TABLE OF CONTENTS

INTRODUCTION 2

TEAM SCIENCE WINNERS 3

- CMS – Center for Computational Study of Excited-State Phenomena in Energy Materials (C2SEPEM) 3
- EFRC – Center for Electrochemical Energy Science (CEES) 4
- EFRC – Inorganometallic Catalyst Design Center (ICDC) 5
- Hub – Joint Center for Artificial Photosynthesis (JCAP) 6
- EFRC – Solid-State Solar-Thermal Energy Conversion Center (S3TEC) 7
- EFRC – Center for Understanding and Control of Acid Gas-induced Evolution of Materials for Energy (UNCAGE-ME) 8

TEAM SCIENCE FINALISTS 9

- EFRC – Argonne-Northwestern Solar Energy Research Center (ANSER) 9
- EFRC – Center for Biological Electron Transfer and Catalysis (BETCy) 10
- EFRC – Center for Gas Separations Relevant to Clean Energy Technologies (CGS) 11
- EFRC – Center for Lignocellulose Structure and Formation (CLSF) 12
- EFRC – Energy Dissipation to Defect Evolution (EDDE) 13
- EFRC – Fluid Interface Reactions, Structures and Transport Center (FIRST) 14
- EFRC – Center for Geologic Storage of CO_2 (GSCO2) 15
- EFRC – NorthEast Center for Chemical Energy Storage (NECCES) 16
- EFRC – Spins and Heat in Nanoscale Electronic Systems (SHINES) 17
- EFRC – Center for Solar Fuels (UNC) 18

CENTER ACRONYMS 19

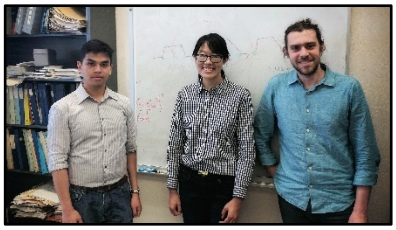
INTRODUCTION TO THE GRADUATE STUDENT AND POSTDOC TEAM SCIENCE CONTEST AT THE 2017 EFRC-HUB-CMS PRINCIPAL INVESTIGATORS' MEETING

Early Career scientists are a significant component of the Energy Frontier Research Center (EFRC), Energy Innovation Hub (Hub), and Computational Materials Sciences Award (CMS) programs. Altogether, these programs involve more than 900 graduate students and 800 postdoctoral researchers. 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 2017 EFRC-Hub-CMS Principal Investigators' Meeting in Washington, D.C. on July 24-25, 2017. 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 that included both theory and experiment. The DOE EFRC, Hub, and CMS management teams selected 16 finalists from more than 25 nominations. In the following pages, early career team members are highlighted in orange; those who presented are underlined. 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, integration of theory and experiment, 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 program websites:

- **Computational Materials Sciences** [http://science.energy.gov/bes/funding-opportunities/closed-foas/computational-materials-sciences-awards/] – Multi-institutional groups of investigators that integrate theory/computation with experiment and provide advanced tools and techniques in support of the Materials Genome Initiative (MGI).
- **Energy Frontier Research Centers** [http://science.energy.gov/bes/efrc] – Multi-institutional groups of investigators that focus on grand challenges and use-inspired science problems of a scope that could not be addressed by a single investigator.
- **Energy Innovation Hubs** [http://science.energy.gov/bes/research/doe-energy-innovation-hubs] – Large groups of investigators spanning basic and applied R&D.

TEAM SCIENCE WINNERS

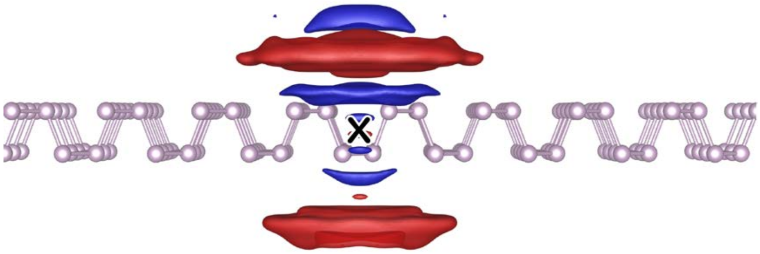

(From left) Iqbal B. Utama,
Diana Y. Qiu, Felipe H. da Jornada

ENVIRONMENTAL SCREENING EFFECTS IN 2D MATERIALS: RENORMALIZATION OF THE BANDGAP, ELECTRONIC STRUCTURE, AND OPTICAL SPECTRA

[CMS – C2SEPEM] Diana Y. Qiu, Felipe H. da Jornada, M. Iqbal B. Utama, Feng Wang, Steven G. Louie
Lawrence Berkeley National Laboratory and UC Berkeley

Few-layer black phosphorus (BP) is a highly promising material for optoelectronic and clean energy technologies. In order to avoid degradation in ambient conditions, it has become common practice to encapsulate these quasi-2D BP devices with wide bandgap insulators. While it is generally assumed that this encapsulation does not significantly affect their electronic and optical properties, we show, in a collaborative effort between ab initio theory and experiment, that the opposite is true [1,2].

We performed the first optical absorption measurements on few-layer BP encapsulated between a sapphire substrate and a boron nitride capping layer. Concurrently, in accordance with the experimental setup, we developed new theoretical and computational techniques to incorporate the screening environment from the substrate and the capping layer in our *ab initio* GW and GW-BSE calculations. We find that, contrary to previous belief, BP is exceptionally sensitive to environmental screening. We showed for the first time that encapsulation reduces the exciton binding energy by as much as 70%, and dramatically changes the nature of the excited states and the qualitative features of the absorption spectrum. This can be seen in the figure below, where we plot the difference between the induced charge density for encapsulated monolayer BP and isolated BP, given an external test charge at “X”



Our discovery and understanding of large environmental screening effects open new pathways for tuning the properties of low-dimensional materials by treating screening and confinement as separately tunable degrees of freedom. Furthermore, the new methods we developed for including substrate screening push the frontiers of state-of-the-art many-body GW and GW-BSE calculations, allowing us not only to accurately account for the experimental environment, but also to calculate excited-state phenomena in incommensurate, layered heterostructures. Finally, in a similar synergetic setup between experiment and theory, we are now studying the role of substrates in the electronic properties of few-layer transition metal dichalcogenides (TMDs).

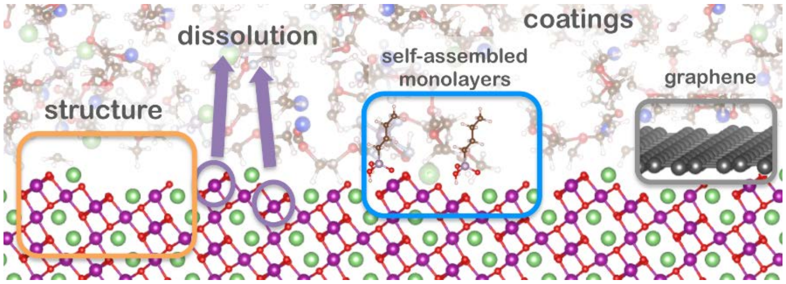
References: [1] L. Li, J. Kim, C. Jin, G. J. Ye, D. Y. Qiu, F. H. da Jornada, Z. Shi, L. Chen, Z. Zhang, F. Yang, K. Watanabe, T. Taniguchi, W. Ren, S. G. Louie, X. H. Chen, Y. Zhang, F. Wang, *Nature Nanotechnology* **12**, 21 (2016). [2] D.Y. Qiu, F.H. da Jornada, and S. G. Louie, submitted to *Nano Letters*.

Contributions: D.Y.Q., F.H.J., S.G.L. developed the theory and performed *ab initio* calculations. M.I.B.U. and F. Wang fabricated and characterized the (TMDs) samples and analyzed the absorption spectra.

(From left on top) Robert Warburton, Bruno Nicolau, Kendra Letchworth-Weaver; (From left on bottom)
Xiao Chen, Kan-Sheng Chen

UNDERSTANDING AND CONTROLLING THE REACTIVITY OF $LiMn_2O_4$-ELECTROLYTE INTERFACES

[EFRC – CEES] Robert Warburton[1], Bruno Nicolau[2], Kendra Letchworth-Weaver[4], Kan-Sheng Chen[3], Aaron Petronico[2], Laila Jaber-Ansari[3], Xiao Chen[4], Yasaman Ghadar,[4] Maria Chan[4], Ralph Nuzzo[2], Andrew Gewirth[2], Jeffrey P. Greeley[1], Mark Hersam[3], Paul Fenter[4]
[1]*Purdue University,* [2]*University of Illinois,* [3]*Northwestern University,* [4]*Argonne National Laboratory*



The spinel $Li_xMn_2O_4$ ("LMO") is a commercial lithium ion battery cathode material whose use is limited by instabilities at the cathode-electrolyte interface. Specifically, LMO undergoes a disproportionation reaction, 2 Mn(III) → Mn(II) + Mn(IV) for $x \geq 1$ where the presence of Mn(II) at the interface is believed to lead to cathode dissolution. These cathode-electrolyte interface reactions are poorly understood and conceptual advances that enable robust mitigation strategies are needed.

In this context, CEES has been working to develop a suite of experimental and conceptual strategies for understanding and controlling this reactivity through coordinated studies of well-defined model systems. The foundation for these studies is a robust understanding of the structure and stability of the different LMO facets. This is obtained by density functional theory (DFT), revealing that the LMO(111) surface facet is the most stable. X-ray reflectivity measurements of model LMO(111) thin film electrodes confirms their use as model electrodes, including the observation of Mn loss upon lithiation for $x>1$ revealing that this chemical instability is observed even in these ideal systems. Phosphonic acid self-assembled monolayers ("SAMs") were used to create artificial cathode electrolyte interface ("CEI") layers at LMO-electrolyte interfaces, in which the length and functionality of the SAM molecule was used to tune the competing needs of maximizing Li ion conductivity but minimizing secondary reactivity. The observed trends in contact angles and cyclic voltammetry were understood using DFT coupled with a continuum electrolyte description that captures the formation of a stable CEI and the interaction of these layers with the electrolyte. This conceptual advance associated with separating charge and ion transfer functionalities was used to create a composite nanostructured graphene/LMO cathode morphology whose improved properties in a working lithium ion battery cell were demonstrated in both half- and full-cell geometries.

Contributions: Warburton and Greeley performed DFT calculations of the structure and relative stability of LMO interfaces. Chen and Fenter probed the structure and reactivity of model LMO thin-film materials under electrochemical control. Nicolau and Gewirth performed experimental studies of the design of model CEI compounds that control the reactivity of LMO. Letchworth-Weaver, Ghadar, and Chan performed computational studies to understand the suppression of LMO dissolution through the choice of model CEI. Chen and Hersam demonstrated that graphene-coatings in composite electrode are effective at suppressing these chemical instabilities.

(From left) Manual A. Ortuna,
Ana E. Platero-Prats, Zhanyong Li

POST-FUNCTIONALIZED METAL–ORGANIC FRAMEWORKS FOR CATALYSIS

[EFRC – ICDC] Manuel A. Ortuño,[1] Zhanyong Li,[2] Ana E. Platero-Prats,[3] Karena W. Chapman,[3] Joseph T. Hupp,[2] Omar. K. Farha,[2] Christopher J. Cramer,[1] Laura Gagliardi[1]

[1]University of Minnesota; [2]Northwestern University; [3]Argonne National Laboratory

Metal–organic frameworks are a versatile family of mesoporous materials used in gas storage, separation, and catalysis. They are comprised by inorganic nodes connected by organic linkers. The vast number of linker–node combinations provides a high degree of tuning to design and predict unique structure topologies. Within this extensive catalog, the Zr-based MOF NU-1000 stands out as an excellent support material to deposit transition metal catalysts via atomic layer deposition (AIM) or solvothermal deposition (SIM) protocols.

The fine-tuning of MOF nodes with transition metals allows us to prepare different catalysts for different transformations, such as ethylene hydrogenation and dimerization (Ni), epoxidation (Mo), methane oxidation (Cu), and propane oxidative dehydrogenation (Co),[1] among others (Figure 1).

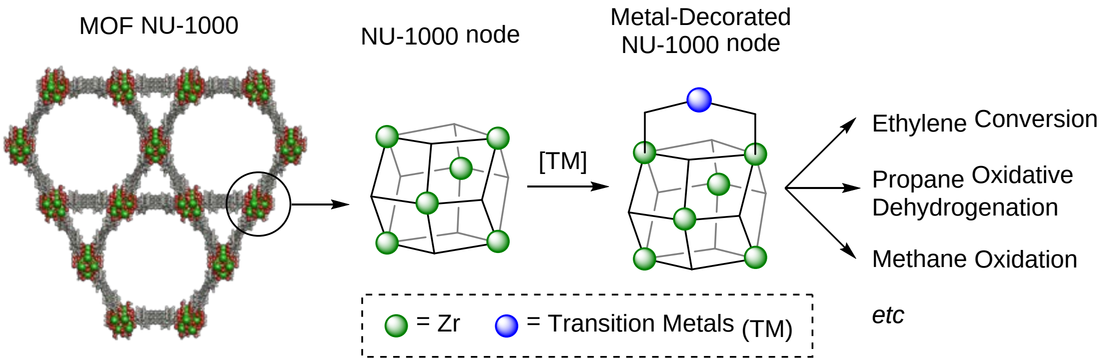


Figure 1. Metal–organic framework (MOF) NU-1000 and further post-functionalization for catalysis.

The synergistic combination of experimental and theoretical techniques becomes crucial to (i) determine the local structure of the post-functionalized materials and (ii) analyze the catalytic reaction mechanisms at the atomic level of precision. These joined efforts would path the way to unravel chemical descriptors and build structure–reactivity relationships leading to rational design of new materials.

Reference: 1. Li, Z.; Peters, A. W.; Bernales, V.; Ortuño, M. A.; Schweitzer, N. M.; DeStefano, M. R.; Gallington, L. C.; Platero-Prats, A. E.; Chapman, K. W.; Cramer, C. J.; Gagliardi, L.; Hupp, J. T.; Farha, O. K. *ACS Cent. Sci.* **2017**, *3*, 31.

Contributions: M. A. O. theoretically modeled structures and reaction mechanisms. Z. L. and A. E. P.-P. carried out the synthesis, characterization, and catalytic testings.

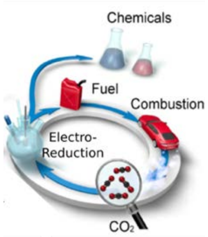
(From left) Zachary W. Ulissi, Daniel A. Torelli, Maryam Farmand, Jeremy T. Feaster, Sean W. Fackler

MATERIALS DISCOVERY, THEORY, AND CHARACTERIZATION OF INTERMETALLICS FOR ELECTROCHEMICAL CO$_2$ REDUCTION

[Hub – JCAP] Jeremy T. Feaster[1,4], Daniel A. Torelli[2,4], Zachary W. Ulissi[1,4], Maryam Farmand[3,4], Sean W. Fackler[3,4], Jeffrey W. Beeman[3], Apurva Mehta[1], Ryan Davis[1], Alan T. Landers[1,4], John C. Lin[1,4], Drew C. Higgins[1,4], Sonja A. Francis[2,4], J. Chance Crompton[2,4], Alnald Javier[2,4], Jonathan R. Thompson[2], Michael T. Tang[1,4], Jianping Xiao[1,4], Xinyan Liu[1,4], Mohammadreza Karamad[1], Robert Sandberg[1,4], Karen Chan[1,4], Christopher Hahn[1,4], Bruce S. Brunschwig[2,4], Manuel P. Soriaga[2,4], Walter S. Drisdell[3,4], Junko Yano[3,4], Thomas F. Jaramillo[1,4], Nathan S. Lewis[2,4], Jens K. Nørskov[1,4]

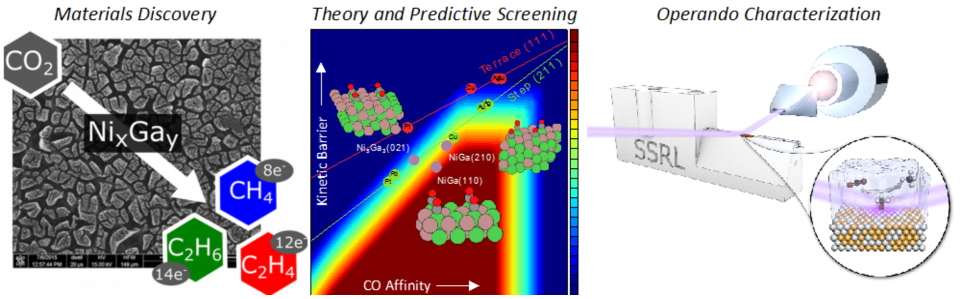
[1]Stanford/SLAC, [2]Caltech, [3]LBNL, [4]JCAP

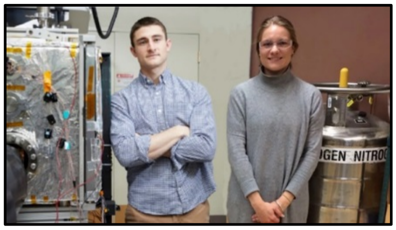
Despite the explosive growth of renewable sources of electricity, making hydrocarbon building blocks and high energy density fuel sources in a renewable fashion is a major challenge. The challenge lies in designing catalysts to perform this hydrogenation selectively in solution. This joint experimental-theoretical work presents the first material with better performance for this reaction than copper, and has required contributions from materials discovery, first-principles theory, and *operando* characterization at the Joint Center for Artificial Photosynthesis.



Our team started with a nickel-gallium intermetallic catalyst known to be active for thermal CO hydrogenation. Nickel-gallium thin films of various stoichiometries were found to reduce CO$_2$ to methane, ethane, and ethylene, at overpotentials lower than the best polycrystalline catalyst, copper. *Ex-situ* characterization was carried out before and after catalysis to demonstrate the stability of the catalysts. It was found that even after long-term polarizations both Ni and Ga are present on the surface and contribute to the observed activity. These experiments raised two questions: what was the active site of these new catalysts, and why did existing theoretical screens not capture their activity for electrochemical CO$_2$ reduction? Answering these questions required modeling the many diverse active sites on these polycrystalline bimetallic samples. Adsorption sites for every stable facet were cataloged. Using machine learning methods, we inferred that most of these facets had similar activity to Ni surfaces but that a few exposed Ni sites surrounded by Ga atoms had a favorable on-top CO configuration with improved kinetics. This motif emerged from the predictive modeling and suggested that these surfaces represent a new class of intermetallic CO$_2$ reduction catalysts. Finally, we used *operando* grazing incidence x-ray absorption and diffraction characterization at the Stanford Synchrotron Radiation Lightsource to compare theoretical and measured reaction rates. These techniques show that kinetically trapped surface oxide species exist at reducing potentials and confirm that the surface structure changes at different reaction conditions. These results provide the foundation for our team at JCAP to screen, characterize, and deploy new catalysts for the most challenging electrochemical reactions.

Contributions: DAT, SAF, JCC, AJ, and JRT performed expt. measurements. JTF, MF, SWF, JWB, AM, RD, AM, RD, ATL, JCL, DCH and CH did the *operando* characterization. ZWU, MTT, JX, XL, MK, RS, and KC did the theory. All authors contributed to the interpretation and presentation. BSB, MPS, WSD, JY, TFJ, NSL, and JKN conceived the problems and approaches.





(From left) David Bierman, Veronika Stelmakh

TAILORING THERMAL EMISSION FOR HIGH PERFORMANCE SOLAR THERMOPHOTOVOLTAIC DEVICES

[EFRC – S3TEC] David M. Bierman[1], Veronika Stelmakh[1], Andrej Lenert[1,2], Veronika Rinnerbauer[1,3], Walker R. Chan[1], Ivan Celanovic[1], Marin Soljacic[1], and Evelyn N. Wang[1]

[1]Massachusetts Institute of Technology; [2]Currently at University of Michigan – Ann Arbor; [3] Currently at Johannes Kepler University Linz

Solar thermophotovoltaics (STPVs) present an enormous opportunity for the efficient conversion of high-grade thermal energy to electricity. These solid-state devices rely on a heat source to generate a tailored thermal emission spectrum which illuminates a photovoltaic cell. The required high temperature operation presents substantial scientific and engineering challenges which have prevented these devices from unlocking their full potential. In this talk, we discuss our development of high temperature stable spectrally engineered surfaces towards the realization of high performance STPV devices (Fig. 1).

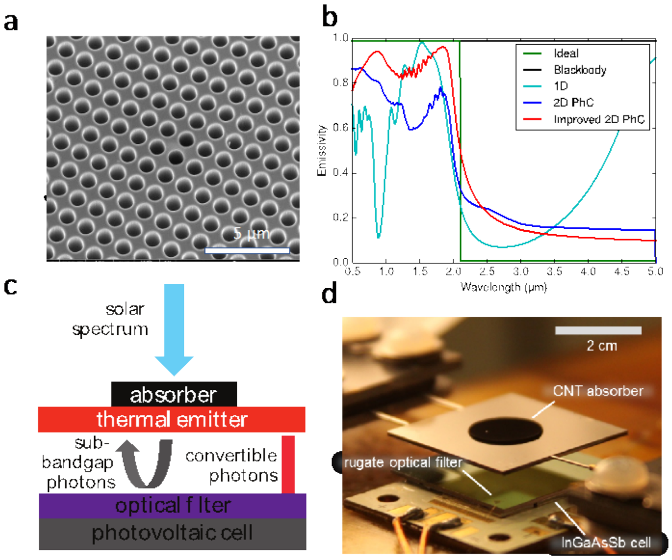


Figure 1: a) SEM of two-dimensional photonic crystal. b) Spectral properties in STPV. c) schematic of STPV energy flow. d) optical image of STPV device

For efficient conversion, the radiative exchange between all components must have a strong spectral dependence. We developed photonic crystal based absorbers and emitters that can withstand temperatures >1200 °C and provide excellent spectral control. We explored different approaches including one-dimensional and two-dimensional photonic crystals to achieve this spectral selectivity (Fig. 1a-b). These consisted of alternating layers of Si and SiO_2 films[1], and patterned refractory metals with arrays of nano-cavities[2], respectively.

We incorporated these photonic crystals for proof-of-principle STPV demonstrations (Fig.2c-d). By coupling a selective emitter with a rugate filter, we demonstrated unprecedented solar-to-electricity conversion efficiencies of 6.8%, exceeding the performance of the same PV cell directly placed under identical solar flux[3]. We also showed that the performance of the device can be improved, and the architecture simplified by incorporating our two-dimensional photonic crystal for both selective solar absorption and thermal emission[4]. Our work suggests a promising route to develop STPVs as a feasible technology to address our sustainable energy needs. We are currently pursuing technology transition opportunities based on this work, including our successful entry into the Cyclotron Road program at Lawrence Berkeley National Laboratory.

References: [1] Chan, W. R. *et al. Proc. Natl. Acad. Sci. U. S. A.* **110,** 5309–14 (2013); [2] Stelmakh, V. *et al. Appl. Phys. Lett.* **103,** 123903 (2013); [3] Bierman, D. M. *et al. Nat. Energy* **1,** 16068 (2016); [4] Rinnerbauer, V. *et al. Adv. Energy Mater.* **4,** (2014).

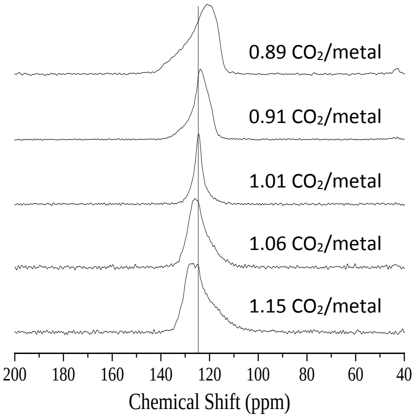
Contributions: V.S. and V.R. fabricated the 2-D photonic crystals, W.R.C. designed the 1-D photonic crystals, D.M.B. and A.L. envisioned, designed, and performed experiments for the solar TPV device. I.C., M.S., and E.N.W. supervised all research.

UNDERSTANDING STRUCTURE AND DYNAMICS OF CO_2 ADSORBED IN OPEN-SITE METAL-ORGANIC FRAMEWORKS

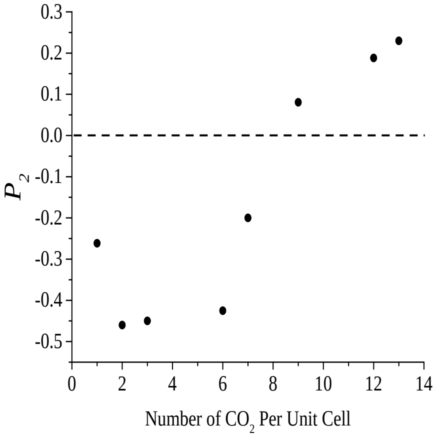
[EFRC – UNCAGE-ME] Robert M. Marti[1], Joshua D. Howe[2], Cody R. Morelock[2], Krista S. Walton[2], Mark S. Conradi[1,3], David S. Sholl[2], Sophia E. Hayes[1]
[1]*Washington University*, [2]*Georgia Institute of Technology*, [3]*ABQMR*

(From left) Joshua D. Howe, Robert M. Marti

Metal-organic frameworks are crystalline organic-inorganic hybrid materials that have been of interest for adsorption applications for their tunability, high crystallinity, and high surface areas. Mg-MOF-74 has long been of interest for its exceptional gravimetric uptake of CO_2 at flue-gas relevant conditions. CO_2 adsorption in Mg-MOF-74 is well studied, but most work has focused on understanding adsorption at the undercoordinated open-metal sites that line the pores. Despite this, loadings of CO_2 in Mg-MOF-74 at even modest partial pressures can exceed one CO_2 per open-metal site, requiring a more nuanced picture to understand the behavior and loading of CO_2. Recent neutron diffraction studies have shown that CO_2 occupies not only these primary adsorption sites, but also “secondary” and even “tertiary” sites that exist within the MOF pore.[1]



Here we present a joint experimental NMR and theory study that demonstrates that higher CO_2 loadings qualitatively alter the structure of adsorbed CO_2 within the MOF pore. Constructing special NMR hardware to deliver gases at variable temperature and pressure, we have found that the ^{13}C NMR lineshape evolves in a predictable fashion as these different sites become occupied. We show that the time-averaged value of the second Legendre polynomial, P_2, which maps to the alignment of CO_2 with respect to the MOF pore axis, allows understanding of the so-called “sign” of the NMR lineshape—which shifts in appearance with loading in a highly sensitive and informative manner. The evolution of the NMR lineshape with CO_2 loading, which probes the aggregate dynamics and structure of adsorbed CO_2, agrees exceptionally well with the DFT-predicted loading-dependent structures of CO_2 within the Mg-MOF-74 pore through analysis in terms of P_2. NMR experiments also point to qualitative differences between the behavior of CO_2 in Mg-MOF-74 and Mg-Cd-MOF-74, which we rationalize in terms of theoretical calculations for mixed-metal MOF-74 systems[2] and our calculations on Mg-MOF-74. Importantly, the NMR spectra are difficult to interpret without the detailed picture of adsorption sites provided by DFT, and the combined effect demonstrates how experiments can reinforce the DFT models of collective CO_2 behavior.



References: [1] Queen, W. L.; Hudson, M. R.; Bloch, E. D.; Mason, J. A.; Gonzalez, M. I.; Lee, J. S.; Gygi, D.; Howe, J. D.; Lee, K.; Darwish, T. A.; James, M.; Peterson, V. K.; Teat, S. J.; Smit, B.; Neaton, J. B.; Long, J. R.; Brown, C. M. *Chem. Sci.* **2014**, *5,* 4569. [2] Howe, J. D.; Morelock, C. R.; Jiao, Y.; Chapman, K. W.; Walton, K. S.; Sholl, D. S. *J. Phys. Chem. C* **2017**, *121*, 627–635.

Contributions: CRM and KSW performed materials synthesis and characterization. RMM, MSC and SEH performed NMR experiments. JDH and DSS conducted DFT calculations. All authors contributed to data analysis and interpretation.

Team Science Finalists

(From left) Gihan Kwon,
Nathan T. La Porte, Kelly L. Materna,
Benjamin Rudshteyn, Jiyun Hong

The Pyridine Alkoxide Ligand Works for Water Oxidation Catalysts Both in Theory and in Practice

[EFRC – ANSER] Benjamin Rudshteyn,[1] Kelly L. Materna,[1] Nathan T. La Porte,[2] Katherine J. Fisher,[1] Ke R. Yang,[1] Svante Hedstrom,[1] Jose F. Martinez,[2] Gihan Kwon,[3] Jiyun Hong,[2] David M. Tiede,[3] Lin X. Chen,[2,3] Michael R. Wasielewski,[2] Robert H. Crabtree,[1] Gary W. Brudvig,[1] Victor S. Batista[1]

[1]Yale University, [2]Northwestern University, [3]Argonne National Laboratory

Catalytic water oxidation is a critical bottleneck in the generation of solar fuels, a challenging reaction that requires active and robust catalysts. Efficient transition metal catalysts require ligands that can stabilize high oxidation states, as necessary for oxidative catalysis and at the same time resist degradation under the harsh oxidative conditions. We find that the ligand 2-(2′-pyridyl)-2-propanoate (pyalk) is an exceptional chelating group that fulfills the necessary requirements. Through collaborative theoretical and experimental efforts of research groups working within the ANSER Center, we have determined the structures and mechanisms for pyalk-containing water-oxidation catalysts. Combining computational modeling and X-ray spectroscopy, we have determined the structure of an active Ir-pyalk dimeric species in solution (Figure 1),[1] and determined the underlying water-oxidation mechanism. Furthermore, we have developed and characterized a catalytic surface-bound species using IR spectroscopy.[2] We have also developed a $Cu^{II}(pyalk)_2$ electrocatalyst and characterized its water-oxidation mechanism.[3] This same suite of collaborative theoretical and experimental methods is now being applied to understanding CO_2 reduction via super-reducing Re-perylenedimiide systems driven with near-infrared light.[4]

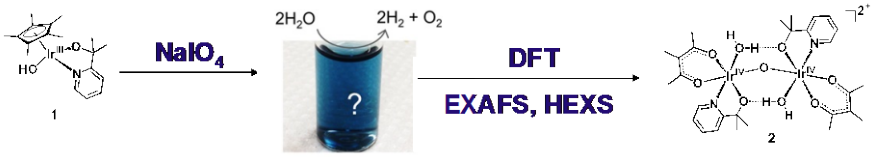


Figure 1. Precatalyst **1** is chemically activated to give an active water-oxidation catalyst. Combined theoretical calculations and experimental X-ray spectroscopies provided the structure of the catalyst, **2**.

References: [1]Ke R. Yang, et al. *J. Am. Chem. Soc.* **2016**, *138*, 5511. [2]Kelly L. Materna, et al. *ACS Catal.* **2016**, *6*, 5371. [3]Katherine J. Fisher, et al. *ACS Catal.* **2017**, *7*, 3384. [4]Nathan T. La Porte, et al. *Chem. Sci*. **2017**, *Advance*: DOI: 10.1039/c6sc05103k.

Contributions: BR, SH, and KRY performed theoretical density functional theory calculations and modeling of spectroscopy. KLM and KJF performed synthesis and characterization by electrochemistry and UV-Vis/IR spectroscopy. NTLP and JFM performed experiments for the Re-PDI project. GK and JH conducted EXAFS experiments. DMT, LXC, MRW, RHC, GWB, and VSB supervised the work. All authors contributed to the discussion and contributed to their respective manuscripts.

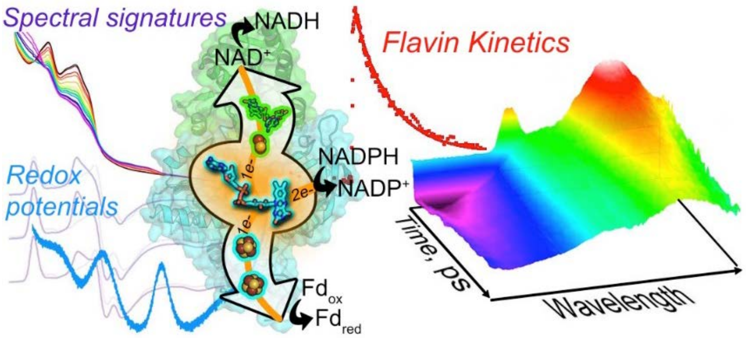
(From left) Jonathan Yuly, Diep Nguyen

MECHANISTIC INSIGHTS INTO ENERGY CONSERVATION BY FLAVIN-BASED ELECTRON BIFURCATION

[EFRC – BETCy] D. Nguyen[1], J. Yuly[2], C. Lubner[3], D. Jennings[4], D. Mulder[3], G. Schut[1], O. Zadvornyy[5], J. Hoben[6], P. Zhang[1], M. Tokmina-Lukaszewska[7], L. Berry[7], G. Lipscomb[1], B. Bothner[7], A. Jones[4,] A. Miller[6], P. King[3], D. Beratan[2], M. Adams[1], J. Peters[5,7]

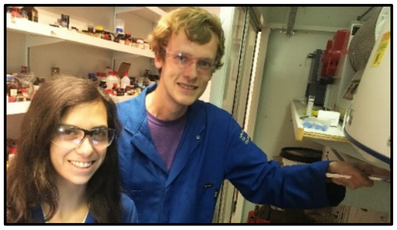
[1]University of Georgia, [2]Duke, [3]National Renewable Energy Laboratory, [4]Arizona State, [5]Washington State, [6]University of Kentucky, [7]Montana State

The recently realized biochemical phenomenon of energy conservation through electron bifurcation provides biology with an elegant means to maximize energy efficiency. Flavin based electron bifurcation couples endergonic and exergonic oxidation-reduction reactions into an overall thermodynamically favorable reaction with minimal energy loss. The catalysts that affect these reactions are enzyme complexes that possess numerous redox cofactors to coordinate electron flow between three diffusible electron carriers. At the inception of the Biological Electron Transfer and Catalysis (BETCy) Energy Frontier Research Center (EFRC) little was known about the mechanism of these unique enzymes. The BETCy EFRC team has used a multidisciplinary approach resulting in profound advances in our mechanistic understanding of flavin-based bifurcation, revealing novel features of redox cofactors. Structure determination using x-ray diffraction, coupled with chemical cross-linking, mass spectrometry, and computational modeling reveals the unique architecture and the arrangement of redox cofactors providing a framework for mechanistic studies. Optical and electron paramagnetic spectroscopy coupled with protein film electrochemistry have revealed unique features of redox cofactors, including highly energetic intermediates and large ranges of cofactor oxidation-reduction potentials invoking low potential electron carriers that have yet to be observed outside of light energy-dependent photosynthesis. Pairs of electrons are bifurcated over more than 1 volt of electrochemical potential by generating a low-potential, highly energetic, unstable flavin semiquinone and directing electron flow to an iron–sulfur cluster with a highly negative potential to overcome the barrier of the endergonic half reaction. Theoretical work supports that gating of electron flow committing the coordination of exergonic and endergonic paths can occur electronically through Marcus inversion. The nature of our results has had transformative effects on understanding this fascinating electron transfer phenomena.



Reference: C.E. Lubner, D.P. Jenning, D.W. Mulder, G.J. Schut, O.A. Zadvornyy, J. Hoben, M. Tokmina-Lukaszewska, L. Berry, D. Nguyen, G.L. Lipscomb, B. Bothner, A.K. Jones, A-F. Miller, P.W. King, M.W.W. Adams, J.W. Peters. "Mechanistic Insights into Energy Conservation by Flavin-Based Electron Bifurcation" *Nature Chem. Bio.* 2017 Apr 10. doi: 10.1038/nchembio.2348

Contributions: Diep Nguyen determined the biochemical properties of the bifurcating enzyme, used genetic tools to generate mutants, provided the bifurcating enzyme to collaborators for spectroscopic, electrochemical and structural analyses, and composed the presentation. Jonathon Yuly contributed to the development of the kinetic models for electron bifurcation, analyzed the electron bifurcation results analysis in collaboration with the experimental team, and composed the presentation.



(From left) Rebecca Siegelman, Alexander Forse

RATIONAL DESIGN OF NEW MATERIALS FOR CARBON DIOXIDE CAPTURE

[EFRC – CGS] Rebecca L. Siegelman,[1] Alexander C. Forse,[1] Phillip J. Milner,[1] Thomas M. McDonald,[1] Miguel I. Gonzalez,[1] Tomče Runčevski,[1] Jeffrey D. Martell,[1] Jarad A. Mason,[1] Jung-Hoon Lee,[1,2] Bess Vlaisavljevich,[1] Walter S. Drisdell,[2] Jeffrey B. Kortright,[2] David Prendergast,[2] Jeffrey B. Neaton,[1,2,3] Berend Smit, Jeffrey A. Reimer,[1] Jeffrey R. Long[1,2]

[1]University of California, Berkeley; [2]Lawrence Berkeley National Laboratory; [3]Kavli Energy NanoSciences Institute at Berkeley

The capture of CO_2 from point-source emitters such as coal-fired power plants has been proposed as a promising strategy to mitigate greenhouse gas emissions. Toward that end, the Center for Gas Separations (CGS) is developing new adsorbents to minimize the energetic costs of CO_2 separations. Initial efforts coupled computation and experiment to study MOF-74 metal–organic frameworks, which bind gases at unsaturated metal(II) sites in the pore interior. These studies showed that high CO_2 capacity and selectivity could be achieved from dry gas streams, but H_2O outcompetes CO_2 at equilibrium. To address this, amine-appended adsorbents capable of maintaining CO_2 capacity under humid conditions were developed. In particular, adsorbents of the form $M_2(dobpdc)(diamine)_2$ (M = Mg, Mn, Fe, Co, Ni, Zn; $dobpdc^{4-}$ = 4,4′-dioxidobiphenyl-3,3′-dicarboxylate) feature step-shaped CO_2 adsorption isotherms. This switch-like adsorption enables the full CO_2 working capacity to be achieved with a minimal pressure or temperature swing. By combining computation, XRD, XAS, IR, and NMR, a co-operative mechanism involving the formation of ammonium carbamate chains was found (Figure 1).

The adsorption thermodynamics of amine-appended MOFs can be tuned by modifying the constituent metal or diamine, enabling rational design of adsorbents for specific CO_2 separations. In this manner, a new material was designed to minimize the energetic cost of CO_2 capture from the flue gas of coal-fired power plants. This material is stable to over 1000 cycles with a high CO_2 working capacity of 2.4 mmol/g and modest regeneration temperature of 100 °C. *In situ* diffraction and NMR methods were developed to characterize the unusual CO_2 adsorption properties of this material and revealed a complex mechanism involving formation of a mixture of ammonium carbamate and carbamic acid pairs. In future efforts, next-generation adsorbents will be designed with the support of computational screening, and diamine-appended frameworks will be incorporated within mixed-matrix membranes.

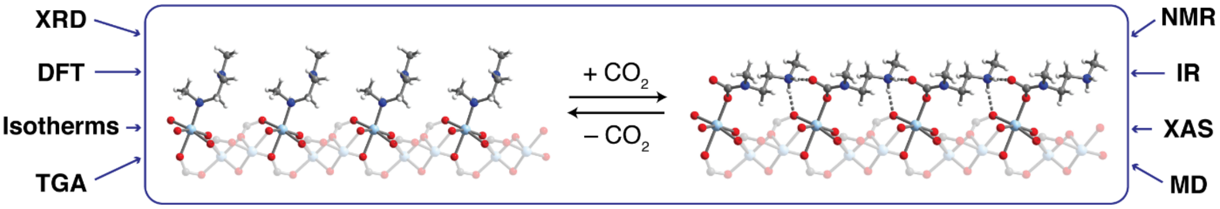
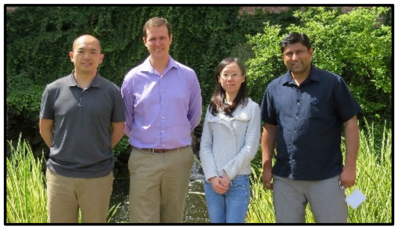


Figure 1. Multidisciplinary approach employed in the CGS to rationally design new materials for energy-efficient CO_2 sorption.

Contributions: R.L.S., P.J.M, J.D.M., T.M.M., and J.A.M. designed, synthesized, and characterized the adsorbents under the advisement of J.R.L. A.C.F. collected and analyzed NMR data with support from J.A.R. R.L.S., M.I.G., T.R., and J.A.M. collected and analyzed the diffraction data. J.-H.L., B.V., J.B.N., and B.S. performed the computational work. W.S.D. and J.B.K. collected and analyzed the XAS data.



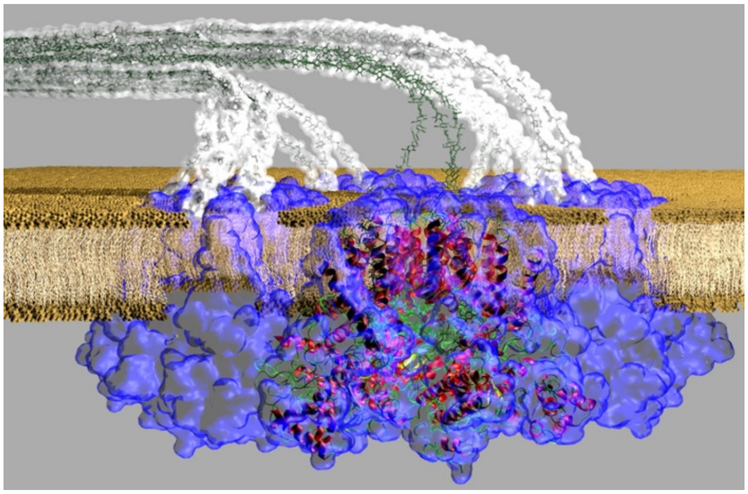
(From left) Hui Yang, Jason Burris, Xiaoran Xin, Abhishek Singh

THE NANOMACHINE THAT SYNTHESIZES CELLULOSE IN PLANTS

[EFRC – CLSF] Abhishek Singh[1], Yaraslova Yingling[1], Jason N. Burris[1], Jonathan K. Davis[1], Alison W. Roberts[2], Candace H. Haigler[1], Xiaoran Xin[3], Ying Gu[3], Hui Yang[3], James D. Kubicki[4], Jochen Zimmer[5]

[1]North Carolina State University, [2]University of Rhode Island, [3]Pennsylvania State University, [4]University of Texas at El Paso, [5]University of Virginia

Using sugar derived from photosynthesis, plants annually produce gigatons of cellulose, a global sink for atmospheric carbon and stored solar energy. Despite its importance as a structural material and a source of renewable energy, many aspects of cellulose synthesis are unresolved. Eighteen β1,4-glucan chains are polymerized in parallel by a remarkable multimeric nanomachine, the cellulose synthase complex (CSC), which is embedded in the cell's plasma membrane, harvests UDP-glucose from the cytoplasm and spins oriented microfibrils outside the cell to construct a complex cell wall. The CSC contains an estimated 18 cellulose synthase proteins (CESAs) in a rosette-like configuration and other protein partners help to regulate CSC activity. Here we report on complementary computational and experimental studies of CSC structure and regulation. Biochemical methods demonstrate the membrane topology of CESA and guide atomistic modeling of CESA with seven transmembrane helices and a predicted substrate-binding motif in the cytoplasm. QM/MM modeling of the catalytic domain gives insights into transition states and activation free energy for glucan polymerization. Using laser scanning confocal microscopy we demonstrate the association of cellulose synthase interactive 1 protein (CSI1) with the CSC. We constructed an atomistic model of CSI1 structure and developed an interaction model in which CSI1 links CESA with cytoskeletal microtubules, providing a means of orienting the direction of cellulose microfibril deposition to the cell wall. These results form the basis for many ongoing experiments in our center, with the goal of manipulating plant cellulose synthesis in beneficial ways.



Right: Molecular model of the CSC embedded in the plasma membrane (brown) and extruding glucan chains (white) to the outside surface of the cell, forming an ordered microfibril.

Contributions: Experiments were designed, implemented, or interpreted as follows: atomistic modeling: A.S., C.H.H, and Y.Y.; biochemistry: J.N.B., J.K.D., A.W.R. and C.H.H.; microscopy: X.X. and Y.G.; and quantum modeling: H.Y., J.D.K. and J.Z.

(From left) Shijun Zhao, Taini Yang, Shi Shi

EFFECTS OF ALLOY COMPLEXITY ON DEFECT PRODUCTION AND MICROSTRUCTURAL EVOLUTION IN CONCENTRATED ALLOYS

[EFRC – EDDE] Shijun Zhao[1], Taini Yang[2], Shi Shi[3], Chenyang Lu[2], Eva Zarkadoula[1], Hongbin Bei[1], Lumin Wang[2], Ian Robertson[3], Yanwen Zhang[1]
[1]Oak Ridge National Laboratory; [2]University of Michigan; [3]University of Wisconsin-Madison

How can we produce structural materials that are more durable in nuclear reactors? What are the keys to governing material degradation mechanisms under radiation? How can we design materials with better radiation tolerance for next-generation reactors? These are central topics in which our Energy Dissipation to Defect Evolution (EDDE) team are interested. Specifically, we are investigating a series of novel concentrated solid-solution alloys (CSAs) to reveal how energy dissipation and defect evolution mechanisms are affected by the random arrangement of mixed atoms with different alloy complexities. We aim to ultimately design alloys that are intrinsically resistant to damage production under different extreme conditions.

We present our findings about the influence of alloy complexity on defect production and microstructure evolution in CSAs based on theoretical models and experimental observations. Through density functional theory, low-energy recoil events in different CSAs are simulated and threshold energies required to knock atoms out of place are determined. We find that threshold energies in CSAs are only slightly influenced by alloy complexity. However, the energetics of interstitial and vacancy defects are strongly related to alloy compositions (specific elemental coupling), which can be interpreted by electronic properties of different constituent elements. Based on *ab initio* molecular dynamics, we show a preferential diffusion of point defects in CSAs, depending on alloy complexity,[1] validated by element segregation observed experimentally.[2] The diffusion of large defect clusters is further studied by classical molecular dynamics simulations and is directly observed in both *in-situ* and *ex-situ* transmission electron microscopy. We found that alloy complexity can effectively modify migration pathways of interstitial defect clusters: from a long-range one-dimensional mode in pure Ni and a simple binary NiCo alloy, to a short-range three-dimensional mode in more compositionally complex CSAs. Such modification leads to enhanced point defect recombination and improved swelling resistance, as shown in Figure 1.[3] Our results underline the importance of both constituent elements and composition in CSAs in determining defect behavior and microstructure evolution.

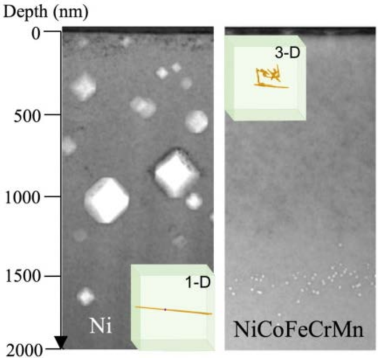
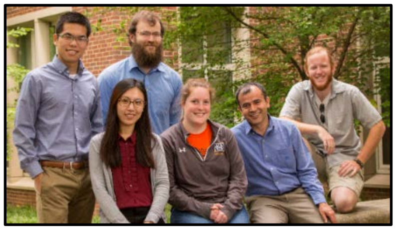


Figure 1: Transmission electron microscopy images showing different defect distributions and microstructure changes in Ni and NiCoFeCrMn CSA.[3]

[1] S. Zhao, Y. Osetsky, Y. Zhang, Acta Mater. 128 (2017) 391–399.
[2] M.-R. He, S. Wang, S. Shi, *et. al.*, Acta Mater., 126 (2017) 182-193 .
[3] C. Lu, L. Niu, N. Chen, *et. al.*, Nat. Commun. 7 (2016) 13564.

Contributions: S. Zhao conducted the theoretical simulations; T. Yang performed the *ex-situ* experiments and S. Shi carried out *in-situ* radiation experiments.



(Standing from left) Yu Zhang, Matt Thompson; (Seated from left) Kun Liu, Katie Van Aken, Naresh Osti, Justin Neal

UNDERSTANDING ROOM TEMPERATURE IONIC LIQUIDS AND THEIR PERFORMANCE IN SUPERCAPACITORS

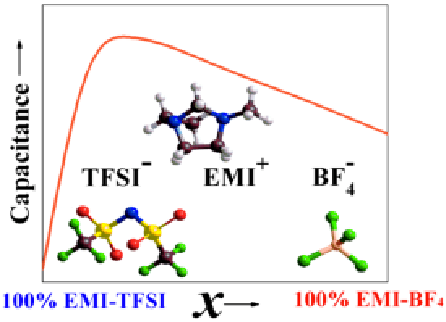
[EFRC – FIRST] Justin Neal[1], Kun Liu[1], Naresh Osti[2], Matthew W. Thompson[3], Katherine Van Aken[4], Yu Zhang[3]

[1]University of California, Riverside, [2]Spallation Neutron Source, Oak Ridge National Laboratory, [3]Vanderbilt University, [4]Drexel University

These graduate students and postdoctoral associates from four of the FIRST Center partner institutions have self-organized into a highly effective team to develop fundamental and predictive understanding of the physicochemical properties of a selection of room temperature ionic liquids and their behavior and performance in nanoporous carbon supercapacitor electrode materials. Through physical meetings at Drexel, ORNL, and U.C. Riverside, as well as numerous teleconferences, they have, with minimal supervision, mapped out and executed a comprehensive research plan that is ongoing, and have published a number of recent joint papers[1-7] briefly summarized below. The team also includes several students and postdoctoral fellows who have now moved on (*e.g.* Cheng Lian and Boris Dyatkin).

Room temperature ionic liquids (RTILs) are a class of molten salts that are liquid at room temperature. Their low vapor pressure and electrochemical stability over a wide voltage window make them viable electrolytes for capacitive energy store. Here, we combine multiscale modeling, electrochemistry, and neutron scattering experiments to probe the fundamental properties of RTILs and how deviations from ideality at the nanoscale affect macroscale properties and capacitive performance.

Classical Density Functional Theory (cDFT) models (figure) predicted that a 20:80 ratio of BF_4^- and Tf_2N^- anions with a common $EMIM^+$ cation exhibited a maximum capacitance over a range of compositions. This result was later confirmed with electrochemistry experiments. cDFT models predict that small concentrations of impurities can boost capacitance energy storage by altering ion affinities and counter-ion adsorption. Molecular dynamics (MD) simulations and cDFT models together predict ion partitioning effects in which larger and smaller ions preferential adsorb into larger and smaller pores, respectively, which help explain capacitance increases observed in electrochemistry experiments.



Quasi-elastic neutron scattering (QENS) measurements revealed the nano-phase separation of an ionic liquid into ionic liquid-rich and solvent-rich phases with a greater diffusivity of ion by the solvent of a higher dipole moment. When confined in functionalized porous carbon, the diffusivity of cation increases significantly. QENS and MD simulations of ions under applied potential in nanoporous carbon demonstrated a totally reversible mechanism of ions immobilized in larger pores (6.7 nm) compared to smaller pores (1.5 nm). These and other emergent nanoconfined RTIL properties are discussed.

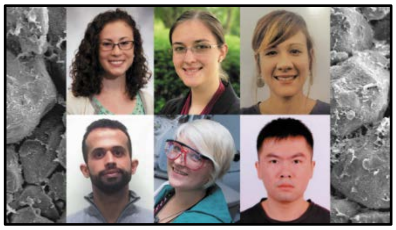
References: [1]B. Dyatkin, Y. Zhang, et al., *J. Phys. Chem. C* (2016) *120*:8730-8741. [2]C. Lian, K. Liu, K. Van Aken, et al., *ACS Energy Letters* (2016) *1(1)*:21-26. [3]K. Liu, J. Wu, *J. Phys. Chem. C* (2016) *120*:24041-24047. [4]K. Liu, C. Lian, et al., *Molecular Physics* (2017) *115*:454-464. [5]J. Neal, et al., *J. Chem. Phys.* (2017), *in press.* [6]N. Osti, K. Van Aken, M.W. Thompson, et al., *J. Phys. Chem. Lett.* (2017) *8*:167-171. [7]S.M. Mahurin, M.W. Thompson, et al., *Appl. Phys. Lett.* (2016) *109*:143111.

Contributions: J.N. and K.L. performed classical density functional theory simulations; N.O. conducted and analyzed neutron scattering experiments; M.W.T. and Y.Z. conducted classical molecular dynamics simulations; K.V.A. conducted electrochemical experiments.

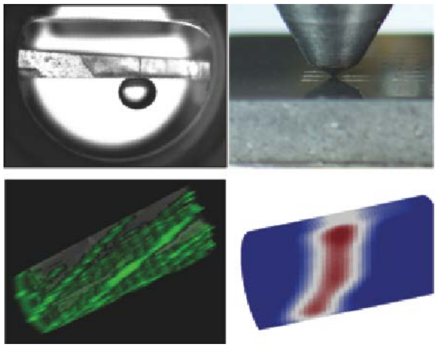
GEOCHEMICAL REACTIONS DURING GEOLOGICAL CARBON SEQUESTRATION CAN DECREASE FRACTURE TOUGHNESS OF RESERVOIR ROCK AND CONTRIBUTE TO MICROSEISMIC EVENTS

[EFRC – GSCO2] L Dalton[1], MG Davila Ordonez[2], S Fuchs[3], P Kabir[2], Z Shi[4], MK Tkach[1], A Akono[2], DM Crandall[1], J Druhan[2], AL Goodman[1], K Jessen[4], T Tsotsis[4], CJ Werth[3]

[1]National Energy Technology Laboratory, [2]University of Illinois at Urbana-Champaign, [3]University of Texas at Austin, [4]University of Southern California



(Top from left) Laura Dalton, Samantha Fuchs, Gabriela Dávila; (Bottom from left) Pooyan Kabir, Mary Tkach, Zhuofan Shi



Many reservoirs proposed for geological storage of carbon dioxide contain reactive minerals that can dissolve under acidic conditions created during CO_2 injection. In some cases, the most reactive minerals act as cementing agents that bind less reactive minerals together. For example, illite clays bind together quartz and feldspar grains in the Mount Simon formation, a siliciclastic storage reservoir being used in a DOE pilot study to geologically sequester carbon dioxide. Bench-scale core studies indicate dissolution and displacement of clays can occur during CO_2 injection, suggesting that this cementing agent can be removed during long-term storage operations. The objectives of our team effort are to quantify the geochemical reactions that occur in reservoir materials during exposure to carbon dioxide, and the subsequent effects on fluid flow paths, the location of geochemical reactions, and reservoir geomechanical properties. Our team is aging common reservoir materials from the Mount Simon formation in supercritical CO_2 and brine at representative pressures and temperatures, under both static and flowing conditions. Pre- and post-aging, we are probing the materials for geochemical and pore-space changes using a suite of gas adsorption, optical, spectroscopic and tomographic methods, including permporometry and CT scanning. During aging, we are mapping preferential flow paths using positron emission tomography (PET scan). We are probing changes in geomechanical properties using a scratch test to measure fracture toughness, as well as triaxial tests that subject rock cores to representative pore fluid and confining pressures. These various experiments span a range of scales, and are being performed by different team members. The results are collectively contributing to our project objectives, and to our collaborative goal of identifying implications of geomechanical weakening on induced microseismicity in the Mount Simon Formation.

Contributions: L. Dalton and M. Tkach are contributing to CT scans of the Mount Simon Material, optical, spectroscopic, and triaxial tests. M. Davila is contributing to PET scan measurements of flow, and geochemical reaction modeling. S. Fuchs is contributing to sample aging and geochemical reaction characterization. P. Kabir is contributing to scratch testing. Z. Shi is contributing to permporometry and strain measurements.

THERMODYNAMIC STABILITY, VOLTAGE AND DIFFUSION KINETICS OF LI$_x$VOPO$_4$ (X=0,1,2) VANADYL PHOSPHATE POLYMORPHS: JOINT FIRST-PRINCIPLES AND EXPERIMENTAL STUDY

[EFRC – NECCES] Yuh-Chieh Lin,[1] Iek-Heng Chu,[1] Marc V. Hidalgo,[2] Carrie Siu,[2] Fredrick Omenya,[2] Natasha A. Chernova,[2] Linda W. Wangoh,[2] Shawn Sallis,[2] Louis F. J. Piper,[2] M. Stanley Whittingham,[1] Shyue Ping Ong[1]
[1]*University of California San Diego,* [2]*Binghamton University*

(From left) Marc Francis Hidalgo, Yuh-Chieh (Paul) Lin, Shawn Sallis

One of the goals of our center is to attain reversible multi-electron transfer in a cathode material using lithium. We focus on vanadyl phosphates because we can utilize both the $V^{3+/4+}$ and $V^{4+/5+}$ redox couples for a theoretical capacity of 318 mAh/g at about 2.5 and 4 V, respectively. The challenge of this system is its great structural diversity; there are seven known polymorphs of $VOPO_4$ and three for $LiVOPO_4$. No Li_2VOPO_4 has been synthesized directly up to now. In order to identify the most stable Li_xVOPO_4 (x=0,1,2) polymorphs, determine their Li intercalation potentials, diffusion pathways and kinetics, we have combined first-principle calculations with experimental studies involving synthesis, structural and electrochemical characterization of three $LiVOPO_4$ polymorphs. We have demonstrated excellent agreement between the calculated and experimental structures, Li intercalation voltages, and also correlated the calculated diffusion barriers with the electrochemical performance (Figure 1). Our studies reveal that β-$LiVOPO_4$, which was previously thought inferior to ε-$LiVOPO_4$, has comparable electrochemical performance. The significant difference between the two is intermediate low-voltage phases $Li_{1.5}VOPO_4$ and $Li_{1.75}VOPO_4$, which form in ε-, but not in β-$LiVOPO_4$. Using a combination of soft and hard absorption / photoelectron spectroscopy we have demonstrated that a prerequisite for the formation of these intermediates is a uniform distribution of Li, which is achieved when $LiVOPO_4$ is used as a starting material, and in this case full reversible cycling of the second Li can be realized.

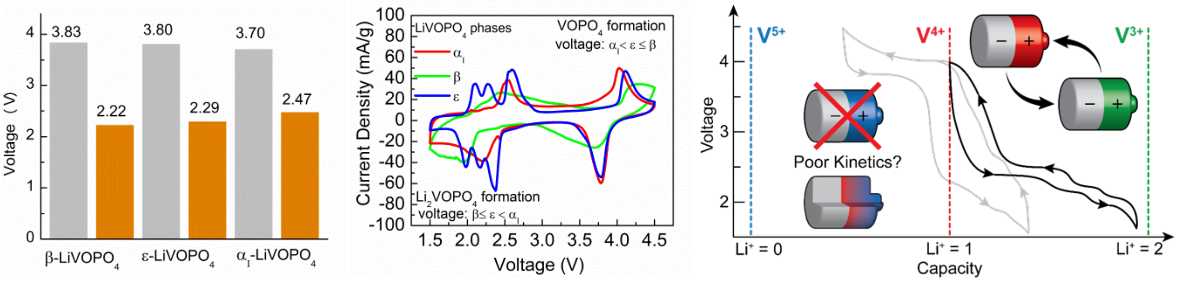


Figure 1 (left) Calculated and (middle) experimental voltages of $LiVOPO_4$ phases. Right: highlight of our ex-situ and operando depth-profile studies confirming full and homogenous second Li^+ insertion and extraction between ε-$LiVOPO_4$ and ε-Li_2VOPO_4 in the low voltage regime.

Contributions: Y.-C.L. performed the first principles calculations, M.V.H. synthesized the samples and performed structural and electrochemical characterization, S.S. acquired and analyzed spectroscopy data. All nominees discussed the results.

(From left) Xin Ma, Gen Yin

MAGNETIC SKYRMIONS IN FERROMAGNETIC/HEAVY-METAL MULTI-LAYERS

[EFRC – SHINES] Gen Yin[1], Xin Ma[2], Kang L. Wang[1] and Xiaoqin Li[2]
[1]University of California, Los Angeles, [2]University of Texas at Austin

Magnetic skyrmions are circular, bubble-like magnetic domains in which the spins on the periphery are polarized vertically, the central spin is polarized in the opposite direction, and, in between, the spins smoothly transition between the two opposite polarizations [Fig. 1(a)]. Due to their amazing properties, magnetic skyrmions are considered to be a competitive candidate to replace the traditional magnetic recording technology used in hard disk drives for higher data density, lower power and faster input/output. The size of skyrmions observed in different material systems varies from ~3nm to ~1000nm, which is mainly determined by the intricate competition between different magnetic interactions. Among all these interactions, Dzyaloshinskii-Moriya interaction (DMI) is an important one. When ferromagnetic (FM) thin films are interfacing with metals (HMs), DMI can be induced in the FM layer. The magnitude of this DMI is strongly determined by the structural and chemical details at the interface, providing a cornucopia of engineering degrees of freedom to fine tune the size, the stability, and the switching difficulty of magnetic skyrmions.

Within SHINES, Dr. Kang L. Wang's research group at UCLA has been pioneering in the field of magnetic skyrmions. The team has demonstrated one of the first multilayer devices that operate magnetic skyrmion bubbles at room temperature, namely, MgO/CoFeB/HM thin films [Fig. 1(b)] [1]. Although these devices function at room temperature, the diameter of skyrmions is typically ∼700 nm, which is too large for memory or recording applications. To optimize the interfacial DMI and to further reduce the size, with their world-leading expertise in Brillouin light scattering (BLS) spectroscopy, Dr. Xiaoqin Li's research team at UT Austin carried out systematic investigations in the interfacial DMI at FM/HM interfaces [2]. This technique measures the spectrum of solid-state elementary excitations (in the present case, spin-wave modes, or magnons) through their interaction to incident phonons [Fig. 1(c)]. Due to DMI, the spectrum shifts its frequency in opposite directions [Fig. 1(e)], therefore the DMI magnitude can be quantitatively extracted [Fig. 1(d)].

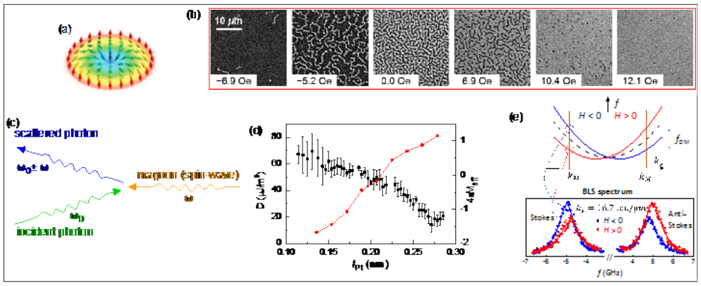


Figure 1: Magnetic skyrmions in ferromagnetic/heavy-metal multilayers. (a) The spin texture of skyrmions in heavy-metal multi-layers. (b) Spin-texture evolution at different magnitudes of applied magnetic fields. (c) Schematic setup of Brillouin-light scattering (BLS) measurement. (d) DMI magnitude at different thickness of HM layers. (e) Rashba-like shift of spin-wave modes and the BLS spectroscopy

Driven by the collaborative platform provided by SHINES, experimental and theoretical resources of different areas were able to combine to systematically investigate the interplay between spin, charge, magnons and phonons. In close collaboration, Wang and Li's research groups were able to design a multilayer structure with two active interfaces and change the magnitude of DMI systematically. Based on these results, the FM/HM material system has been further optimized. Small magnetic skyrmion bubbles of ∼ 70nm have been experimentally observed.

References: [1] G. Yu, P. Upadhyaya, X. Li, et al. Nano Lett. 17, 261 (2017); [2] X. Ma, G. Yu, X. Li, et al. Phys. Rev. B 94, 180408(R) (2016).

Contributions: The UCLA team (G.Y. and K.L.W) modeled, fabricated and tested the skyrmion hosting multi-layer devices. The UT Austin team (X.M. and X.L.) carried out BLS measurements. All team members contributed to the design of the experiment and data analysis.

(From left) Lesheng Li, Taylor Moot

IDENTIFICATION AND PASSIVATION OF THE DEFECT STATES IN NiO FOR PHOTOVOLTAIC AND SOLAR FUEL APPLICATIONS

[EFRC – UNC] Taylor H. Moot[1], Lesheng Li[1], Aaron D. Taggart[1], Bing Shan[1], Shannon M. McCullough, Carrie L. Donley[1], Thomas J. Meyer[1], Yosuke Kanai[1], James F. Cahoon[1]

[1]*University of North Carolina at Chapel Hill*

Nickel oxide (NiO) is one of the most common wide-bandgap p-type semiconductors, and it is often used in photovoltaic devices as either a hole-transporting layer or a photocathode. Despite its ubiquitous use, NiO is plagued with a large trap-state density, which turns this wide band gap material black, gives rise to fast recombination, and lowers solar-cell efficiency. These problems are of particular concern for the use of NiO as a photocathode, such as in p-type dye sensitized solar cells (p-DSSCs) or in tandem solar fuel devices for water splitting or CO_2 reduction.

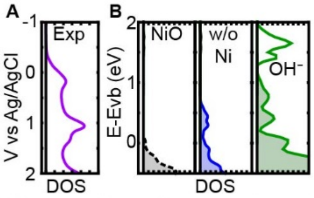


Figure 1. Density of states of A) experimental NiO and B) DFT calculations as labeled.

Although the problem of trap states in NiO has been anecdotally known for years, the exact character and number of trap states has been widely debated. We first focused on the fundamental question of what defects may be responsible for the experimentally-resolved trap states. To identify plausible defects, first-principles calculations were performed. Realizing the well-known failure of density-functional theory (DFT) for later-transition metal oxides, a DFT+*U* scheme was employed, where a local Hubbard correction augments the DFT Hamiltonian to correct erroneous electron delocalization in DFT. From these calculations, it was determined that defects, which give rise to a majority of the trap states, likely arise from a combination of Ni vacancies with and without a hydroxyl group that give rise to oxygen-localized electronic states.[1,2]

Beyond identifying plausible trap states, the calculated density of states (DOS) also shows states directly above the valence band edge of the semiconductor, which matches experimental measurements and explains the black color of NiO. With an understanding of the character and implications of the trap states, subsequent work to minimize the trap-state density was undertaken. By using a low-temperature, vapor-phase method termed targeted atomic deposition (TAD),[2] aluminum was placed at the most reactive, defect sites of NiO. As predicted by the first-principles calculations, the TAD Al-treated NiO turned white, indicative of minimizing trap states. The power conversion efficiency of fabricated p-DSSCs nearly tripled, primarily driven by an increase in V_{OC} to ~300 mV.[2]

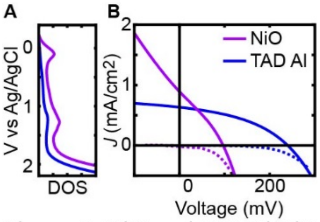


Figure 2. NiO and TAD Al NiO A) DOS and B) JV curves.

1. **Moot, T.H.**; **Li, L.**; Shan, B.; McCullough, S. M., Taggart, A. D.; Donley, C.L.; Meyer, T.J.; Kanai, Y.; Cahoon, J. F. Probing the Valence Band Density of States of NiO to Understand Photovoltaic Performance. *In Preparation.*
2. Flynn, C. J.; McCullough, S. M.; Oh, E. E.; **Li, L.**; Mercado, C. C.; Farnum, B. H.; Li, W.; Donley, C. L.; You, W.; Nozik, A. J.; McBride, J. R.; Meyer, T. J.; Kanai, Y.; Cahoon, J. F. Site-Selective Passivation of Defects in NiO Solar Photocathodes by Targeted Atomic Deposition. *ACS Appl. Mater. Interfaces* **2016,** *8* (7), 4754-4761. DOI: 10.1021/acsami.6b01090

Contributions: T. Moot, A. Taggart, C. Flynn, B. Shan, and C.L Donley collected the experimental data and L. Li was responsible for all computational work.

2017 EFRC-Hub-CMS PI Meeting – Center Acronyms

Types of Basic Energy Sciences Centers

CMS	Computational Materials Sciences Award
EFRC	Energy Frontier Research Center
Hub	Energy Innovation Hub

Basic Energy Sciences Centers

[EFRC – ANSER] Argonne-Northwestern Solar Energy Research Center
Michael Wasielewski, Northwestern University
Award Period: 2009 – 2014; 2014 - 2018

[EFRC – BETCy] Center for Biological Electron Transfer and Catalysis
John Peters, Montana State University
Award Period: 2014 - 2018

[CMS – C2SEPEM] Center for Computational Study of Excited-State Phenomena in Energy Materials
Steven Louie, Lawrence Berkeley National Laboratory
Award Period: 2016 - 2020

[EFRC – C3Bio] Center for Direct Catalytic Conversion of Biomass to Biofuels
Maureen McCann; Purdue University
Award Period: 2009 – 2014; 2014 - 2018

[EFRC –CASP] Center for Advanced Solar Photophysics
Victor Klimov, Los Alamos National Laboratory
Award Period: 2009 – 2014; 2014 - 2018

[EFRC – CAST] The Center for Actinide Science and Technology
Thomas Albrecht-Schmitt, Florida State University
Award Period: 2016 - 2020

[EFRC – CBES] Center for Bio-Inspired Energy Science
Samuel Stupp, Northwestern University
Award Period: 2009 – 2014; 2014 - 2018

[EFRC – CCDM] Center for the Computational Design of Functional Layered Materials
John Perdew, Temple University
Award Period: 2014 - 2018

[EFRC – CCEI] Catalysis Center for Energy Innovation
Dionisios Vlachos, University of Delaware
Award Period: 2009 – 2014; 2014 - 2018

[CMS – CDMFTS] Center for Computational Design of Functional Strongly Correlated Materials and Theoretical Spectroscopy
Gabriel Kotliar, Brookhaven National Laboratory
Award Period: 2015 - 2019

[EFRC – CE] Center for Excitonics
Marc Baldo, Massachusetts Institute of Technology
Award Period: 2009 – 2014; 2014 - 2018

[EFRC – CEES] Center for Electrochemical Energy Science
Paul Fenter, Argonne National Laboratory
Award Period: 2009 – 2014; 2014 - 2018

[EFRC – CES] Center for Emergent Superconductivity
Peter Johnson, Brookhaven National Laboratory
Award Period: 2009 – 2014; 2014 - 2018

[EFRC – CFSES] Center for Frontiers of Subsurface Energy Security
Larry Lake, University of Texas at Austin
Award Period: 2009 – 2014; 2014 - 2018

[EFRC – CGS] Center for Gas Separations Relevant to Clean Energy Technologies
Jeffrey Long, University of California, Berkeley
Award Period: 2009 – 2014; 2014 - 2018

[EFRC– CHWM] Center for Hierarchical Wasteform Materials
Hans-Conrad zur Loye, University of South Carolina
Award Period: 2016 - 2020

2017 EFRC-HUB-CMS PI MEETING – CENTER ACRONYMS

[EFRC – CLSF] Center for Lignocellulose Structure and Formation
Daniel Cosgrove, Pennsylvania State University
Award Period: 2009 – 2014; 2014 - 2018

[EFRC – CME] Center for Molecular Electrocatalysis
R. Morris Bullock, Pacific Northwest National Laboratory
Award Period: 2009 – 2014; 2014 - 2018

[EFRC – CNGMD] Center for Next Generation of Materials by Design: Incorporating Metastability
William Tumas, National Renewable Energy Laboratory
Award Period: 2014 - 2018

[CMS - CPSFM] Center for Predictive Simulation of Functional Materials
Paul Kent, Oak Ridge National Laboratory
Award Period: 2016 - 2020

[EFRC – EDDE] Energy Dissipation to Defect Evolution
Yanwen Zhang, Oak Ridge National Laboratory
Award Period: 2014 - 2018

[EFRC – EFree] Energy Frontier Research in Extreme Environments
Russell Hemley, Carnegie Institution of Washington
Award Period: 2009 – 2014; 2014 - 2018

[EFRC – FIRST] Fluid Interface Reactions, Structures and Transport Center
David Wesolowski, Oak Ridge National Laboratory
Award Period: 2009 – 2014; 2014 - 2018

[EFRC – GSCO2] Center for Geologic Storage of CO_2
Scott M. Frailey, University of Illinois at Urbana-Champaign
Award Period: 2014 - 2018

[EFRC – ICDC] Inorganometallic Catalyst Design Center
Laura Gagliardi, University of Minnesota
Award Period: 2014 - 2018

[EFRC – IDREAM] Interfacial Dynamics in Radioactive Environments and Materials
Sue Clark, Pacific Northwest National Laboratory
Award Period: 2016 - 2020

[EFRC – IMASC] Integrated Mesoscale Architectures for Sustainable Catalysis
Cynthia Friend, Harvard University
Award Period: 2014 - 2018

[Hub – JCAP] Joint Center for Artificial Photosynthesis
Harry Atwater, California Institute of Technology
Award Period: 2010 – 2015; 2015 - 2020

[Hub – JCESR] Joint Center for Energy Storage Research
Georgy Crabtree, Argonne National Laboratory
Award Period: 2012 – 2017

[EFRC – LMI] Light-Material Interactions in Energy Conversion
Ralph Nuzzo, California Institute of Technology
Award Period: 2009 – 2014; 2014 - 2018

[EFRC – m2M] Center for Mesoscale Transport Properties
Esther Takeuchi, Stony Brook University
Award Period: 2014 - 2018

[CMS – MAGICS] MAterials Genome Innovation for Computational Software
Priya Vashishta, University of Southern California
Award Period: 2015 - 2019

[CMS – MICCoM] Midwest Integrated Center for Computational Materials
Giulia Galli, Argonne National Laboratory
Award Period: 2015 - 2019

[EFRC – MSA] Materials Science of Actinides
Peter Burns, University of Notre Dame
Award Period: 2009 – 2014; 2014 - 2018

2017 EFRC-HUB-CMS PI MEETING – CENTER ACRONYMS

[EFRC – NCGC] Center for Nanoscale Controls on Geologic CO_2
Donald DePaolo, Lawrence Berkeley National Laboratory
Award Period: 2009 – 2014; 2014 - 2018

[EFRC – NECCES] NorthEast Center for Chemical Energy Storage
M. Stanley Whittingham, Binghamton University
Award Period: 2009 – 2014; 2014 - 2018

[EFRC – NEES] Nanostructures for Electrical Energy Storage
Gary Rubloff, University of Maryland
Award Period: 2009 – 2014; 2014 - 2018

[EFRC – PARC] Photosynthetic Antenna Research Center
Robert Blankenship, Washington University in St. Louis
Award Period: 2009 – 2014; 2014 - 2018

[EFRC – S3TEC] Solid-State Solar-Thermal Energy Conversion Center
Gang Chen, Massachusetts Institute of Technology
Award Period: 2009 – 2014; 2014 - 2018

[EFRC – SHINES] Spins and Heat in Nanoscale Electronic Systems
Jing Shi, University of California, Riverside
Award Period: 2014 - 2018

[EFRC – UNC] Center for Solar Fuels
Thomas Meyer, University of North Carolina
Award Period: 2009 – 2014; 2014 - 2018

[EFRC – UNCAGE-ME] Center for Understanding and Control of Acid Gas-induced Evolution of Materials for Energy
Krista Walton, Georgia Institute of Technology
Award Period: 2014 - 2018

[EFRC - WastePD] Center for Performance and Design of Nuclear Waste Forms and Containers
Gerald. Frankel, Ohio State University
Award Period: 2016 - 2020