los Angeles
Class: 2018 – 2022

[SHINES] Spins and Heat in Nanoscale Electronic Systems
Jing Shi, University of California, Riverside
Class: 2014 – 2020