Graduate Student and Postdoctoral Team Science Contest

Introduction:

There are more than 1,600 graduate students and postdoctoral researchers involved in the current Energy Frontier Research Centers (EFRC), BES energy storage and fuels from sunlight Energy Innovation Hubs, BES Computational Materials Sciences awards (CMS), and BES Computational Chemical Sciences awards (CCS). 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 2021 Virtual EFRC-Hub-CMS-CCS Principal Investigators' Meeting on October 18-19, 2021. Each Director was invited to nominate a team of two or more graduate student and/or postdoctoral researchers to present a joint virtual talk about their center research. The DOE EFRC management team selected 9 teams to give talks. The rest were invited to give posters.

Team Science Talks:

Student and Postdoc Team in orange; Speakers underlined

T-1: Entropic Control of HD Exchange Rates over Dilute Pd-In-Au Alloy Nanoparticle Catalysts

[EFRC – IMASC] Jessi E. S. van der Hoeven[1], Hio Tong Ngan[2], Austin Taylor[1], Nathaniel M. Eagan[3], Joanna Aizenberg[1], Philippe Sautet[2]; Robert J. Madix[1], Cynthia M. Friend[1]

[1]Harvard University; [2]University of California, Los Angeles; [3]Tufts University

FULL ABSTRACT

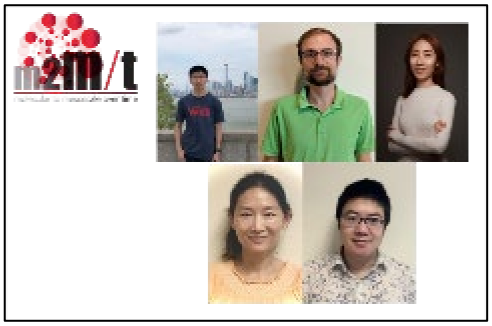
(from left) Jessi E. S. van der Hoeven and Hio Tong Ngan

T-2: Tunable Porous Electrode Architectures for Enhanced Li-Ion Storage Kinetics in Thick Electrodes

[EFRC – m2M/t] Xiao Zhang[1], Zeyu Hui[2], Steven King[3], Lei Wang[4], Zhengyu Ju[1], Jingyi Wu[1], Kenneth J. Takeuchi[3,4], Amy C. Marschilok[3,4], Alan C. West[2], Esther S. Takeuchi[3,4], Guihua Yu[1]

[1]University of Texas at Austin; [2]Columbia University; [3]Stony Brook University; [4]Brookhaven National Laboratory

FULL ABSTRACT



(from upper left) Zeyu Hui, Steven King, Xiao Zhang
(from lower left) Jingyi Wu, Zhengyu Ju

T-3: INTEGRATED COMPUTATIONAL ENGINEERING TOWARDS ACCELERATED SCREENING AND OPTIMIZATION FOR NANOPOROUS MATERIALS

[CCS – NMGC] Kaihang Shi[1], Yangzesheng Sun[2], J. Ilja Siepmann[2], Randall Q. Snurr[1]
[1]Northwestern University; [2]University of Minnesota

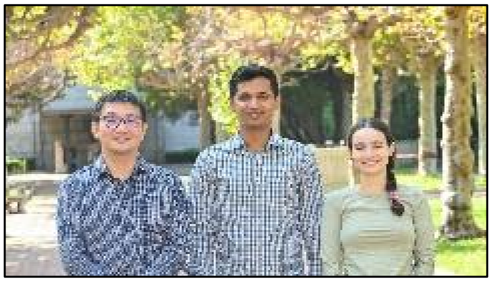
FULL ABSTRACT

(from left) Kaihang Shi and Yangzesheng Sun

T-4: NATURE OF NOVEL MOIRÉ EXCITON STATES IN TRANSITION METAL DICHALCOGENIDE HETEROBILAYERS

[CMS – C2SEPEM] Mit H. Naik[1,2], Emma C. Regan[1,2], Zhenglu Li[1,2], Felipe H. da Jornada[3], Feng Wang[1,2], Steven G. Louie[1,2]
[1]University of California at Berkeley; [2]Lawrence Berkeley National Laboratory; [3]Stanford University

FULL ABSTRACT

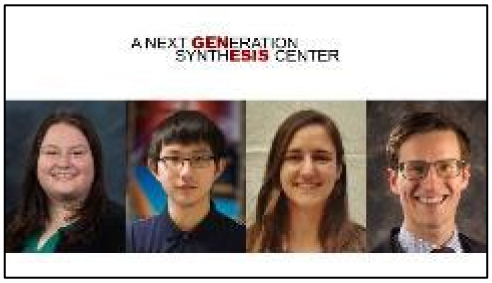


(from left) Zhenglu Li, Mit H. Naik, and Emma C. Regan

T-5: THIN FILM PARADIGM TO PROBE DIFFUSION DURING SOLID-STATE METATHESIS REACTIONS

[EFRC – GENESIS] Rebecca D. McAuliffe[1], Guanglong Huang[2], David Montiel[2], Apurva Mehta[3], Ryan C. Davis[3], Victoria Petrova[4], Matthew J. McDermott[5], Katie L. Browning[1], James R. Neilson[6], Kristin A. Persson[5], Ping Liu[4], Katsuyo Thornton[2], Gabriel M. Veith[1]
[1]Oak Ridge National Laboratory; [2]University of Michigan; Ann Arbor; [3]SLAC National Accelerator Laboratory; [4]University of California-San Diego; [5]University of California, Berkeley; [6]Colorado State University

FULL ABSTRACT



(from left) Rebecca D. McAuliffe, Guanglong Huang, Victoria Petrova, and Matthew J. McDermott

T-6: RADIOLYSIS ACROSS MULTIPLE TIMESCALES IN EXTREME ENVIRONMENTS

[EFRC – IDREAM] Lixin Lu[1]; Emily Nienhuis[2], Andrew Wildman[1], Xiaosong Li[1,2], William Smith[3], Aurora Clark[3,2], Jay LaVerne[4], Thomas Orlando[5], Greg Kimmel[2], Xin Zhang[2], Carolyn Pearce[2,1], Linda Young[6]
[1]University of Washington; [2]Pacific Northwest National Laboratory; [3]Washington State University; [4]Notre Dame University; [5]Georgia Institute of Technology; [6]Argonne National Laboratory

FULL ABSTRACT

(from upper left) Emily Nienhuis and William Smith
(from lower left) Andrew Wildman and Lixin Lu

T-7: Harvesting Oxygen Vacancies in Cobaltites for Low Power Neuromorphic Devices

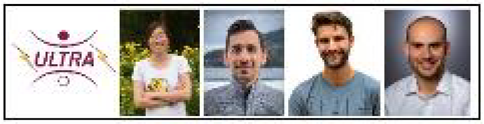
[EFRC – Q-MEEN-C] Shenli Zhang[1], I-Ting Chiu[2], Min-Han Lee[3], Shaobo Cheng[4], Brandon Gunn[3], Hien Vo[1], Mingzhen Feng[2], Larry Heki[5], Zhen Zhang[6], Yahya Mohtashami[5], Pavel N. Lapa[3], Padraic Shafer[7], Alpha T. N'Diaye[7], Apurva Mehta[8], Shriram Ramanathan[6], Jon A Schuller[5], Yimei Zhu[4], Alex Frañó[3], Ivan K. Schuller[3], Yayoi Takamura[2], Giulia Galli[1,9]
[1]The University of Chicago; [2]University of California, Davis; [3]University of California, San Diego; [4]Brookhaven National Laboratory; [5]University of California, Santa Barbara; [6]Purdue University; [7]Lawrence Berkeley National Laboratory; [8]SLAC National Accelerator Laboratory; [9]Argonne National Laboratory

(from left) I-Ting Chiu and Shenli Zhang

Full Abstract

T-8: Thermal Properties of Ultrawide-band-Gap Nitride Material Heterostructures

[EFRC – ULTRA] W. Peng[1], J. Wright[2], M. Malkoutian[3], D. Field[4], R. Wilson[1], D. Jena[2], H. G. Xing[2], S. Chowdhury[3], M. Kuball[4]
[1]Univerisy of California – Riverside; [2]Cornell University; [3]Stanford University; [4]Univeristy of Bristol

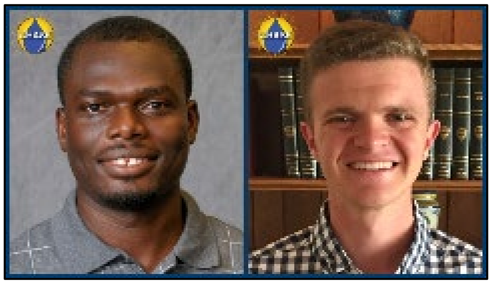


(from left) Wanyue Peng, Mohamadali Malakoutian, Daniel Field, and John Wright

Full Abstract

T-9: Using Di-Copper Molecular Compounds to Investigate Intermediates in CO Reduction to C_2 Products

[Hub – CHASE] Mawuli Deegbey[1], Walter Johnsen[2], Karen I. Goldberg[2], Elena Jakubikova[1], Thomas E. Mallouk[2]
[1]North Carolina State University; [2]University of Pennsylvania



(from left) Mawuli Deegbey and Walter Johnsen

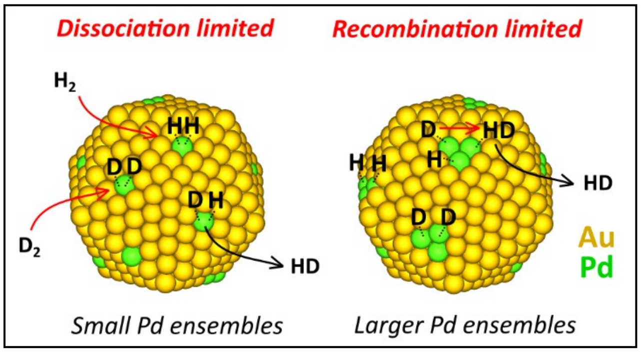
Full Abstract

Team Science Talk Abstracts

T-1: ENTROPIC CONTROL OF HD EXCHANGE RATES OVER DILUTE PD-IN-AU ALLOY NANOPARTICLE CATALYSTS

[EFRC – IMASC] Jessi E. S. van der Hoeven[1], Hio Tong Ngan[2], Austin Taylor[1], Nathaniel M. Eagan[3], Joanna Aizenberg[1], Philippe Sautet[2]; Robert J. Madix[1], Cynthia M. Friend[1]
[1]Harvard University; [2]University of California, Los Angeles; [3]Tufts University

Dilute Pd-in-Au alloy catalysts are promising materials for selective hydrogenation catalysis and have been a focus of IMASC over the past years. Previous surface science studies have contributed mechanistic insight on the energetic aspect of hydrogen dissociation, migration and recombination on dilute alloy systems. Yet translating these fundamental concepts to the kinetics and free energy of hydrogen dissociation on nanoparticle catalysts operating at ambient pressures and temperatures remains challenging. Here, the effect of the Pd concentration and Pd ensemble size on the catalytic activity, apparent activation energy and rate limiting process is addressed by combining experiment and theory. Experiments in a flow reactor show that a compositional change from 4 to 8 atm% Pd of the Pd-in-Au alloy catalyst leads to strong increase in activity, albeit with an increase in apparent activation energy. First-principles calculations show that the rate and apparent activation enthalpy for HD exchange increase when increasing the Pd ensemble size from single Pd atoms to Pd trimers in a Au surface, suggesting that the ensemble size distribution shifts from mainly single Pd atoms on the 4 atm% Pd alloy to larger Pd ensembles of at least three atoms for the 8 atm% Pd/Au catalyst. The DFT studies also indicated that the rate-controlling process is different: H_2 (D_2) dissociation determines the rate for single atoms whereas recombination of adsorbed H and D determines the rate on Pd trimers, similar to bulk Pd. Both experiment and theory suggest that the increased reaction rate with increasing Pd content and ensemble size stems from an entropic driving force. Altogether, this study shows that the rate-controlling step for a catalytic mechanism can be tuned by the formation of specific metastable ensembles at the surface of the alloy that are maintained during reaction at moderate temperature, opening the promise for the rational control of hydrogenation reactions through optimal active ensembles.

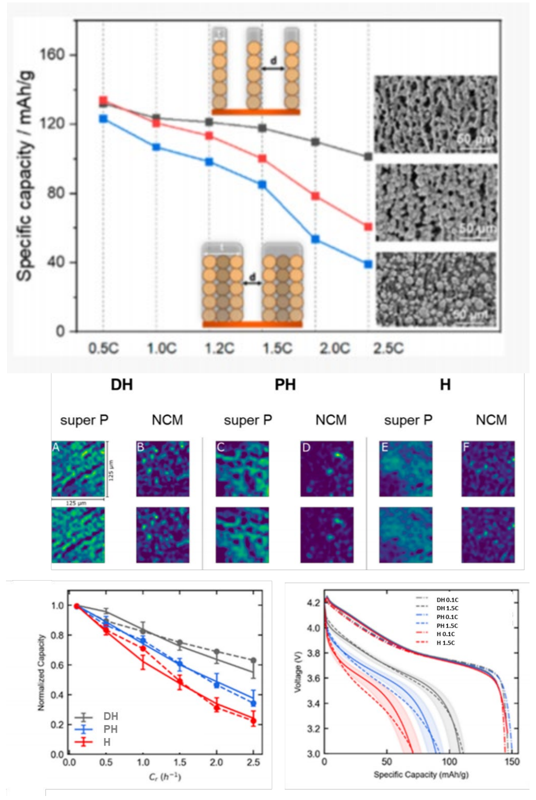


Contributions: Jessi E. S. van der Hoeven prepared and characterized the catalysts and conducted the catalysis experiments. Hio Tong Ngan performed the DFT calculations.

T-2: TUNABLE POROUS ELECTRODE ARCHITECTURES FOR ENHANCED LI-ION STORAGE KINETICS IN THICK ELECTRODES

[EFRC – m2Mt] Xiao Zhang[1], Zeyu Hui[2], Steven King[3], Lei Wang[4], Zhengyu Ju[1], Jingyi Wu[1], Kenneth J. Takeuchi[3,4], Amy C. Marschilok[3,4], Alan C. West[2], Esther S. Takeuchi[3,4], Guihua Yu[1]

[1]University of Texas at Austin; [2]Columbia University; [3]Stony Brook University; [4]Brookhaven National Laboratory



A challenge in design of battery electrodes is the tradeoff between increased energy content and diminished power as the thickness of the electrode is increased. Thick electrodes can suffer from incomplete utilization of active material due to inhibited electrolyte access where the redox reactions are restricted to the electrode surface. The design of porous electrode architectures offers a promising solution, but detailed understanding of the electrode structure and associated transport properties become increasingly critical for accurate prediction of their electrochemical behavior.

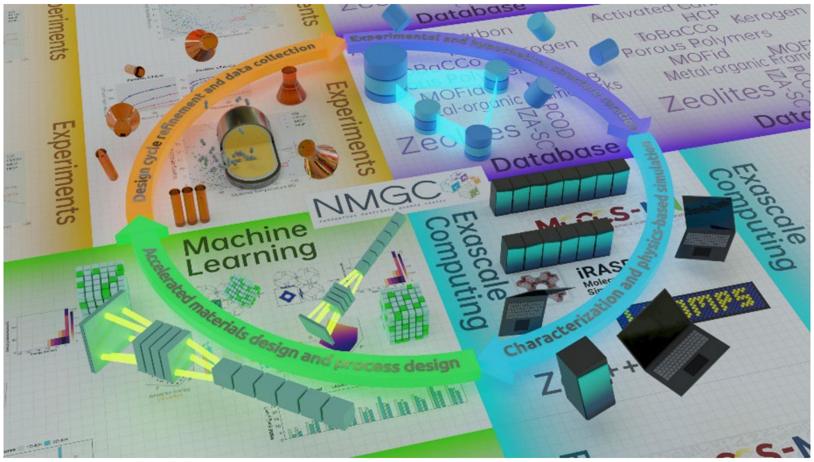
This study brought together expertise in electrode design and fabrication (UTA), detailed 3-dimensional characterization of the electrodes using confocal Raman microscopy paired with NMF analysis (SBU/BNL), and continuum modeling predicting the electrochemistry of the resultant electrodes (CU). The team investigated the relationship among the solvent used (H = water, PH = propanol, DH = DMSO) in the preparation of binder-free, ice-templated porous electrodes, their resultant morphology as determined by Confocal 3D Raman and electrochemical function as predicted by continuum modeling for a model NMC111 system. The pore width, wall thickness, and NMC distribution of the electrodes were characterized using scanning electron microscopy and confocal Raman microscopy. Electrodes with thinner walls were demonstrated to outperform electrodes of comparable porosities but greater wall thickness at elevated C-rates, exhibiting approximately 70% capacity retention under 2.5 C cycling conditions. Continuum simulation models including the wall thickness and channel width were developed and accurately predicted the rate capability and voltage profiles. Modeling suggested the superior function resulted from a reduced Li concentration gradient throughout the electrodes with thinner walls and wider pores. The results move closer toward the goal of achieving simultaneous high energy density and high power.

Contributions: XZ provided the electrode fabrication and electrochemical testing, ZH conducted the continuum modeling, and STK did the Raman mapping/NMF analysis. All contributed equally to this work.

T-3: INTEGRATED COMPUTATIONAL ENGINEERING TOWARDS ACCELERATED SCREENING AND OPTIMIZATION FOR NANOPOROUS MATERIALS

[CCS – NMGC] Kaihang Shi[1], Yangzesheng Sun[2], J. Ilja Siepmann[2], Randall Q. Snurr[1]
[1]Northwestern University; [2]University of Minnesota

Integration of data science, machine learning (ML), and molecular simulation has the potential to facilitate the exploration of nanoporous materials for energy storage, chemical separation, sensing, and catalysis. Predicting the adsorption capacity using molecular simulation is usually the rate-limiting step in the materials design process. Here we present novel two-dimensional energy histogram (2D-EH) features for ML to fast predict the adsorption capacity of a variety of adsorbates in diverse families of nanoporous materials, including those in crystalline and amorphous forms. The 2D-EH features encode critical energetic and structural information of the guest-host system and lead to highly accurate ML models (determination of coefficient R^2~0.96–0.99) for single-component adsorption of spherical molecules and linear and branched alkanes over a wide range of temperatures and pressures. With the help of such high-fidelity ML predictive models, high-performing materials can be quickly identified by computational screening. Another challenging task is to find the optimal operation conditions for a given application. To efficiently search the thermodynamic state space, we present the development of a meta-learning model that jointly predicts the hydrogen uptake for multiple nanoporous materials over a continuous space of pressure and temperature, using data obtained from high-throughput, exascale-ready simulation software [*Sci. Adv.* 2021, **7** (30)].Meta-learning gives higher accuracy and improved generalization compared to fitting a model separately to each material and allows us to identify the optimal hydrogen storage temperature with the highest working capacity for a given pressure/temperature swing. We demonstrate that the combination of meta-learning and molecular simulation accurately predicts the optimal hydrogen storage condition for a cation-exchanged zeolite in good agreement with experiments. The closed-loop workflow involving robust and accurate ML models, databases, and high-throughput simulations developed by NMGC researchers is accelerating screening and de novo design of nanoporous materials.



Acknowledgment: This research is supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Chemical Sciences, Geosciences and Biosciences under award DE-FG02-17ER16362 as part of the Computational Chemical Sciences Initiative.

Contributions: K.S. and R.Q.S. are the lead authors on the 2D energy histogram. Y.S. and J.I.S. are the lead authors on meta-learning for hydrogen storage. K.S. and Y.S. wrote the abstract with revisions from all of the authors.

T-4: NATURE OF NOVEL MOIRÉ EXCITON STATES IN TRANSITION METAL DICHALCOGENIDE HETEROBILAYERS

[CMS – C2SEPEM] Mit H. Naik[1,2], Emma C. Regan[1,2], Zhenglu Li[1,2], Felipe H. da Jornada[3], Feng Wang[1,2], Steven G. Louie[1,2]
[1]University of California at Berkeley; [2]Lawrence Berkeley National Laboratory; [3]Stanford University

Moiré superlattices of transition metal dichalcogenide heterobilayers are an ideal platform to support unusual, correlated electron and exciton physics. Previously, our team established experimentally the existence of novel moiré exciton states in WS_2/WSe_2 moiré superlattices through the observation of multiple emergent peaks in the absorption spectra, but the exact origin and nature of these states remains difficult to probe. A theoretical understanding of the moiré excitons has been limited until now to parameterized continuum models, owing to the challenge of calculating the photo-excited states of a system of thousands of atoms in the moiré unit cell including accurate electron-hole interactions from first principles. In this work, we combine predictive, parameter-free *GW* plus Bethe-Salpeter equation (*GW*-BSE) calculations with experimental reflection contrast measurements to study exciton resonances in WS_2/WSe_2 moiré superlattices. The exciton states, calculated using a novel computational strategy to tackle large-size superlattices, explain the experimentally measured spectrum. From the GW-BSE calculations, we discover that moiré excitons possess distinct characters: some are of a modulated Wannier character and others are of a previously unidentified intralayer charge-transfer character (Figure 1).

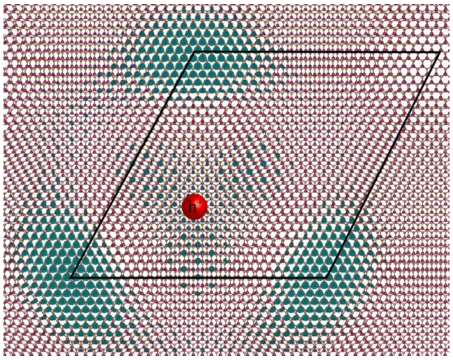


Fig. 1. Calculated electron density isosurface (4% of maximum) for a particular moiré exciton with the hole coordinate fixed at a point (red sphere), showing the charge-transfer character. The solid lines enclose the moiré primitive unit cell.

Further, we identify signatures of these distinct excitonic states and measure them in the doping-dependence and circular dichroism of the reflection contrast spectrum. Each of the excitonic resonances has a unique doping dependence, directly correlated to the site that the doped electron and hole occupy in the moiré pattern. The theoretical method developed is currently being extended in our Center to study moiré exciton dynamics and the formation of hybrid excitons in other moiré heterostructures in synergy with experiments.

Contributions: S.G.L. conceived the project; M.H.N., Z.L., F.H.J. and S.G.L. developed the theory and performed the GW-BSE calculations; E.C.R., Z.Z. and F.W. fabricated the sample and measured the reflection contrast spectra.

Reference:

M. H. Naik*, E. C. Regan*, Z. Zhang*, Y. Chan, Z. Li, D. Wang, Y. Yoon, C. S. Ong, W. Zhao, S. Zhao, M. I. B. Utama, B. Gao, X. Wei, M. Sayyad, K. Yumigeta, M. Blei, K. Watanabe, T. Taniguchi, S. Tongay, F. H. da Jornada, F. Wang and S. G. Louie, *Nature of novel moiré exciton states in transition metal dichalcogenide heterobilayers,* to be submitted (2021).

T-5: Thin Film Paradigm to Probe Diffusion during Solid-State Metathesis Reactions

[EFRC – GENESIS] Rebecca D. McAuliffe[1], Guanglong Huang[2], David Montiel[2], Apurva Mehta[3], Ryan C. Davis[3], Victoria Petrova[4], Matthew J. McDermott[5], Katie L. Browning[1], James R. Neilson[6], Kristin A. Persson[5], Ping Liu[4], Katsuyo Thornton[2], Gabriel M. Veith[1]

[1]Oak Ridge National Laboratory; [2]University of Michigan; Ann Arbor; [3]SLAC National Accelerator Laboratory; [4]University of California-San Diego; [5]University of California, Berkeley; [6]Colorado State University

The team is focused on understanding and predicting how bulk, surface, gas-phase, and grain boundary diffusion processes mediate nucleation and growth of reaction products during low-temperature solid-state metathesis reactions. The approach involves the synergetic integration of experiments with thin film samples to confine the diffusion pathways and simplify the reaction processes and simulations through phase field modeling. A prototypical metathesis reaction between FeCl2 and Na2S2 to form NaCl and FeS2 was selected as the model system. The synthesis of model films (Na2S2 and FeCl2) was performed through physical vapor deposition, which was assisted by density functional theory calculations to identify and understand growth conditions and extensive characterization of the resulting structures and defects. Film heterostructures were built from successive layers of these materials. The diffusion and product formation as a function of temperature were evaluated using in situ reflectometry, electrochemical impedance, microscopy, and phase field simulations from GENESIS team members. The data show a surprising change in the reaction process between traditional bulk powders and the thin film heterostructures. Specifically, the thin-film samples exhibited an interfacial reaction that blocked further solid-state diffusion through the films at temperatures up to 350oC. In contrast, powder samples reacted to completion in a few hours at 250oC. Together the results point to a multifaceted set of transport processes mediating this reaction. The knowledge gained is being integrated into a complex model to predict reaction pathways that also considers intermediates for other metathesis reactions.

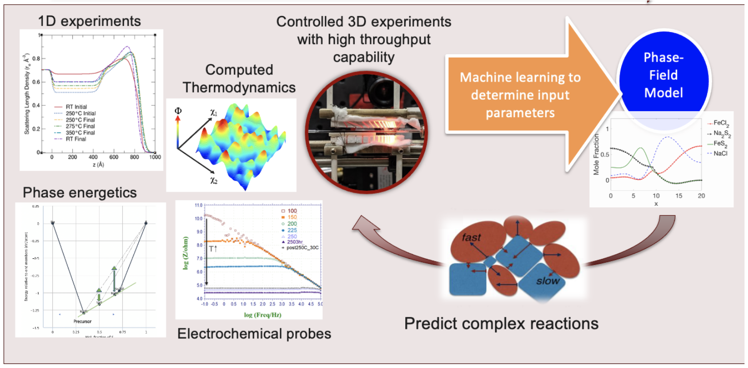


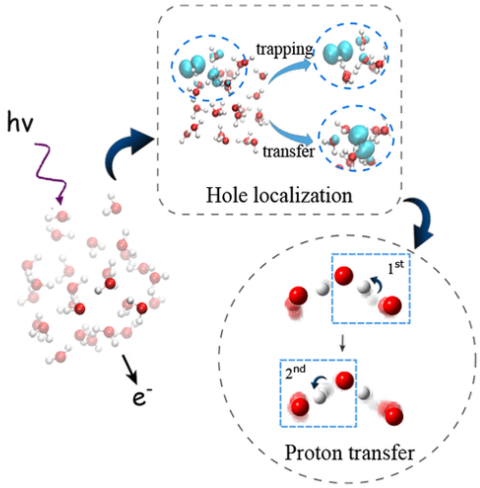
Fig. 1: A schematic of the collaborative effort in GENESIS EFRC, integrating theory, experiments, simulations, and machine learning to elucidate complex reaction pathways and enable control of synthesis.

Contributions: R.D.M. fabricated the heterostructures, performed and analyzed the X-ray reflectivity and analyzed the X-ray photoelectron spectroscopy data with guidance from G.M.V. R.C.D. and A.M. assisted in the setup and collection of XRR data and A.M. and K.L.B. assisted in the analysis of the XRR data. V.P. performed and analyzed the AC impedance data with guidance from P.L. **G. H. performed phase-field modeling calculations with guidance from D.M. and K.T. M.J.M. performed formation energy calculations with guidance from K.A.P. J.R.N. assisted in understanding the data and discussing reaction processes in metathesis reactions.**

T-6: RADIOLYSIS ACROSS MULTIPLE TIMESCALES IN EXTREME ENVIRONMENTS

[EFRC – IDREAM] Lixin Lu[1]; Emily Nienhuis[2], Andrew Wildman[1], Xiaosong Li[1,2], William Smith[3], Aurora Clark[3,2], Jay LaVerne[4], Thomas Orlando[5], Greg Kimmel[2], Xin Zhang[2], Carolyn Pearce[2,1], Linda Young[6]
[1]University of Washington; [2]Pacific Northwest National Laboratory; [3]Washington State University; [4]Notre Dame University; [5]Georgia Institute of Technology; [6]Argonne National Laboratory

Understanding radiation-induced chemical processes in condensed phase has importance for applications ranging from cancer therapies and space travel to environmental remediation of legacy nuclear waste. High-energy irradiation can ionize and electronically excite target atoms and molecules. These excitations undergo complex relaxation and energy transfer processes that ultimately determine how the system responds to the deposited excess energy and the subsequent chemical reactions and transformations. Our quantum dynamic simulations have provided unprecedented insight into the ultrafast dynamics and reactive events initiated by the radiolysis of water, including ultrafast hole trapping and transfer, large-OH oscillations, proton transfer and subsequent relay, formation of metastable Zundel complexes, and long-lived coherence [DOI: 10.1021/acs.jpclett.0c02987]. These early-time dynamics trigger chemical processes within complex energetic landscapes that drive subsequent reactions. For example, joint experiment-theory efforts in IDREAM revealed that intermolecular Coulomb decay (ICD) and electron-transfer mediated decay (ETMD) pathways under non-equilibrium conditions at water/boehmite interfaces led to efficient energy transfer and soft ionization of the interfacial water molecules instead of damage to the nanoplatelets [DOI: 10.1021/acs.jpclett.0c02911]. These efforts provide the foundation for new experiments at the Linear Coherent Light Source (LCLS) that will investigate ultrafast dynamics in highly alkaline aqueous environments, and the surprising differences in interfacial reactivity of aluminum oxyhydroxides nanoparticles. New and unique x-ray pump/x-ray probe capabilities at the LCLS allow us to track the aforementioned processes, down to the sub-picosecond timescale, and thus understand the origin and fate of reactive species in these complex environments [DOI: 10.3390/app11020701]. We aim to resolve radiation driven processes from ultrafast non-equilibrium dynamics to long-time chemical transformation, developing a fundamental understanding of interfacial energy exchange to explain chemical and physical behavior in complex and multiphasic extreme environments.



Using Ehrenfest dynamics, we successfully predicted the chemical processes that occur during the photoionization of water on the femtosecond time scale.

Contributions: L. Lu, E. Nienhuis, A. Wildman, W. Smith: conceptualization, data analysis, investigation, methodology, visualization, writing—original draft, writing—review and editing. X. Li and A.E. Clark (Theory), J. LaVerne, T. Orlando, G. Kimmel, L. Young, and C. Pearce (Experimental): conceptualization, funding acquisition, supervision, project administration, writing—original draft, writing—review and editing.

T-7: HARVESTING OXYGEN VACANCIES IN COBALTITES FOR LOW POWER NEUROMORPHIC DEVICES

[EFRC – Q-MEEN-C] Shenli Zhang[1], I-Ting Chiu[2], Min-Han Lee[3], Shaobo Cheng[4], Brandon Gunn[3], Hien Vo[1], Mingzhen Feng[2], Larry Heki[5], Zhen Zhang[6], Yahya Mohtashami[5], Pavel N. Lapa[3], Padraic Shafer[7], Alpha T. N'Diaye[7], Apurva Mehta[8], Shriram Ramanathan[6], Jon A Schuller[5], Yimei Zhu[4], Alex Frañó[3], Ivan K. Schuller[3], Yayoi Takamura[2], Giulia Galli[1,9]

[1]The University of Chicago; [2]University of California, Davis; [3]University of California, San Diego; [4]Brookhaven National Laboratory; [5]University of California, Santa Barbara; [6]Purdue University; [7]Lawrence Berkeley National Laboratory; [8]SLAC National Accelerator Laboratory; [9]Argonne National Laboratory

Transition metal oxides (TMO) are promising materials to realize low-power neuromorphic devices. The cobaltites $La_{1-x}Sr_xCoO_{3-\delta}$ (LSCO) are of particular interest, since they display a unique metal-to-insulator transition (MIT) under the action of physical stimuli and they offer the opportunity of designing desirable resistive switching states. Through a combination of theory and experiments, we investigated[1] the role played by oxygen vacancies in determining the conditions which facilitate the MIT. Upon annealing under highly reducing conditions, a series of topotactic transformations are observed from perovskite to brownmillerite (BM) and finally Ruddlesden-Popper phases, each with their own distinct magnetic and electronic properties.[1] The complex interplay between the changes in magnetic and electronic properties and the transformation of the crystal structure was unraveled by first principles calculations[2]. We found that cooperative, rather than local, structural distortions occur during the topotactic transformation between the perovskite and BM phases, which are accompanied by a magnetic state transition, ultimately responsible for driving the MIT. Using our first principles results we then developed a model[3] to predict the required electrical bias to drive such a transition, and provided strategies to minimize the electrical bias needed to design and optimize neuromorphic devices. Our work helped establish general computational strategies to study TMOs[4]. Finally, we combined experiments and theory to identify fingerprints of oxygen vacancies in LSCO based materials, by analyzing X-ray absorption spectra and we provided a robust protocol to determine oxygen stoichiometry in promising TMOs for neuromorphic devices[5].

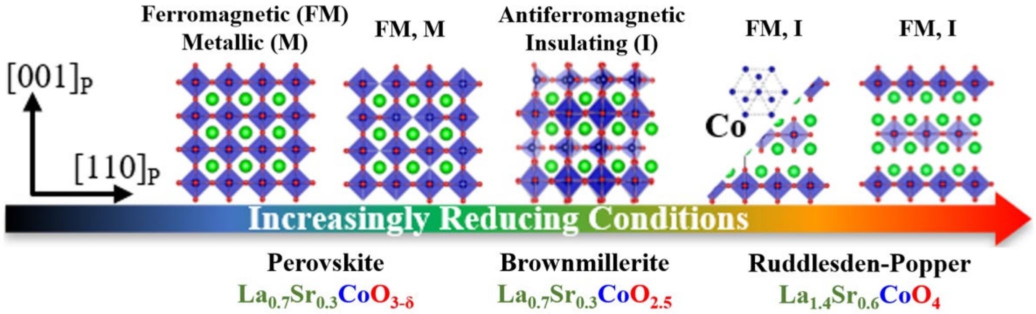


Figure 1 Crystal structure diagrams for the annealed LSCO films along with their associated magnetic and electrical properties.

References: [1] Chiu, I.-T. *et al., Phys. Rev. Mater.* **5**, 064416 (2021). [2] Zhang, S. & Galli, G. *npj Comput. Mater.* **6**, 170 (2020). [3] Zhang, S., Vo, H. & Galli, G. *Chem. Mater.* **33**, 3187–3195 (2021). [4] Vo, H., Zhang, S., Wang, W. & Galli, G. *J. Chem. Phys.* **154**, 174704 (2021). [5] Zhang, S *et al.*, in preparation.

Contributions: I. Chiu performed the main experimental work involved in the study. S. Zhang conducted the first-principles calculations. I. Chiu and S. Zhang both contributed to the abstract writing and figure design.

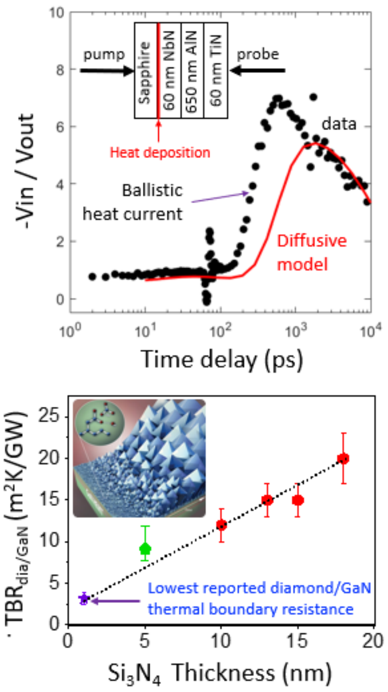
T-8: THERMAL PROPERTIES OF ULTRAWIDE-BAND-GAP NITRIDE MATERIAL HETEROSTRUCTURES

[EFRC – ULTRA] W. Peng[1], J. Wright[2], M. Malkoutian[3], D. Field[4], R. Wilson[1], D. Jena[2], H. G. Xing[2], S. Chowdhury[3], M. Kuball[4]

[1]Univerisy of California – Riverside; [2]Cornell University; [3]Stanford University; [4]Univeristy of Bristol

The high breakdown voltage of ultra-wide band gap materials provides the basis to enable power electronics with reduced size, increased reliability, and lower on-resistances. The ULTRA EFRC seeks to improve fundamental understanding of ultra-material phenomena so such devices can reach their full potential. A challenge we must overcome is that device performance is limited by the efficiency of heat conduction in a complex multilayered heterostructure.

Our work seeks to understand the effects of synthesis, interfaces, defects, and ballistic vs. diffusive transport on heat conduction in nitride heterostructures. We closely integrate sample synthesis, thermal characterization, and simulation efforts. This allows us to design experiments that separate how different phenomena control conduction. For example, our theoretical simulations of conduction in sub-micron thick AlN layers predict that transport occurs via a combination of ballistic and diffusive heat-currents. But our standard thermal metrologies could not confirm this prediction. We overcame this obstacle by developing a new thermal metrology. Our approach relies on integrating an epitaxial buried heater layer into an AlN heterostructure during sample growth. We used MBE to grow an epitaxial 60nm-TiN/650nm-AlN/60nm-NbN tri-layer on sapphire. We then performed nanoscale laser flash measurements of heat conduction across the AlN. We monitor the time-evolution of the surface TiN layer's temperature after ultrafast heating of the buried NbN layer (top panel of figure). By comparing our experimental data to theoretical simulations, we were able to quantify the importance of sub-continuum transport effects. We find that, at room temperature, ~25% of the heat-current across the AlN is ballistic.



Similarly, close integration of simulation, synthesis, and thermal experiments led to our discovery of a method for enhancing heat conduction in N-polar and Ga-polar nitride device heterostructures. Our simulations predicted that depositing a diamond layer on top of an AlGaN/GaN heterostructure could improve performance if thermal boundary resistance (TBR) is small. To test this, we grew polycrystalline diamond on Si_3N_4/GaN/AlGaN heterostructures. Then, we prepared the samples for transient thermoreflectance measurements. We used Si_3N_4 as a thermal interface material between the diamond and GaN to improve their thermal contact. By growing polycrystalline diamond on a series of samples with different Si_3N_4 layer thicknesses, we were able to separate the effects of the interface vs. the Si_3N_4 layer on transport (bottom panel of figure). We observed record low TBR of ≈ 3 m^2-K/GW between diamond and the GaN. Finally, we used Raman thermometry to show that, consistent with thermal simulations, the diamond top-layer decreased device temperature by >25%. Our work shows how co-design of heat-transfer experiments by synthesis experts, thermal scientists, and theorists allows otherwise intractable problems to be overcome.

Contributions: W. P. and R. W. performed thermal simulations and characterization of AlN. J. W., D. J., and G. H. X. prepared nitride-metal/AlN samples. M. M. and S. C. synthesized diamond/GaN structures. D. F. and M. K. performed thermal characterization and thermal simulations of diamond/GaN samples.

T-9: Using Di-Copper Molecular Compounds to Investigate Intermediates in CO Reduction to C_2 Products

[Hub – CHASE] Mawuli Deegbey[1], Walter Johnsen[2], Karen I. Goldberg[2], Elena Jakubikova[1], Thomas E. Mallouk[2]

[1]North Carolina State University; [2]University of Pennsylvania

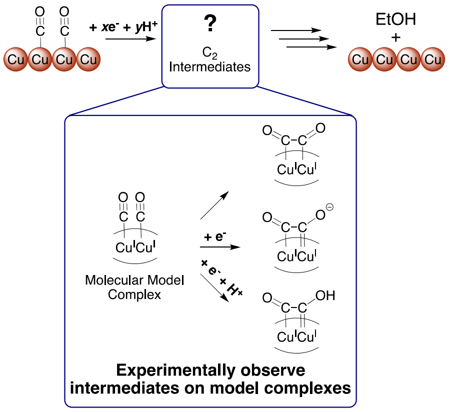
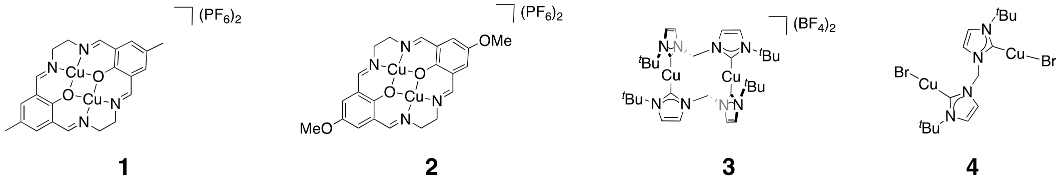


Figure 1: Molecular model complexes are used to investigate intermediates in CO reduction reaction.

The reduction of CO to multi-carbon products on heterogenous copper electrocatalysts offers an environ-mentally benign method to produce carbon-containing liquid fuels. Poor understanding of the reaction mechanism, including the formation of the C-C bond, inhibits the design of efficient and selective catalysts. To address this gap, we use molecular di-copper complexes as functional models for copper surfaces (Fig. 1). Molecular complexes, unlike heterogenous structures, have easily tuned electronic and steric properties and proposed catalytic intermediates may be synthetically accessible.

Complexes **1** and **2** were selected as copper surface models for their short Cu-Cu distances (< 2.9 Å) and ease of synthesis (Fig. 2). Voltametric experiments and density functional theory (DFT) calculations suggest that **1** and **2** coordinate two CO molecules upon two electrochemical reductions in an ECEC mechanism. Subsequent electrochemical studies showed that **1** and **2** are not stable in acidic reducing conditions. Stability in acid is necessary for the complexes to be functional models of the copper surfaces, thereby preventing **1** and **2** from being further investigated as models.



1 **2** **3** **4**

Figure 2: Complexes investigated as models for the copper surface.

Computational analysis was used to screen potential model complexes for electrochemical properties and acid stability. The results of the initial screening led to the selection of complexes **3** and **4**. Initial experiments characterized by ^1H NMR suggest both **3** and **4** react with CO. Isolation of the products from these reactions is ongoing.

This project sits at the center of two of the three CHASE Thrusts: Cascades and Microenvironments. Multiple catalytic cascades under investigation by CHASE to convert CO_2 to liquid fuels proceed through CO intermediates. The information garnered from characterizing the formation of the C-C bond between CO molecules will aid the development of cascades for reduction of CO_2 to multi-carbon products. In parallel, the high tunability of the primary and secondary coordination spheres of the molecular complexes will allow for thorough analysis of the influence microenvironment has on CO reduction.

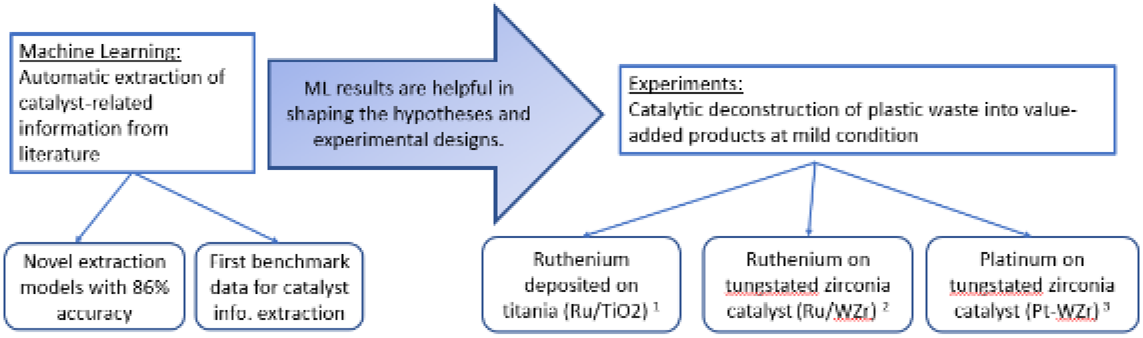
Contributions: This project was conceived by M.D., K.I.G., E.J., W.D.J., and T.E.M. W.D.J. synthesized model compounds and performed experimental studies. M.D. carried out all computational experiments. W.D.J. and M.D. prepared this abstract with input from all authors.

Team Science Poster Abstracts

T1-A-1: DATA SCIENCE-LEVERAGED CATALYTIC DECONSTRUCTION OF PLASTIC WASTE INTO VALUE-ADDED PRODUCTS AT MILD CONDITIONS

[EFRC – CPI] Cong Wang, Yue Zhang, Brandon C. Vance, Pavel A. Kots, Zachary R. Hinton, Mya Soukaseum, Dionisios G. Vlachos, Thomas H. Epps, III, LaShanda T. J. Korley, Hui Fang
University of Delaware

The environmental impact of plastics waste is a major global challenge. Polyolefins, such as poly(ethylene) and poly(propylene), comprise the highest volume of the plastics waste stream and also have a very low recycling rate. Chemical recycling, specifically catalytic polymer deconstruction, has the potential to combat this polyolefin plastics waste problem, but one challenge associated with advancing these efforts is that prior literature on the topic is minimal. Therefore, experimentalists must rely on a very large volume of partially-relevant articles to shape their hypotheses and experimental designs, a time-consuming task that limits the applicability of these prior findings. To tackle this challenge, machine learning (ML) researchers along with catalyst and polymer experimentalists within the Center for Plastics Innovation (CPI) have teamed up to develop novel data science tools. The models developed by the CPI team can automatically extract condensed, relevant information from a large pool of scientific literature and present the information in a user-friendly, structured format. These tools have improved the learning curve and substantially accelerated the progress of experiments within CPI, thanks to the interdisciplinary synergy. In the past year, this collaborative approach has aided experimentalists in identifying high-performance catalysts that can efficiently decompose plastics waste through distinct reaction pathways, leading to impactful publications[1-3] with more on the horizon. Current team efforts are focused on translating these ML approaches to polymer upgrading strategies.



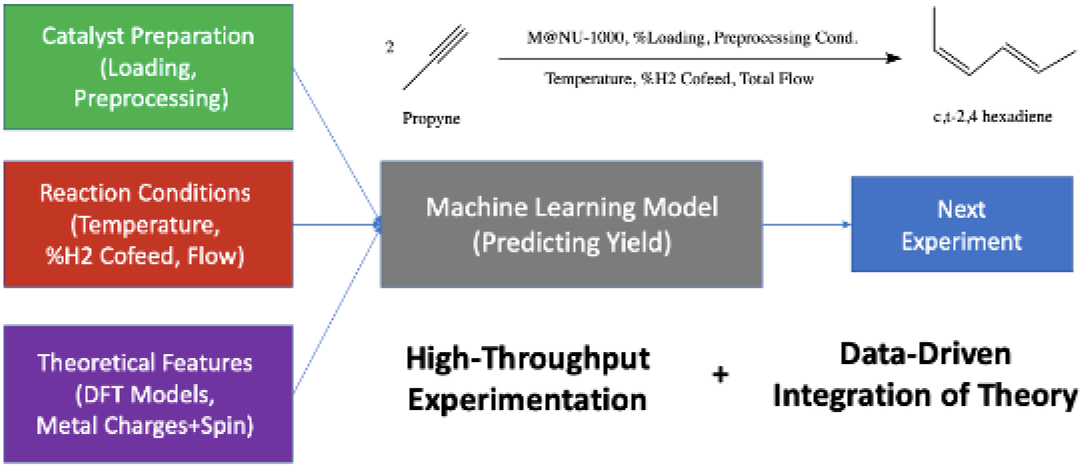
1. Kots, P. A.; Liu, S.; Vance, B. C.; Wang, C.; Sheehan, J. D.; Vlachos, D. G., Polypropylene Plastic Waste Conversion to Lubricants over Ru/TiO2 Catalysts. *ACS Catalysis* **2021,** *11* (13), 8104-8115.
2. Wang, C.; Xie, T.; Kots, P.; Vance, B.; Yu, K.; Kumar, P.; Fu, J.; Liu, S.; Tsilomelekis, G.; Stach, E.; Zheng, W.; Vlachos, D., Polyethylene Hydrogenolysis at Mild Conditions Over Ruthenium on Tungstated Zirconia. *JACS Au* **Under Review**.
3. Vance, B. C.; Kots, P. A.; Wang, C.; Hinton, Z. R.; Quinn, C. M.; Epps, T. H.; Korley, L. T. J.; Vlachos, D. G., Single Pot Catalyst Strategy to Branched Products via Adhesive Isomerization and Hydrocracking of Polyethylene over Platinum Tungstated Zirconia. *Applied Catalysis B: Environmental* **2021**, 120483.

Contributions: Experimentalists (CW, BV, PK, ZH, MS, DV, TE and LK) conducted catalytic experiments and developed high-performance catalysts for plastic waste deconstruction. ML researchers (YZ and HF) developed novel algorithms that can automatically extract catalyst information from scientific literature using input from experimentalists.

T1-A-2: A Data-Driven High-Throughput Framework for Discovery of Transition Metal Catalysts on NU-1000

[EFRC – ICDC] King, D.S.[1], McCullough, K.M.[2], Ricardo, A.M.[1], Ferrandon, M.S.[2], Gagliardi, L.[1], Farha, O.[3], Delferro, M.[2]

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



Transition metal systems deposited on highly porous metal-organic frameworks (MOFs) have the unique opportunity to unite the benefits of homogeneous and heterogeneous catalysis. However, the active sites of these catalysts are often extremely difficult to characterize, and catalytic activity can often change drastically as a function of experimental synthesis and preprocessing conditions. These factors present a great challenge for standard theoretical approaches, which generally require the active site to be well-defined. To overcome this issue, we take a multi-faceted approach to developing transition metal catalysts on the MOF NU-1000 which combines high-throughput experimentation and computational modeling united by a machine-learning framework. Instead of theoretical approaches being used to characterize the active site, they are used to develop features for a machine learning model which are combined with experimental conditions directly to predict figures of merit such as conversion and yield, for untested experiments. Here, we present the data generated using this coupled approach to target the dimerization of propyne through the deposition of 18 different transition metals. We believe this approach has the potential greatly speed up the discovery of promising MOF catalysts over the standard “synthesize-characterize-explain” regime of standard development, and can be expanded to a wide range of industrially relevant chemical reactions.

Contributions:

King, D.S.; Ricardo, A.M. – Machine learning modeling and development
Katie, M.; Ferrandon, M. S. – Experimental synthesis, pretreatment, and reaction
Delferro, M.; Farha, O.; Gagliardi, L. – Project oversight

T1-B-3: UNDERSTANDING STRUCTURE AND COMPOSITION OF DES IMPACTS ON BATTERY ELECTROLYTE PERFORMANCE

[EFRC – BEES] Derrick N. Poe[1], Brian W. Doherty[2], Ibrahim A. Alfurayj[3], William Dean[3], Raziyeh Ghahremani[3], Benworth B. Hansen[4], Stephanie Spittle[4], Mark E. Tuckerman[2], Burcu Gurkan[3], Clemens Burda[3], Joshua Sangoro[4], Edward J. Maginn[1], Robert F. Savinell[3]

[1]Notre Dame; [2]New York University; [3]Case Western Reserve University; [4]University of Tennessee

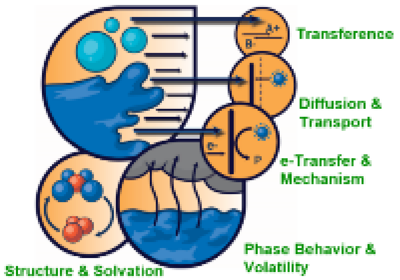


Fig 1. Target DES properties to be optimized for RFB

Renewable energy is an integral component of current and future energy generation across the globe, though the next generation of electrochemical energy storage systems will require a new class of electrolytes to match and facilitate the growing green energy demand. This is the motivation behind this EFRC, Breakthrough Electrolytes for Energy Storage (BEES). Deep eutectic solvents (DESs) are a class of liquids, comprised of a hydrogen bond donor (HBD) and hydrogen bond acceptor (HBD), that possesses an incredibly wide chemical design space. A goal of BEES is to develop a comprehensive understanding of how DES composition results in their diverse physiochemical and electrochemical properties, as indicated in Figure 1. Ultimately, an engineered DES electrolyte functionalized with redox active groups and favorable physical properties will allow for high power and energy dense next-generation RFBs.

BEES has capitalized on the collaborative nature of an EFRC with numerous multidisciplinary research projects resulting in several publications[1-8]. A comprehensive understanding of the varied and complex structural and dynamic behaviors of hallmark DESs Ethaline and Glyceline was achieved through combined experimental and simulation techniques.[1,2,5,6] Furthermore, while water was typically believed to be a contaminant, properties were found to be enhanced at relatively low to medium water concentrations.[8] Advancements have also been made in understanding redox molecules behavior in DESs with different polar environments to improve battery performance.[3,4,7] To achieve this, BEES employed an array of techniques including broadband dielectric spectroscopy, classical molecular dynamics, *ab initio* molecular dynamics, nuclear magnetic resonance spectroscopy, wide angle neutron scattering, differential scanning calorimetry, ultrafast spectroscopy, viscometry, densitometry, and electrochemical measurements. The publications resulting from the BEES EFRC have resulted in a better understanding of fundamental DES behavior and have provided numerous avenues for further research. Ongoing research efforts include precise mapping and understanding of DES liquid-solid phase diagrams, impacts of alternative HBD-HBA pairs on bulk and interfacial behavior, precise design of ideal redox active candidates, and developing a precise understanding of structure-property relationships of the HBDs.

[1] Gurkan B. *et al. J. Phys. Chem. Lett.* 2019, 10, 24, 7956–7964; **[2]** Zhang Y. *et al. J. Phys. Chem. B* 2020, 124, 25, 5251–5264; **[3]** Klein M. *et al. J. Phys. Chem*. B 2020, 124, 29, 6348–6357; **[4]** Chen, B. *et al. Mol. Syst. Des. Eng*., 2020,5, 1147-1157; **[5]** Hansen B. *et al. Chem. Rev.* 2021, 121, 3, 1232–1285; **[6]** Dean W. *et al. 2021 J. Electrochem. Soc.* 168 026503; **[7]**; Sinclair N. *et al.* et al 2021 *J. Electrochem. Soc*. 168 020527; **[8]** Alfurayj I *et al. J. Phys. Chem. B* 2021 125 (31), 8888-8901

Contributions: D.N.P. and E.J.M. performed classic molecular dynamics simulations. B.W.D. and M.E.T. conducted *ab initio* molecular dynamics simulations. I.A.A. and C.B. performed ultrafast laser spectroscopy measurements and polarity measurements. W.D. and B.G. collected physical property data and performed interfacial analysis. R.G. and B.G. performed electrochemical characterizations. B.B.H. and J.S. carried out differential scanning calorimetry. S.S. and J.S. performed broadband dielectric spectroscopy. E.J.M. oversaw the *Team Science Competition* team. R.F.S. served as EFRC director while B.G. and E.J.M served as Lead and Deputy Lead for Thrust 1, respectively. D.N.P prepared the abstract submission with review and contributions from all authors.

T1-B-4: EFFECTS OF INTERLAYER CONFINEMENT AND HYDRATION ON CAPACITIVE CHARGE STORAGE IN BIRNESSITE

[EFRC – FIRST] S. Boyd[1], K. Ganeshan[2], W.-Y. Tsai[3], T. Wu[4], S. Saeed[1], J. Fortunato[1], D.-E. Jiang[4], N. Balke[3], A.C.T. van Duin[2], V. Augustyn[1]

[1]North Carolina State University; [2]Penn State University; [3]Oak Ridge National Laboratory; [4]University of California, Riverside

Birnessite is a low-cost electrode material of interest for high power energy storage. In its nanostructured form, birnessite exhibits high specific capacitance and nearly ideal capacitive behavior in aqueous electrolytes. The mechanism of electrochemical capacitance in birnessite has been described as both Faradaic (involving redox) and non-Faradaic (involving only electrostatic interactions). To understand the capacitive mechanism of birnessite in aqueous electrolytes, we combined experimental characterization (including in situ Raman spectroscopy and operando atomic force microscopy) with computational methods (density functional theory and ReaxFF reactive force field-based molecular dynamics and grand canonical Monte Carlo simulations). The combination of experimental and computational studies enabled us to propose an atomistic-level perspective for capacitive charge storage in birnessite as being enabled by the presence of cation intercalation into a nanoconfined and hydrated interlayer.[1] Moreover, we were able to use the combination of electrochemical characterization and simulation to deconvolute the role of cations and protons in the capacitive charge storage mechanism.[2] These studies provide critical insight into the understanding of the electrochemical interface under confinement.

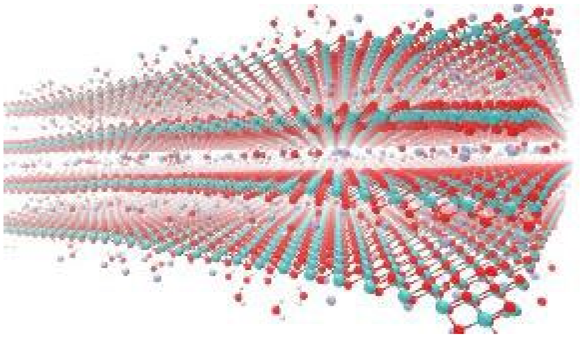


Figure 2. Structure of birnessite showing the hydrated interlayer environment responsible for the capacitive behavior in aqueous electrolytes. (blue: manganese, red: oxygen, white: hydrogen, lavender:

References

1. Boyd, S.; **Ganeshan, K.**; **Tsai, W.-Y.**; Wu, T.; **Saeed, S.**; Jiang, D.E.; Balke, N.; van Duin, A.C.T.; Augustyn, V. “Effects of Interlayer Confinement and Hydration on Capacitive Charge Storage in Birnessite.” *Nature Mater.* DOI: 10.1038/s41563-021-01066-4.
2. **Saeed, S.**; **Fortunato, J.**; **Ganeshan, K.**; van Duin, A.C.T.; Augustyn, V. “Decoupling Proton and Cation Contributions to Capacitive Charge Storage in Birnessite in Aqueous Electrolytes.” *under review.*

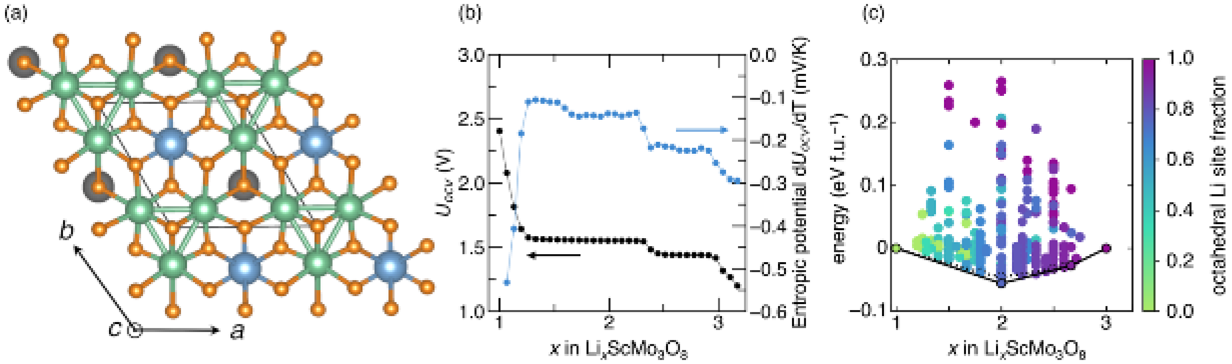
Contributions: **K. Ganeshan**: ReaxFF simulations; **W.-Y. Tsai**: *operando* atomic force microscopy dilatometry; **S. Saeed**: aqueous & non-aqueous electrochemistry; **J. Fortunato**: *in situ* and *ex situ* Raman spectroscopy

T1-B-5: LINKING ELECTROCHEMISTRY TO LITHIUM ORDERING IN THE LOW-STRAIN MO-CLUSTER COMPOUND LISCMO$_3$O$_8$

[EFRC – SCALAR] Kira E. Wyckoff[1], Jonas L. Kaufman[1], Sun Woong Baek[2], Joshua J. Zak[3], Rebecca C. Vincent[1], Kimberly A. See[3], Laurent Pilon[2], Anton Van der Ven[1], Ram Seshadri[1]
[1]University of California, Santa Barbara; [2]University of California, Los Angeles; [3]California Institute of Technology

The mission of the SCALAR EFRC is to design materials that revolutionize the performance of energy storage systems by expanding the range of materials systems and chemistries that can be employed in next generation batteries. One of the focus areas of SCALAR is on electrode materials that intrinsically display efficient electron and ion transport in order to enhance performance. Degradation in many promising systems has been attributed to chemomechanics associated with structural changes accompanying repeated cycling. Materials that exhibit minimal structural changes with (de)lithiation are rare. Here we present a chemical bonding principle to aid the search for such materials.

Metal-metal bonding is a distinct feature of some refractory metal oxides that has been largely underutilized in electrochemical energy storage. Here we establish $LiScMo_3O_8$, a compound containing triangular clusters of metal-metal bonded Mo atoms as a potential new anode material in Li^+–ion batteries. We demonstrate that electrons are localized across the structurally rigid Mo_3 triangles (rather than on individual metal atoms) upon lithiation, resulting in minimal structural change. We use this model system to investigate how the Mo–Mo bonding impacts electrochemistry, reversibility of cycling, and fast rate capabilities. We capitalize on the complementary expertise within our center to employ advanced *operando* and *ex-situ* experimental characterization techniques, in conjunction with detailed computational studies, to develop strategies to promote efficient electron and ion transport in electrode materials.



(a) Crystal structure of $LiScMo_3O_8$ (space group is *P*3*m*1, No. 156) contains alternating layers of triangular clusters of metal-metal bonded Mo atoms (green) and Li (grey)/Sc (blue), (b) $U_{ocv}(x,T)$ and entropic potential $\partial U_{ocv}(x,T)/\partial T$ during lithiation, (c) calculated formation energies of distinct Li-vacancy orderings in $Li_xScMo_3O_8$. Points are colored by the fraction of Li in the structure that occupy octahedral sites. The solid black line is the convex hull.

Contributions: K.E.W and R.S. conceived the idea. K.E.W. prepared the material and performed some of the electrochemistry experiments. R.C.V. performed the *operando* X-ray diffraction experiment. K.E.W. prepared *ex-situ* synchrotron X-ray diffraction samples and analyzed the data. J.J.Z. performed the *operando* Raman experiment with input from K.A.S. S.W.B. performed the *operando* calorimetry measurements with input from L.P. J.L.K. carried out all modeling and DFT calculations with direction from A.V.

T1-B-6: INVESTIGATING THE CHARGE-STORAGE MECHANISM OF CA-IONS IN NASICON-STRUCTURED $NaV_2(PO_4)_3$

[Hub – JCESR] Lauren Blanc[1], Yunyeong Choi[2], Sanghyeon Kim[3], Prakash Parajuli[4], Haesun Park[3], Bob Jin Kwon[3], Brian J. Ingram[3], Peter Zapol[3], Robert F. Klie[4], John T. Vaughey[3], Liang Yin[3], Saul H. Lapidus[3], Linda F. Nazar[1], Gerbrand Ceder[2]

[1]University of Waterloo; [2]University of California, Berkeley; [3]Argonne National Laboratory; [4]University of Illinois, Chicago

Recent reports of reversible calcium plating and stripping have rekindled interest in the development of Ca-ion batteries (CIBs) as next-generation energy storage devices. This technology has the potential to overcome limitations of conventional Li-ion batteries, but CIBs are plagued by a paucity of suitable positive electrode (cathode) materials. To date, NASICON-structured $NaV_2(PO_4)_3$ has been demonstrated as a successful cathode candidate, exhibiting reversible (de)intercalation of 0.6 mol Ca^{2+} along with stable cycling performance. However, a complex multi-phase mixture forms on discharge so that the Ca-ion charge storage mechanism in the NASICON framework is poorly understood. In this work, the structure and/or Na^+/Ca^{2+} environment(s) in these materials were investigated through the chemical preparation of a wide variety of NASICON $Ca_xNa_yV_2(PO_4)_3$ phases which were characterized using synchrotron XRD, SEM-EDX, ^{23}Na NMR and TEM. Highly calciated $CaV_2(PO_4)_3$, $Ca_{1.5}V_2(PO_4)_3$, $CaNaV_2(PO_4)_3$ phases can be prepared at high temperature, but – unlike $Ca_{0.6}NaV_2(PO_4)_3$ – these structures are electrochemically inactive. To better understand the fundamental factors impacting successful Ca^{2+} electrochemistry in this system, DFT was employed to examine the $Ca_xNa_yV_2(PO_4)_3$ phase diagram and Ca^{2+} diffusion mechanism. Theoretical insights show that a cooperative push-pull process enables reversible electrochemistry in $Ca_xNa_yV_2(PO_4)_3$, as Na^+-assisted Ca^{2+} migration is critical for successful performance. This investigation of fundamental principles affecting reversible Ca^{2+} (de)intercalation in $Ca_xNa_yV_2(PO_4)_3$ allows for the development of design principles to enable the discovery of a variety of successful cathodes for CIBs.

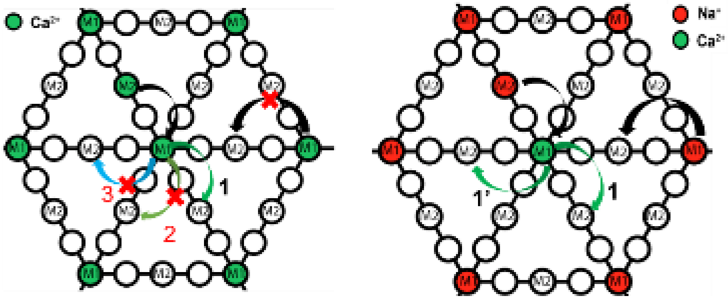


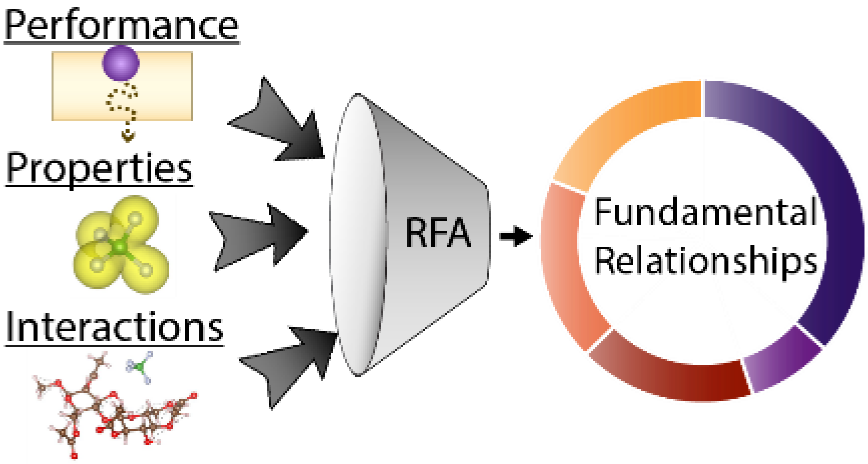
Figure 3: Schematic of diffusion pathways through NASICON framework comparing Ca^{2+}- vs. Na^+-assisted Ca^{2+} diffusion.

Contributions: LFN, JTV, and BJI, GC conceived the idea and supervised the electrochemical and computation experiments. LB, SK, and BJK synthesized performed electrochemical experiments and YC and HP performed computational studies in parallel. ZP supervised computational studies. PP carried out the STEM experiments under the supervision of RFK. LY performed high resolution diffraction under the supervision of SHL. All of the authors contributed to the research.

T1-C-7: MACHINE LEARNING ENABLES THE DISCOVERY OF KEY ION SELECTIVITY MECHANISMS IN POLYMERIC MEMBRANES WITH SUB-NANOMETER PORES

[EFRC – CENT] Cody L. Ritt[1], Mingjie Liu[2], Heather J. Kulik[2], Menachem Elimelech[1]
[1]Yale University; [2]Massachusetts Institute of Technology

Designing single-species selective membranes for high precision separations requires a fundamental understanding of the molecular interactions governing solute transport in sub-nm pores. Deconvoluting the role of intrinsic ion properties in selective transport has remained largely clouded due to the complex and inhomogeneous nature of confined polymer networks. To address this, we comprehensively assess molecular-level features that influence the separation of 18 anions of different size and shape by nanoporous cellulose acetate membranes. Our analysis identifies the limited ability of bulk solvation characteristics to explain ion transport, highlighted by the poor correlation between anion hydration energy and the measured permselectivity ($R^2 = 0.37$). Entropy is found to be critically important as it accounts for more than half of the total free energy barrier ($\Delta G^{\ddagger}$) for most anions. Entropy–enthalpy compensation (EEC) spans a range of 40 kJ mol^{-1}, leading to a $\Delta G^{\ddagger}$ variation of only ~8 kJ mol^{-1} across all anions. We leverage machine learning techniques, such as Recursive Feature Addition (RFA), to determine important descriptors for energetic barriers from a set of 126 features collected from cheminformatics, literature, and first-principles simulations. Notably, electrostatic features account for 75% of the overall features used to describe $\Delta G^{\ddagger}$, despite the relatively uncharged state of cellulose acetate. Our findings call for a paradigm shift in the approach to studying ion transport across membranes with sub-nm pores to enable the design of ion-selective membranes.

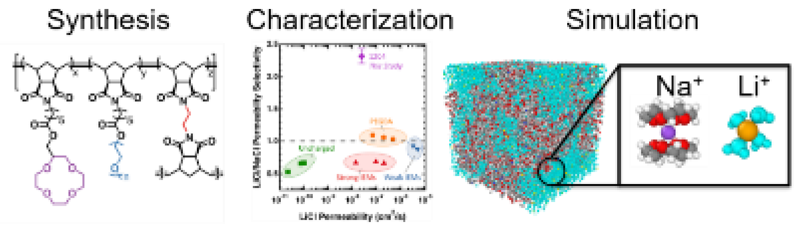


Contributions: C.L.R. and M.E. designed experimental research; C.L.R. performed experimental research; M.L. and H.J.K. designed and carried out computational and machine learning research.

T1-C-8: UNRAVELING THE INFLUENCE OF SPECIFIC MOLECULAR INTERACTIONS ON ION SELECTIVITY IN POLYMER MEMBRANES

[EFRC – M-WET] Everett S. Zochak[1], Samuel J. Warnock[2], Rahul Sujanani[1], Christopher M. Bates[2], Mahdi Abu-Omar[2], Lynn Katz[1], Benny D. Freeman[1]
[1]The University of Texas at Austin; [2]University of California, Santa Barbara

Effective treatment of non-traditional and highly contaminated water would markedly expand access to fit-for-purpose water and contribute to resource recovery. For example, recovery of lithium from produced water would provide new domestic sources of lithium for batteries. However, membranes with high selectivity for lithium salts (e.g., LiCl) over other salts (e.g., NaCl or $MgCl_2$) are required. While synthetic polymer membranes are attractive for such separations because they are highly energy efficient, readily scalable, and can be incorporated into compact, modular systems, they cannot discriminate between ions of the same valence (e.g., Li^+ vs. Na^+). In striking contrast to synthetic membranes, biological membranes show remarkable ion selectivity, with potassium ion channels achieving K^+/Na^+ selectivities $\sim 10^4$ due to precise pore sizes and ion-specific interactions within the channels. Inspired by these design principles, we incorporated ion-specific functional groups into polymers to produce a membrane having the highest LiCl/NaCl selectivity reported in polymer membranes.[1,2] However, the basic science relating polymer structure to ion-polymer interactions and ion transport remains poorly understood.



Here, we highlight results from M-WET's coordinated and collaborative polymer synthesis, membrane characterization, and molecular simulation studies to design and characterize ion specific polymer membranes. 12-crown-4, a ligand exhibiting highly specific complexation with alkali cations, was incorporated into a versatile and flexible polymer membrane platform to permit independent tuning of membrane hydration and cation selectivity. We prepared a material with a LiCl/NaCl permeability selectivity of ~2.3, which is a reversal from the traditional order of salt permeation in hydrated membranes and is the largest LiCl/NaCl selectivity reported to date in polymers.[1] Atomistic simulations revealed the origin of this remarkable selectivity to be strong complexation between sodium ions and 12-crown-4 moieties in aqueous environments, while lithium ions are relatively unaffected by the presence of 12-crown-4 groups in the membrane.[1,2] These interactions enhanced partitioning of NaCl into the membrane and significantly impeded NaCl diffusion, leading to LiCl/NaCl permeability selectivity.[1,2] These results support M-WET's broad goals of discovering basic science insights needed to design advanced membranes for resource extraction from non-traditional water sources. Moreover, the results may contribute to significant advances in understanding for applications beyond membrane separations (e.g., ion exchange, affinity chromatography, and biomimetic materials).

References: 1. S.J. Warnock et al., PNAS, 118 (37), e2022197118, (2021). 2. E.S. Zofchak et al., ACS Macro Letters, 10, 1167-1173, (2021).

Contributions: SJW synthesized polymers used for these studies. RS performed membrane characterization experiments. ESZ performed simulations and modeling. CMB, MO, LK, and BDF helped design and supervise these studies.

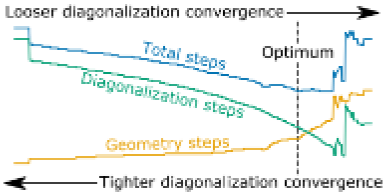
T1-D-9: APPLICATION OF A NOVEL SADDLE POINT OPTIMIZATION ALGORITHM ON SURFACE REACTIONS INVOLVING BIDENTATE ADSORBATES

[CCS – EEC] Eric D. Hermes[1], Katrín Blöndal[2], Bjarne Kreitz[3], Khachik Sargsyan[1], Habib N. Najm[1], Judit Zádor[1], C. Franklin Goldsmith[2], Richard H. West[4]

[1]Sandia National Laboratories; [2]Brown University; [3]Technical University of Clausthal; [4]Northeastern University

The development of reaction networks for heterogeneous catalytic chemical transformations is a crucial step in the computational modeling of heterogeneous catalysis. Traditionally, these reaction networks have been assembled manually through chemical intuition, a tedious and error-prone process. Recently, tools that automate the construction of reaction networks such as RMG (Reaction Mechanism Generator)[1] have been developed. RMG uses a database of known reaction families and tabulated activation energies to predict new reactions and estimate their rates. To extend the capabilities of RMG, it is necessary to provide it with additional energetic information for previously unrepresented reaction families.

There is currently a lack of data on surface reactions involving bidentate adsorbates in the literature; therefore, we computationally produce kinetic data for such reactions on a Pt(111) surface. This will provide important information for improving the predictive capabilities of RMG for heterogeneous catalysis. A set of 19 reactions, involving 7 H/C/O containing bidentate species are calculated. Transferability to other metal surfaces is explored by looking at linear scaling relationships of the bidentate adsorbate binding energies across nine metals including Pt. Following optimization of the initial and final state geometries, constraint force interpolation (CFI) is used to produce approximate saddle point geometries which are refined with Sella.[2] The resulting reaction and activation energies will be used in RMG to improve its ability to assess the importance of pathways including bidentate adsorbates for many relevant heterogeneous processes.



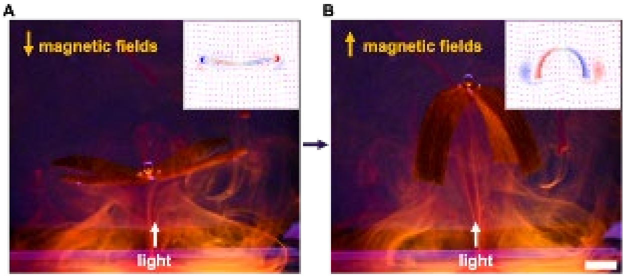
Refinement of saddle point geometries is the most computationally expensive step in the calculation of reaction rate constants under transition state theory. Commonly used saddle point optimization methods rely on iterative diagonalization of the Hessian matrix to identify the direction of lowest curvature. However, these methods typically fail to fully capitalize on the curvature information obtained during the diagonalization procedure, reducing overall performance of the optimization algorithm. We have developed a new optimization algorithm that fully incorporates into an approximate Hessian all curvature information obtained during the iterative diagonalization procedure. This algorithm has been implemented in Sella, a new open-source software package for locating saddle point geometries on the potential energy surfaces of molecules, solids, and heterogeneous systems.[2]

Contributions: E. D. H. developed Sella and the saddle point optimization algorithm implemented therein. K. B. set up and performed all electronic structure theory calculations.

[1] Liu, M., et al. Reaction mechanism generator v3.0: Advances in automatic mechanism generation. Journal of Chemical Information and Modeling, 61(6):2686–2696, 5 2021. doi:10.1021/acs.jcim.0c01480.
[2] Hermes, Eric D., et al. Accelerated Saddle Point Refinement through Full Exploitation of Partial Hessian Diagonalization. Journal of Chemical Theory and Computation, 15(11):6536–6549, 11 2019. ISSN 1549-9618. doi:10.1021/acs.jctc.9b00869.

T1-D-10: SWIMMING ROBOTIC HYDROGELS POWERED BY LIGHT AND MAGNETIC FIELDS

[EFRC – CBES] S. Doruk Cezan, Aaveg Aggarwal, Monica Olvera de la Cruz, Samuel I. Stupp
Northwestern University



Swimming motion of hybrid hydrogel robots. The motion of the swimming hydrogel consists of cycles of expansion (A) and contraction (B) of legs achieved by applying oscillating magnetic fields (160 Oe at 0.5 Hz). White arrows represent the direction of irradiation, and yellow arrows indicate the direction of applied magnetic fields. Rhodamine B dye was added to the water tank to visualize the wake structures. The inset shows the finite element model of the system. The surface color indicates the vorticity, and the arrow surface represents the velocity field. The scale bar is 5 mm.

The design of robotic soft matter is experiencing a paradigm shift with the incorporation of energy conversion strategies inspired by living organisms, which use external sources of energy to generate locomotion and shape transformations. Encoding soft matter with such life-like functionalities could enable new types of soft robotics or control over chemical reactions. Functionalized hydrogels are excellent candidates for such materials since they can operate in water and are highly responsive to their environment, but their response times can be slow. In this work, we report the design of photo-responsive hybrid hydrogels that integrate supramolecular nanofibers and ferromagnetic nanowires that couple to magnetic fields. Compared to our previous CBES-supported work,* these hydrogels have much faster response times enabled by the supramolecular skeleton and create materials capable of swimming underwater. Interestingly, we also discovered that these robotic hydrogels spontaneously swim towards an external light source, a phenomenon reminiscent of the known natural phototactic behaviors. To analyze the complex behavior of these robots, we developed a continuum model that incorporates the coupling between the physics of polymer hydrogels, photoactive chemical reactions, and magnetism. The model is solved using finite element methods, and the theoretical results agree with experimental data. We expect this model will facilitate the design of future robotic soft matter with even more complex functionalities.

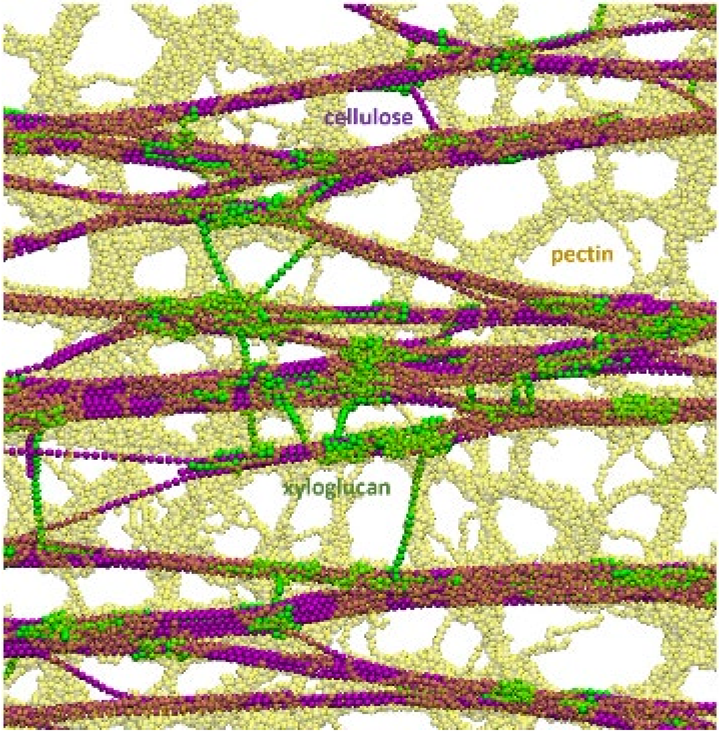
References: *Li, C., *et al*. Supramolecular-Covalent Hybrid Polymers for Light-Activated Mechanical Actuation *Nature Materials* **19,** 900 (2020); Li, C., *et al*. “Fast and programmable locomotion of hydrogel-metal hybrids under light and magnetic fields”. *Science Robotics* **5**, eabb9822 (2020); Li, C.. *et al*. Synergistic Photoactuation of Bilayered Spiropyran Hydrogels for Predictable Origami-Like Shape Change *Matter* **4,** 1377 (2021).

Contributions: SDC designed and carried out the experimental work; AA designed and performed the simulations; SIS and MOdlC directed the research.

T1-D-11: MOLECULAR BASIS OF CELL WALL STRETCHING BEHAVIOR IN PLANTS: COMPUTATIONAL AND EXPERIMENTAL INSIGHTS

[EFRC – CLSF] Yao Zhang[1], Jingyi Yu[1], Joshua T. Del Mundo[1], Fabien Deligey[2], Enrique Gomez[1], Esther Gomez[1], Tuo Wang[2], Sulin Zhang[1], Daniel J. Cosgrove[1]
[1]Penn State University; [2]Louisiana State University

The plant cell wall is a complex polylamellate structure constructed of layers of aligned crystalline cellulose nanofibrils separated by highly hydrated acidic and neutral polysaccharides. It has complex physical and mechanical properties whose structural basis is uncertain. To gain new insights into its molecular structure, we developed a coarse-grained molecular dynamics (CGMD) model of the wall[1] based on new analyses of wall mechanics and ssNMR-based composition[2]. Bead-and-spring models of cellulose (purple), pectin (yellow) and xyloglucan (green) were parameterized to correspond to their physical characteristics such as binding properties, modulus and flexibility. When allowed to self assemble, chains formed networks with morphologies resembling actual cell walls (see image).



We then stretched the CGMD wall to measure its stress-strain behavior and compared this with parallel experimental measurements. The model captured the experimental behavior very well, leading us to conclude that (a) simple noncovalent binding interactions are able to generate bundled cellulose networks observed in cell walls and (b) the complex mechanical behaviors emerge from the collective physical interactions incorporated in the model. These include stress-dependent elasticity, stiffening, and plasticity beyond a yield threshold. In the model, plasticity originates from fibril-fibril sliding in aligned cellulose networks. In additional experimental work, the wall was stretched by up to 50% and wall structure was analyzed by X-ray scattering. Small angle and wide angle X-ray scattering results corroborate the model by providing evidence of microfibril rearrangement under strain. Extension of the CGMD model to the growth of plant cell walls under chemomechanical conditions is underway. This physical model provides quantitative insights into fundamental questions of plant mechanobiology and reveals design principles of biomaterials that combine stiffness with yielding and extensibility.

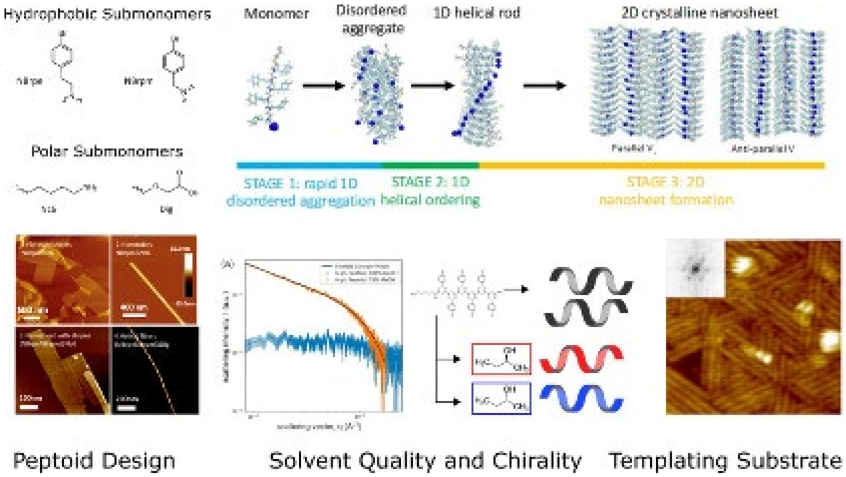
[1] Zhang, Y. *et al.* Molecular insights into the complex mechanics of plant epidermal cell walls. *Science* **372**, 706-711 (2021).
[2] Wilson, L. A., Deligey, F., Wang, T. & Cosgrove, D. J. Saccharide analysis of onion outer epidermal walls. *Biotechnol Biofuels* **14**, 66 (2021).

Contributions: YZ: CG model development; JY: material preparation and mechanics, refinement of the model and simulations; JDM X-ray scattering analysis; FD: ssNMR analysis

T1-D-12: STRUCTURAL TRANSITION OF PEPTOID SELF-ASSEMBLY

[EFRC – CSSAS] Mingfei Zhao[1], Kacper Lachowski[2], Renyu Zheng[2], Shuai Zhang[2,3], Sarah Alamdari[2], Chris Mundy[2,3], Chun-Long Chen[2,3], Jim DeYoreo[2,3], Lilo Pozzo[2], Jim Pfaendtner[2,3], Andrew Ferguson[1]
[1]University of Chicago; [2]University of Washington; [3]Pacific Northwest National Laboratory

Polypeptoids, or poly-N-substituted glycines, are a class of synthetic peptidomimetic polymers that are regioisomers of natural polypeptides with side chains attached to amide nitrogens instead of α-carbons. Their physicochemical properties are predominantly defined by side chain chemistry, which can be easily modulated. Together with inherent biocompatibility, thermal processability, and capacity of assembling into diverse supramolecular morphologies such as spheres, helices, tubes, ribbons, sheets, etc., these properties have made peptoids extremely attractive biomaterials in numerous biochemical, biomedical, and bioengineering fields. However, the mechanisms of peptoid hierarchical self-assembly remain largely unclear. This work comprises multi-thrust efforts within CSSAS blending our center's expertise in theory, computation, and in-situ characterization. We integrate computation and experiments to develop a fundamental understanding of the emergence of order and hierarchy in peptoid self-assembly. By examining the sequence-dependent mechanical properties of peptoid sheets, we resolve sequence-property relationships. In addition, we evaluate the influence of solvents upon supramolecular chirality of peptoid structures. We also extend our peptoid library of self-assembly in solution and on templating surfaces with peptoid blocks having diverse hydrophobicity. Our research opens a new avenue to expand the design space of peptoid side-chain chemistry blending all-atom and coarse-grained molecular simulation and in-situ characterizations.



References:
Zhao, M., Lachowski, K., Alamdari, S., Sampath, J., Mu, P., Pozzo, L.D., Chen, C.L., Pfaendtner, J., Mundy, C.J. and Ferguson, A.L.. (2021). Submitted.
Zhao, M., Sampath, J., Alamdari, S., Shen, G., Chen, C.L., Mundy, C.J., Pfaendtner, J. and Ferguson, A.L.. (2020). J. *Phys. Chem. B*, 124(36), 7745-7764.
Li, Z., Cai, B., Yang, W., & Chen, C. L. (2021). *Chemical Reviews*. Accepted.

Contribution: M.Z., K.L., R.Z., S.Z., C.C., L.P., and A.L.F. conceived the research. K.L., R.Z., and S.Z. carried out the characterizations. M.Z. and A.L.F. carried out the simulations. M.Z., K.L., R.Z., S.Z., S.A., C.M., J.D., J.P., C.C., L.P., and A.L.F. contributed to the data interpretation and result analysis.

T1-E-13: CORROSION AND IRRADIATION OF CHROMIUM-ALLOYS IN MOLTEN SALT REACTORS

[EFRC – FUTURE] Nathan Bieberdorf[1], Sean H. Mills[1], Elena Romanovskaia[2], Ho Lun Chan[2], Ryan Hayes[1], Mark Asta[1], Laurent Capolungo[2], Andrew M. Minor[1], John R. Scully[2]
[1]University of California, Berkeley; [2]Los Alamos National Laboratory; [3]University of Virginia

The FUTURE EFRC aims to develop a multiscale understanding of how structural materials evolve under simultaneous corrosion and irradiation seen in nuclear reactor environments. In molten-salt reactor environments, previous experimental work has shown that Cr dealloying is strongly coupled to the microstructure evolution of these alloys [1,2]. However, the trends associated with varying salt chemistry, temperature, and irradiation dose are not intuitive, and a mechanistic understanding of the associated thermodynamics and kinetics remains unknown.

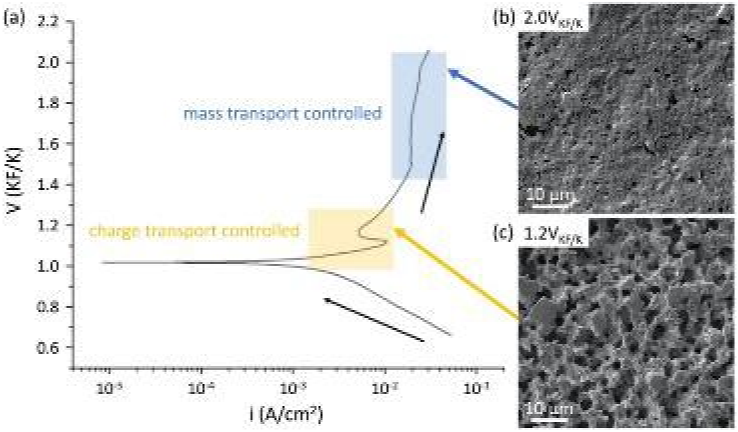


Figure 4. Electrochemical corrosion behavior of Cr in FLiNaK at 600°C: a) Potentiodynamic polarization plot; SEM of Cr surface hold at b) $2.0V_{KF/K}$ and c) $1.2V_{KF/K}$

The present work aims to understand, through experiments and modeling, what the rate limiting steps are in the dissolution of Cr in LiF-NaF-KF eutectic salts (FLiNaK), and how they are correlated to microstructure evolution in the metal. Electrochemical experiments conducted on pure Cr samples in FLiNaK at 600 C have concluded that Cr dissolution can be both charge-transport-controlled and mass-transport-controlled, corresponding to the formation of Cr^{2+} and Cr^{3+} charge states, respectively (Fig. 1). The thermodynamic stability of these Cr valence states in FLiNaK has been verified using a newly developed molten fluoride Pourbaix diagram. When the corrosion of pure Cr in FLiNaK is mass-transport controlled, the metal/salt interface remains relatively planar (Fig. 1b), while in the charge-transport-controlled regime, a faceted morphology develops (Fig. 1c), illustrating the importance of crystallography on this dissolution process.

Phase field modeling within FUTURE has shown that these microstructural coupling trends vary for selective dissolution from a binary (e.g. Cr dissolution from NiCr). In the mass-transport-limited regime (where the corrosion front is known to be highly topological [2]), our results show that grain boundary migration is a key dealloying mechanism, and that in the interface-reaction-rate-limited regime, the corrosion front will remain relatively planar. Additionally, when mass-transport in the bulk metal is high, our phase field modeling shows how the metal/salt interface becomes passivated, offering an explanation for experiments that show irradiation-decelerated corrosion [1]. To build on these findings, in situ NiCr sample mass loss experiments and ex situ SEM, 4D-STEM, and EDX/EELS characterization are being used to reveal how corrosion morphology is controlled by point defect migration in the metal and by oxidant and Cr diffusion in FLiNaK. By combining experiments and modeling, this work aims to show how the corrosion front can be decelerated through the manipulation of the metal/salt interface reaction, and also highlight key knowledge-gaps for future studies to target.

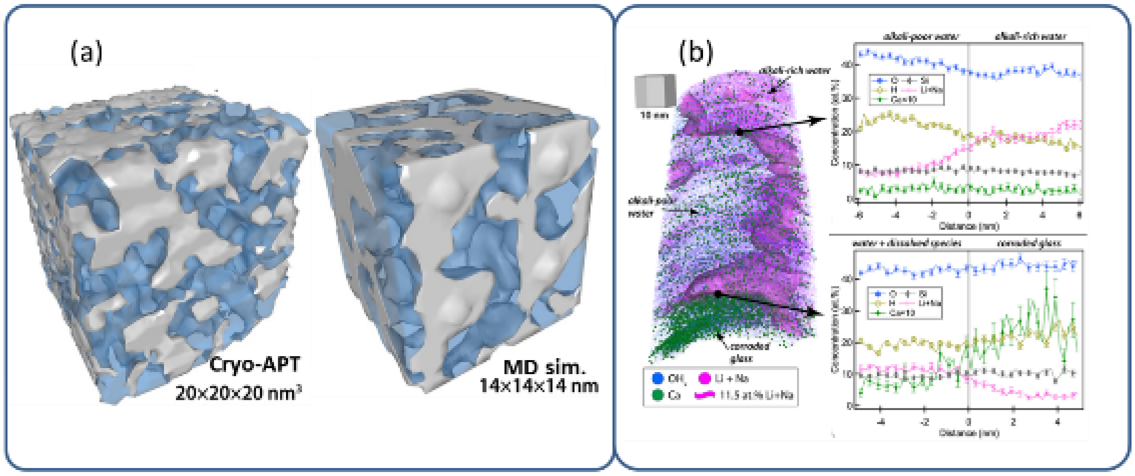
References: [1] Zhou, et al. Nature Comms 11 3430 (2020). [2] Liu et al. Nature Comms 12 3441 (2021).

Contributions: E.R. and H.L.C. conducted the electrochemical experiments on Cr, N.B. performed the phase field modeling, S.M. and R.H are performing dealloying experiments on NiCr.

T1-E-14: MULTISCALE INVESTIGATION OF STRUCTURE AND STABILITY OF NANOPOROUS GEL LAYER ON NUCLEAR WASTE GLASS

[EFRC – WastePD] Thiruvillamalai S. Mahadevan[1], Xiaonan Lu[2], Dien Ngo[3], Huseyin Kaya[3], Daniel K. Schreiber[2], Danny E. Perea[2], Jincheng Du[1], Joseph V. Ryan[2], John Vienna[2], Stephane Gin[4], Seong H. Kim[3]
[1]University of North Texas; [2]Pacific Northwest National Laboratory; [3]Pennsylvania State University; [4]CEA France

Aqueous corrosion of borosilicate glass, used for immobilization of nuclear wastes, leads to the formation of a nano-structured, gel-like alteration layer at the interface. The dynamics of formation and destruction of this alteration layer determine the stability of the glass in corrosive conditions. Understanding chemical reactions and transport phenomena in this layer is important to design durable glass for processing and disposal of nuclear waste. The non-equilibrium multiphase environments dictate that a combination of atomistic simulations and nano-structure characterization is required to achieve a detailed understanding of this alteration layer. The structure of a representative alteration layer in a borosilicate glass was imaged using cryo-atom probe tomography (cryo-APT) and the pore size distribution was characterized using spectroscopic ellipsometry (SE). Reactive molecular dynamics (MD) simulations were used *in-silico* to create equivalent silicate structures and elucidate transport of water in these constrained geometries. The vibrational spectra of water inside the pores were correlated to the distribution of the hydrogen bond network structure using sum frequency generation (SFG) spectroscopy. The evolution of interfacial stress in the alteration layer was investigated with SE and IR spectroscopy. Reactive transport of water molecules in the alteration layer was modeled after accounting for constraints affecting diffusion in open and closed pores. The results from multi-scale computational and experimental studies were combined to construct comprehensive understanding of physical properties of nano-porous gel-like alteration layer and to predict their implications on the passivity and stability of the alteration layer.



(a) Nanostructure characterization by cryo-APT and MD simulation show the qualitative equivalence of the simulated structure. (b) Chemical characterization by cryo-APT shows alkali dissolution

Contributions: T.M. wrote the abstract and poster with guidance from S.K. T.M., X.L and J.D performed the MD simulations, D.N, H.K and S.K did SFG, SE, and IR measurements, D.S. and D.P. did the cryo-APT imaging and S.G performed the pore size measurements.

T1-F-15: MAGNETIC AXION INSULATOR AND EXOTIC SURFACE STATES IN EuIn$_2$As$_2$

[EFRC – CATS] S. X. M. Riberolles[1], T. V. Trevisan[1,2], B. Kuthanazhi[1,2], T. W. Heitmann[3], F. Ye[4], D. C. Johnston[1,2], S. L. Bud'ko[1,2], D. H. Ryan[5], P. C. Canfield[1,2], A. Kreyssig[1,2], A. Vishwanath[6], R. J. McQueeney[1,2], L. -L. Wang[1,2], P. P. Orth[1,2], B. G. Ueland[1]

[1]The Ames Laboratory; [2]Iowa State University; [3]University of Missouri; [4]Oak Ridge National Laboratory; [5]McGill University; [6]Harvard University

Magnetic topological materials are a central topic of research in condensed-matter physics, where the emergence of magnetic-crystalline symmetries promotes exotic properties associated with the band topology. A primary goal of the CATS program is to discover and investigate magnetic topological materials, and we recently identified EuIn$_2$As$_2$ as a promising platform to explore the interplay between magnetism and topology [S. X. M. Riberolles, *et al.* Nat. Comm. **12**, 999 (2021)]. A combination of neutron diffraction experiments, density-functional theory (DFT) calculations, and detailed magnetic-symmetry analysis unveil an intricate helical magnetic order in EuIn$_2$As$_2$ which promotes an exotic magnetic axion-insulator state. Neutron diffraction data find that EuIn$_2$As$_2$ adopts both 60°-helix and broken-helix orders, with a broken-helix ground state [Fig. (b)]. Continuity of the magnetic structure [Fig. (a)] and the band gap between the A-type antiferromagnetic axion insulator and 60°-helix magnetic orders guarantees the existence of the axion insulator state in the helical phases. In the helical phases, the axion state is protected by the combination of time-reversal symmetry and a two-fold rotation, i.e., 2' in the families of topological crystalline insulators. Such a state has unique surface features: some of the surfaces host gapped states with half-quantized anomalous Hall conductivity. Surfaces normal to the 2' axis, however, exhibit exotic gapless Dirac states that are unpinned from time-reversal-invariant momenta [Fig. (c)] and can be moved around in the surface Brillouin zone via an external magnetic field. EuIn$_2$As$_2$ promises to satisfy a high-level CATS goal to manipulate magnetic topological materials, as we predict that the surface states can be switched by applying a moderate magnetic field.

Contributions: S.X.M.R. conducted neutron scattering experiments, refined the data and determined the magnetic structure. T.V.T. performed symmetry analyses concerning the topologically protected properties. B.K. synthesized crystals and performed magnetization and resistance measurements.

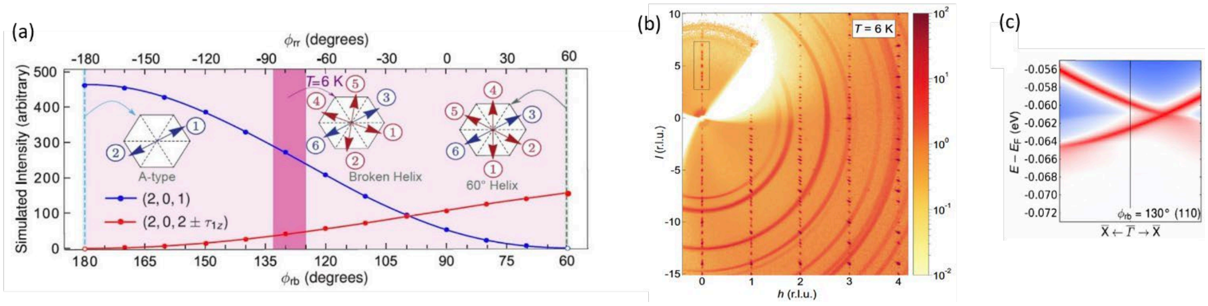
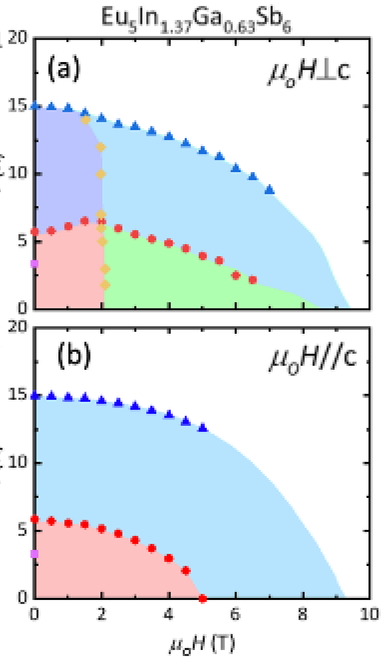


Figure. (a) Simulated neutron diffraction intensities for different turning angles continuously interpolates between different magnetic orders. (b) Neutron diffraction data in the broken-helix phase as measured on Corelli at the Spallation Neutron Source. (c) DFT calculation shows the Dirac cone in the (110) surface is shifted away from the time-reversal invariant point $\bar{\Gamma}$.

T1-F-16: ENGINEERING MAGNETIC TOPOLOGICAL INSULATORS IN EU-BASED ZINTL COMPOUNDS

[EFRC – IQM] Nicodemos Varnava[1], Tanya Berry[2], Vincent C. Morano[2], Rishi Bhandia[2], Anaëlle Legros[2], Jiahao Liang[2], N. Peter Armitage[2], Collin L. Broholm[2], Tyrel M. McQueen[2], David Vanderbilt[1]
[1]Rutgers University; [2]Johns Hopkins University

Fig. 1



In Zintl materials, the rocksalt-like charge separation between the cationic and anionic frameworks offers vital ingredients to explore magnetic topological insulators. When the cations are magnetic and the anions are non-magnetic, it often causes the materials to behave as two independent subunits, with separate magnetic and electronic behaviors (Fig. 2). In addition, the clear separation between the electronic and magnetic energy scales allows us to tune the electronic structure of the polyanionic network and then consider the effect of magnetism. This band engineering approach is achieved by employing doping, element substitution, pressure, and epitaxial strain. Specifically, starting from the trivial antiferromagnetic insulator $Eu_5In_2Sb_6$, we utilize density functional theory (DFT) to engineer band inversions by applying chemical pressure via isoelectronic substitution. We find three good antiferromagnetic topological insulator (AFM TI) candidates: $Eu_5Ga_2Sb_6$, $Eu_5Tl_2Sb_6$, and $Eu_5In_2Bi_6$. Furthermore, we show that pressure and epitaxial strain can be used to control the bulk energy gaps. On the experimental side, $Eu_5In_2Sb_6$ crystals are synthesized and then substituted with Ga (Fig 1). Transport and optical measurements of these crystals confirmed the insulating nature of the Ga-substituted samples. In addition, neutron scattering, magnetization measurements, and DFT+U calculations are employed to identify the complex magnetic structure in $Eu_5In_2Sb_6$ (Fig. 3) and $Eu_5In_{2-x}Ga_xSb_6$, which determines whether a given surface will be gapless, hosting Dirac cones, or gapped, possessing half-integer anomalous Hall conductivity.

Fig. 2

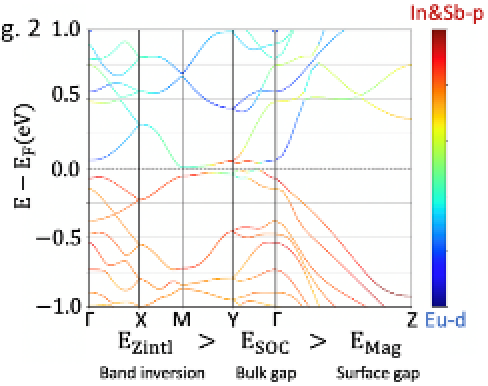
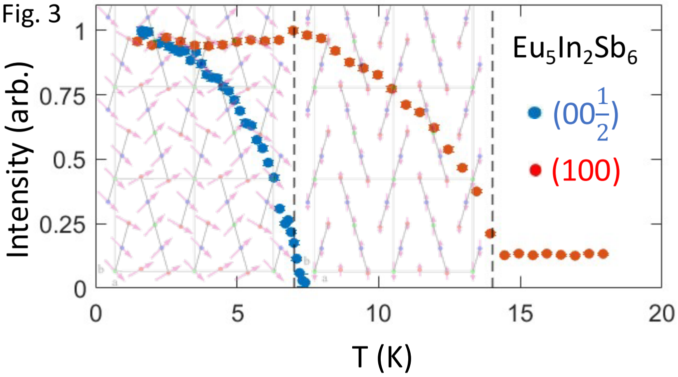


Fig. 3



Contributions: N.V., T.B., D.V., N.P.A., C.L.B., and T.M.M. conceived the project. N.V. and D.V. performed all theoretical calculation. T.B. and T.M.M. synthesized single crystals. T.B. and T.M.M. solved single crystal structures. T.B. and T.M.M. performed magnetization measurements. V.C.M. and C.L.B. performed and analyzed neutron diffraction measurements. T.B., A.L., R.B., and J.L., performed transport measurements. A.L. and R.B. performed optical measurements on the sample.

T1-F-17: Imaging Gate-Tunable Tomonaga-Luttinger Liquids in 1H-MoSe$_2$ Mirror Twin Boundaries

[EFRC – NPQC] Tiancong Zhu[1,2,†], Wei Ruan[1,2,3,†], Yan-Qi Wang[1,2,†], Hsin-Zon Tsai[2], Shuopei Wang[4,5], Canxun Zhang[2,6], Tianye Wang[1,2], Franklin Liou[2,6], Kenji Watanabe[7], Takashi Taniguchi[7], Jeffrey B. Neaton[1,2], Alex Weber-Bargioni[1] , Alex Zettl[2], Ziqiang Qiu[1,2], Guangyu Zhang[4,5,8], Feng Wang[1,2,6], Joel E. Moore[1,2,6], Michael F. Crommie[1,2,6]

[1]Lawrence Berkeley National Laboratory; [2]University of California, Berkeley; [3]Fudan University; [4]Beijing National Laboratory for Condensed Matter Physics; [5]Songshan Lake Materials Laboratory; [6]Kavli Energy Nano Sciences Institute; [7]National Institute for Materials Science; [8]University of Chinese Academy of Sciences; [†]These authors contributed equally to this work.

One-dimensional electron systems (1DESs) host unique quantum coherent state that are fundamentally different from those in higher-dimensions. For example, electron-electron interactions in 1DESs have been predicted to induce Tomonaga-Luttinger liquid (TLL) behavior. Naturally-occurring grain boundaries in single-layer semiconducting transition metal dichalcogenides provide 1D conducting channels that have been proposed to host TLL, but charge density wave physics has also been suggested to explain their behavior. Clear identification of the electronic ground state of this system has been hampered by an inability to electrostatically gate such boundaries and thereby tune their charge carrier concentration. Here we present a scanning tunneling microscopy/spectroscopy (STM/STS) study of gate-tunable mirror twin boundaries (MTBs) in single-layer 1H-MoSe$_2$ devices. Gating here enables STM spectroscopy to be performed for different MTB electron densities, thus allowing precise characterization of electron-electron interaction effects. Visualization of MTB electronic structure under these conditions allows unambiguous identification of collective density wave excitations having two distinct velocities. Theoretical analysis based on finite-length TLL model quantitatively explained the experimental observations originated from spin-charge separation. Our collaborative experimental and theoretical efforts demonstrated a novel pathway to measure, manipulate, and understand correlated quantum coherence at engineered interfaces of 2D materials.

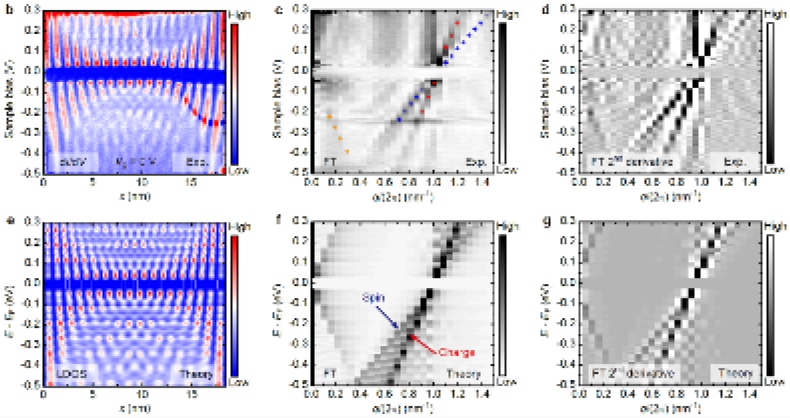


Figure 1. Experimental data (upper panel) and theoretical calculation (lower panel) of the charge density modulation and spin-charge separation in a MoSe$_2$ mirror twin boundary.

Contributions: T.Z., W.R., F.W., and M.F.C. initiated and conceived this project. W.R., T.Z. carried out STM/STS measurements under the supervision of M.F.C. Y.-Q.W. and W.R. performed theoretical analysis and numerical calculation under the supervision of J.E.M. T.Z performed MBE growth. All authors contributed to the scientific discussion.

T1-F-18: KRAMERS-WEYL FERMIONS IN THE CHIRAL CHARGE DENSITY WAVE MATERIAL (TaSe$_4$)$_2$I

[EFRC – QSQM] Soyeun Kim[1], Robert C. McKay[1], Nina Bielinski[1], Chengxi Zhao[1], Meng-Kai Lin[1], Joseph A. Hlevyack[1], Xuefei Guo[1], Sung-Kwan Mo[2], Peter Abbamonte[1], Tai C. Chiang[1], Andre Schleife[1], Daniel P. Shoemaker[1], Barry Bradlyn[1], Fahad Mahmood[1]

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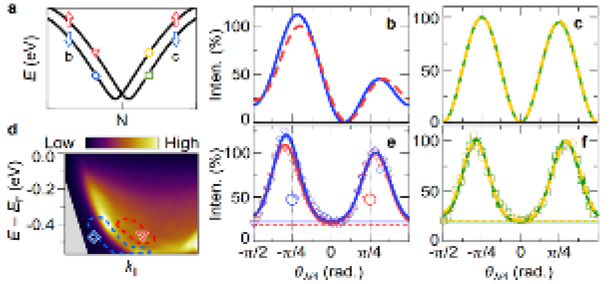
One of the core missions of the QSQM is to use advanced quantum sending techniques to understand the electrodynamic signatures of topological crystalline insulators (TCI). A recent TCI candidate material is the putative axion insulator, (TaSe$_4$)$_2$I. In preparation for the commissioning of our quantum sensing instruments, we are performing spectroscopic studies on this material. In this work we use a suite of experimental and theoretical tools to identify new topological fermions in (TaSe$_4$)$_2$I.



(a) Tight-binding model near the N point along the N'-N-N' path. Arrows indicate up/down (pseudo-)spin. (b,c) Theoretical photoemission intensities vs. light helicity for bands to the left (b) and right (c) of the N point. (d) ARPES spectra near the N-point along the chain direction. (e,f) Integrated photoemission intensity for bands to the left (e) and right (f) of the N point

Electrons in crystals can be made to behave like exotic particles called Weyl fermions. Weyl fermions have topological charge, meaning each is either a sink or a source of the pseudo-magnetic field known as Berry curvature. A way to guarantee that a crystal will contain Weyl fermions is through combining chiral crystal symmetry and time-reversal symmetry, leading to the existence of Kramers-Weyl (KW) fermions. However, direct observations of KW fermions have remained elusive. The material (TaSe$_4$)$_2$I has the benefit that at sufficiently low temperatures, the interaction between electrons and phonons becomes strong, leading to a charge-density wave (CDW) order. Thus, (TaSe$_4$)$_2$I is a promising candidate to explore KW fermions with interactions. Our collaborative project identifies properties of a KW fermion by analyzing experimental data from helicity-dependent laser-based angle resolved photoemission spectroscopy (ARPES) and comparing it to theoretical calculations.

First, the Shoemaker group synthesized a sample of (TaSe$_4$)$_2$I using chemical vapor transport. Next, the Chiang group preformed synchrotron ARPES experiments to confirm the previously reported linear energy dispersion. The Abbamonte group performed x-ray diffraction to find the CDW transition temperature. The Schleife group provided density functional theory (DFT) calculations, accompanied by the Bradlyn group's tight-binding calculations, to compare to the Mahmood group's laser ARPES data.

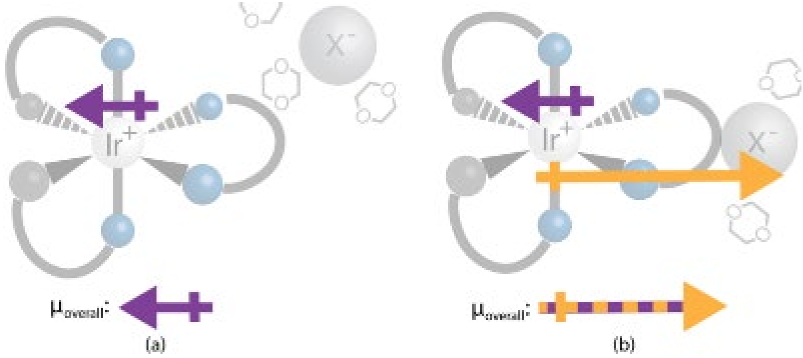
QSQM postdoc Dr. Soyeun Kim then preformed the helicity-dependent laser-based ARPES experiment to observe properties of a KW fermion. Since this experiment is (pseudo)spin-sensitive, it provides signatures of a KW fermion which acquires a spin texture from spin-orbit coupling. QSQM graduate student Robert McKay modeled this photoemission process starting from Fermi's Golden Rule and a tight-binding model. Both the experimental data and theoretical prediction are shown in Fig. 1. Data is shown for the left and right sides of a KW node, where both theory and experiment phenomenologically agree. On one side, the helicities show a difference in intensities across the two bands, while the other side does not exhibit this. This distinctive asymmetry confirms the presence of KW fermions in (TaSe$_4$)$_2$I. Interestingly, we also reveal that this distinctive asymmetry decreases with the onset of CDW order indicating that KW fermions of opposite Weyl charge likely mix due to CDW correlations. Our work has been submitted and is currently in review (Kim et. al. arXiv:2108.10874).

Contributions: Soyeun Kim performed the laser-ARPES experiments, the corresponding data analysis and lead the collaboration and synergy between all the groups involved. Robert McKay developed the theoretical methods, the tight-binding model, and the theoretical analysis. Soyeun Kim and Robert McKay wrote the submitted manuscript with input from all the authors.

T1-G-19: MICROWAVE SPECTROSCOPY REVEALS TIGHT ION PAIRING IN IRIDIUM PHOTOREDOX CATALYSIS

[EFRC – BioLEC] Justin D. Earley[1,2], Nick Shin[3], Anna Zieleniewska[1], Hunter H. Ripberger[3], Megan S. Lazorski[3,4], Hannah Sayre[3], Robert R. Knowles[3], James K. McCusker[5], Obadiah G. Reid[1,2], Garry Rumbles[1,2]
[1]National Renewable Energy Lab; [2]University of Colorado Boulder; [3]Princeton University; [4]Metropolitan State University of Denver; [5]Michigan State University

At BioLEC, we use advanced spectroscopic techniques and expertise to elucidate all aspects of the reaction process and have recently developed time-resolved dielectric loss spectroscopy to understand the spatial separation of charges in a molecular system. This spectroscopic technique adds to the tools available to BioLEC for understanding the mechanistic processes that underlie photoredox catalysis and enables the development of superior photoredox catalysts. In this study, we report evidence of excited-state ion pair reorganization in a cationic iridium (III) photoredox catalyst in 1,4-dioxane and its effect on the electron transfer kinetics. Microwave-frequency dielectric-loss measurements combined with accurate simulation of dipolar relaxation time allow us to assign both ground and excited-state molecular dipole moments in solution. These measurements show significant changes in ground-state dipole moment between $[Ir[dF(CF_3)ppy]_2(dtbpy)]PF_6$ (10.74 Debye) and $[Ir[dF(CF_3)ppy]_2(dtbpy)]BAr^F_4$ (4.86 Debye). After photoexcitation, relaxation to the lowest lying excited-state leads to a negative change in the dipole moment for $[Ir[dF(CF_3)ppy]_2(dtbpy)]PF_6$ and a positive change in dipole moment for $[Ir[dF(CF_3)ppy]_2(dtbpy)]BAr^F_4$. These observations are consistent with a sub-nanosecond reorganization with the PF_6^- counter-ion, which cancels the intramolecular dipole moment of the lowest lying excited-state, a process which is absent for the BAr^F_4 counter-ion. A comparison of these observations suggest contact-ion pair formation between the cationic metal complex and the PF_6^- anion and not with the $BAr^F_4{}^-$ anion. The dynamic ion pair reorganization we observe with the PF_6^- counter-ion modifies the kinetic behavior for electron transfer in both oxidative and reductive quenching studies as observed by Stern-Volmer steady-state quenching measurements. Understanding the impact of ion pairing in photoredox catalysis could provide useful tunability when tailoring the reactivity of both new and extant photocatalysts.



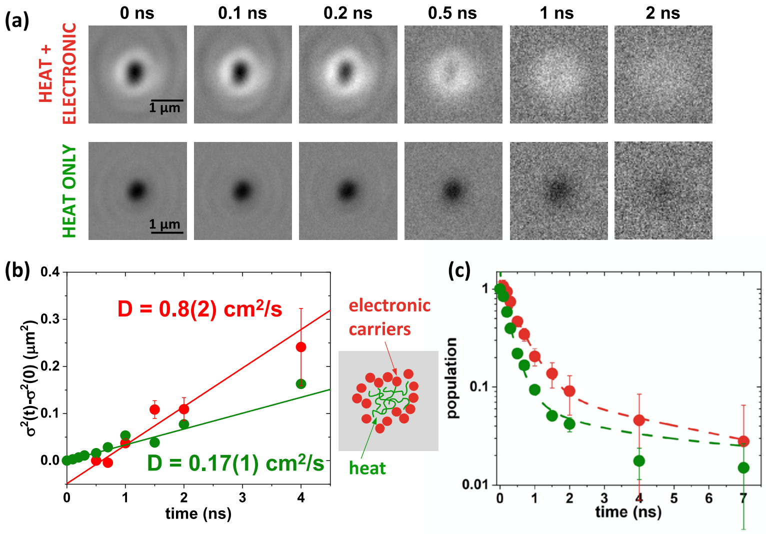
Contributions: J.D.E. designed and built the microwave experiment and wrote the dipolar relaxation simulation. N.S. performed Stern-Volmer quenching studies and quantum yield studies. A.Z. did the sample preparation, microwave measurements, and data analysis. H.H.R. synthesized the IrBArF complex and carried out theoretical calculations. H.S. conducted ultrafast spectroscopy on the Ir complex.

T1-G-20: Mapping Nanoscale Energy Transport in Low Dimensional Materials with Stroboscopic Scattering Microscopy

[EFRC – PTL] Hannah L. Weaver[1], Cora M. Went[2], Joeson Wong[2], Dipti Jasrasaria[1], Aidan L. O'Beirne[3], Tony F. Heinz[3], Eran Rabani[1], Harry A. Atwater[2], Naomi S. Ginsberg[1]
[1]University of California, Berkeley; [2]California Institute of Technology; [5]Stanford University

Understanding how energy interconverts and transports at the nanoscale is vital for pushing the operating limits of active materials in photonic thermodynamic cycles. This collaborative project studies energy transport and transduction in low-dimensional thermoelectric materials via stroboSCAT, a novel time-resolved scattering microscopy that enables direct tracking of different carrier types (e.g. free charges, excitons, heat) in a variety of materials over four orders of magnitude in time. With the synthesis expertise of the Atwater and Heinz groups, the characterization expertise of the Ginsberg group and the theoretical expertise of the Rabani group, we directly measure and interpret how electronic and thermal energy propagate and interplay in few-layer MoS_2. To be able to observe this microscopic heat transport for the first time in few-layer MoS_2, we tune the stroboSCAT probe wavelength far from excitonic resonances. We then capture a complementary measurement at a probe wavelength just detuned from the exciton resonances where stroboSCAT is sensitive to both electronic and thermal energy (Fig. 1a). We decouple the electronic (bright) and heat (dark) contributions to the stroboSCAT signal and find that electronic and thermal expansion are well-separated after ~500 ps (Fig. 1b). At early times (<200 ps), electronic transport is dominated by Auger-Meitner interactions while heat transfers across the interface to surrounding hexagonal boron nitride (hBN) on a similar time scale. At late times (>1 ns), we observe the few-ns decay of long-lived indirect excitons with temperature decaying due to heat transfer limited by diffusion in hBN (Fig. 1c). We capture these effects with a spatiotemporal model that includes the electronic excited state dynamics in addition to the transport of heat and electronic species and their cross-couplings. We also show preliminary results tracking anisotropic heat and electronic transport in black phosphorus which has an intrinsic enhanced thermoelectric capability. With the ability to visualize and decouple heat and electronic transport on relevant spatiotemporal scales, we are able to understand novel properties of thermoelectric materials at a fundamental level so that they may be more efficiently optimized and leveraged for cutting-edge applications.

Figure 1. Decoupling heat and electronic dynamics in 4L MoS_2



a, stroboSCAT image sequences near resonance (top row) and far-detuned from resonance (bottom row). **b,** mean squared expansion and **c,** population decays of the decoupled populations.

Contributions: C.M.W., J.W. and A.L.O. prepared the samples. H.L.W. carried out the experiments and analyzed the data. D.J. developed the kinetic model. H.A.A., E.R., T.F.H. and N.S.G. supervised the research and coordinated the work.

T1-G-21: Tracking Dynamic Morphological Changes of Cu Nanocatalysts during Electrochemical CO_2 Reduction

[Hub – LiSA] Soohong Lee[1,2], Jaime E. Avilés Acosta[1,3], Hui Li[2], Egon Campos Dos Santos[1,3], David M. Larson[1,2], Anthony Y. Fong[3], Christopher J. Tassone[3], Frank Abild-Pedersen[1,3], Thomas F. Jaramillo[1,3], Walter S. Drisdell[1,2]

[1]Liquid Sunlight Alliance; [2]Lawrence Berkeley National Laboratory; [3]SLAC National Accelerator Laboratory

Electrochemical CO_2 reduction (CO_2R) offers an efficient strategy to upcycle anthropogenic CO_2 gases into value-added fuels. While Cu-based electrocatalysts can form desirable C_{2+} products, they have shown drastic changes in morphology and crystal structure during CO_2R which limits durability. The Liquid Sunlight Alliance (LiSA) hub aims to understand the detailed thermodynamics, kinetics, and mechanisms of degradation to achieve solar fuels generating systems operating stably beyond several weeks.

To gain insights into the dynamic phenomena of degradation, *operando* and *in situ* characterization is essential to catch the transient evolution of Cu electrocatalysts under various reaction conditions. Herein, we tracked morphological changes of Cu nanoparticles during CO_2R by using the synchrotron-based small-angle X-ray scattering (SAXS) technique. Monodisperse 8 nm Cu nanocubes are used as starting material to make it simpler to characterize the evolution of a nanoparticle ensemble. An *in situ* cell is designed to simulate the catalyst microenvironment and performance of a lab-based cell. By analyzing *in situ* SAXS data, the changes in size, distribution, morphology, volume fraction, and number density can be obtained for different reaction conditions. Coupling these measurements to kinetic Monte Carlo simulations using energetics obtained from the α-scheme theory will yield detailed atomic-scale insights into the degradation process. We expect to glean fundamental insights on the relationship between the morphological evolution and the degradation mechanisms of Cu catalysts. This fundamental mechanistic information will feed into predictive theories and scaling laws for degradation of catalysts and photocatalysts, enabling the co-design of stable solar fuels systems as part of the LiSA mission.

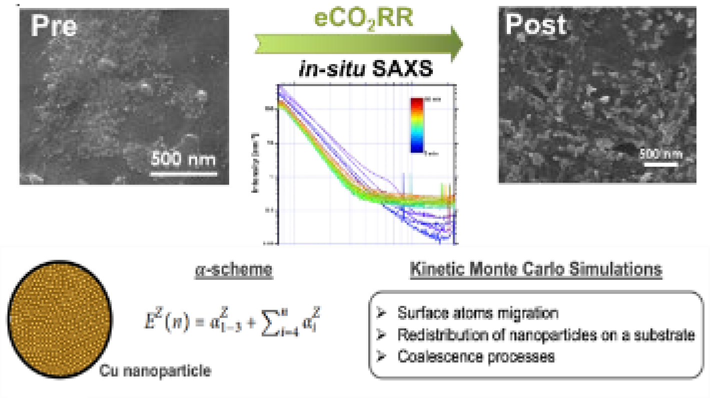


***Figure 1.** a) Illustration of the morphological changes of Cu nanoparticles during CO_2RR observed by pre-and post-catalysis imaging, and* in situ *SAXS data. b) Schematic showing how the alpha parameters co-derived from machine learning and density functional theory predict energetics for modelling Cu nanoparticle redistribution and coalescence durina CO2R.*

Contributions: S.L. and J.E.A.A designed *in-situ* cell and evaluated electrochemical CO_2RR performance. S.L. and J.E.A.A performed *in-situ* SAXS measurements and analyzed data with fitting. E.C.D.S. carried out machine learning-based density functional theory (DFT) calculations and Monte Carlo simulations.