Science for our Nation's Energy Future

Energy Frontier Research Centers
Energy Innovation Hubs
Computational Materials and Chemical Sciences Projects
Principal Investigators' Meeting

October 18-19, 2021
Virtual Meeting

U.S. DEPARTMENT OF ENERGY | Office of Science

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2021 EFRC-Hub-CMS-CCS Virtual PI Meeting

Free and Open to the Public

October 18, 2021: Plenary Session

11:00 am - 4:30 pm Eastern **Click Here to Join via Zoom**

11:00 – 11:10 am	**Welcome from the Office of Science** Harriet Kung, *Deputy Director for Science Programs*
11:10 – 11:20 am	**Remarks from the DOE** David Turk, *Deputy Secretary of Energy*
11:20 – 12:00 pm	**Can the US Compete in Basic Energy Sciences? Critical Research Frontiers and Strategies** Cynthia Friend, *The Kavli Foundation and Harvard University (on leave)*
12:00 – 12:30 pm	**Update from Basic Energy Sciences (BES)** Andy Schwartz, *Office of Basic Energy Sciences*
12:30 – 1:00 pm	**Break**
1:00 – 1:45 pm	**Recent BES Basic Research Needs Reports** Jillian Dempsey, *University of North Carolina Chapel-Hill* Liquid Solar Fuels Roundtable Cynthia Jenks, *Oak Ridge National Laboratory* Transformative Manufacturing Workshop Karren More, *Oak Ridge National Laboratory* Carbon-Neutral Hydrogen Roundtable
1:45 – 2:45 pm	**Connections across DOE** Sunita Satyapal, *EERE Hydrogen and Fuel Cell Technologies Office* Jennifer Wilcox, *Office of Fossil Energy and Carbon Management* Eric Hsieh, *Office of Electricity* Mike McKittrick, *EERE Advanced Manufacturing Office*
2:45 – 3:15 pm	**Break**
3:15 – 4:15 pm	**Data Science for Basic Sciences** Kristin Persson, *Lawrence Berkeley National Lab*, EFRC and Hub PI John Gregoire, *California Institute of Technology*, Hub PI Giulia Galli, *Argonne National Lab/University of Chicago*, CMS and EFRC PI Roberto Car, *Princeton University*, CCS PI
4:15 – 4:30 pm	***Science in the Time of Covid* Graphic Art Contest Winners**

2021 EFRC-Hub-CMS-CCS Virtual PI Meeting

By Invitation Only

Register at https://www.orau.gov/2921efrcpi

October 18, 2021: EFRC, Hub, CMS, CCS Mixer

7:00 – 8:00 pm EST GatherTown Student and Postdoc Network Mixer

October 19, 2021: EFRC, Hub, CMS, CCS Poster Sessions

11:00 am - 5:30 pm Eastern

11:00 – 1:00 pm **Technical Poster Session 1** *(GatherTown)*

Center Overview Posters (*Room: **Overview Posters**, no presenters*)

Student and Postdoc Team Science Posters (*Room: **Team Posters***)

A. Catalysis and Polymer Science (*Room: **1AE***)
B. Energy Storage (*Room: **1B***)
D. Materials/Chemistry by Design and Synthesis (*Room: **1D***)
E. Nuclear Science (*Room: **1AE***)
F. Quantum Science and Microelectronics (*Room: **1F***)

1:00 – 2:40 pm **Student and Postdoc Team Science Contest Talks**

(Enter Zoom through GatherTown)

Student and Postdoc Team in orange, Speakers underlined

1:00 - 1:10 pm **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

1:11 - 1:21 pm **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

1:22 - 1:32 pm **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

1:33 - 1:43 pm

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

1:44 - 1:54 pm

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

1:55 - 2:05 pm

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

2:06 - 2:16 pm

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

2:17 - 2:27 pm

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

2:28 - 2:38 pm

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

2:40 – 3:00 pm

Student and Postdoc Team Science Q&A *(GatherTown)*

3:00 – 3:30 pm **Break**

3:30 – 5:30 pm **Technical Poster Session 2** *(GatherTown)*

Center Overview Posters (*Room:* ***Overview Posters****, no presenters*)

A. Catalysis and Polymer Science (*Room:* ***2AG***)
C. Energy-Water (*Room:* ***2C***)
D. Materials/Chemistry by Design and Synthesis (*Room:* ***2D***)
F. Quantum Science and Microelectronics (*Room:* ***2F***)
G. Solar Energy (*Room:* ***2AG***)

GATHERTOWN STUDENT AND POSTDOC NETWORK MIXER

Come join us at the **“GatherTown Student and Postdoc Network Mixer"** for the 2021 PI Meeting! The event will be hosted by the **BES Early Career Network** on the virtual platform of Gather Town — an old school arcade-style 2D virtual world. You will be able to roam freely in the world while bumping into your colleagues for lively conversations of your choosing. It will be an excellent opportunity to expand your network in an informal setting with peers from across the nation. We also will be having a fun, short trivia game in one of the rooms for those who are interested. The mixer is on **October 18 from 7-8 p.m. EST**, and the **trivia game will be held at 7:30 p.m.** in a designated trivia room in GatherTown.

To learn more about the BES Early Career Network (ECN), please follow the link below:
https://www.energyfrontier.us/bes-ecn

We hope to see you there!

BES ECN Virtual Mixer Committee
Dayton (Jon) Vogel, UNCAGE-ME (EFRC)
Lixin Sun, IMASC (EFRC)
Ashlyn Hale, M2QM (EFRC)
Hanu Arava, Q-MEEN-C (EFRC)
Eric Cueny, CHASE (Hub)
Kunyu Wang, CGS (EFRC)
Tyler Jaynes, CBES (EFRC)

To receive announcements about BES Early Career Network (ECN) events, please subscribe to the BES Early Career Network GovDelivery list.

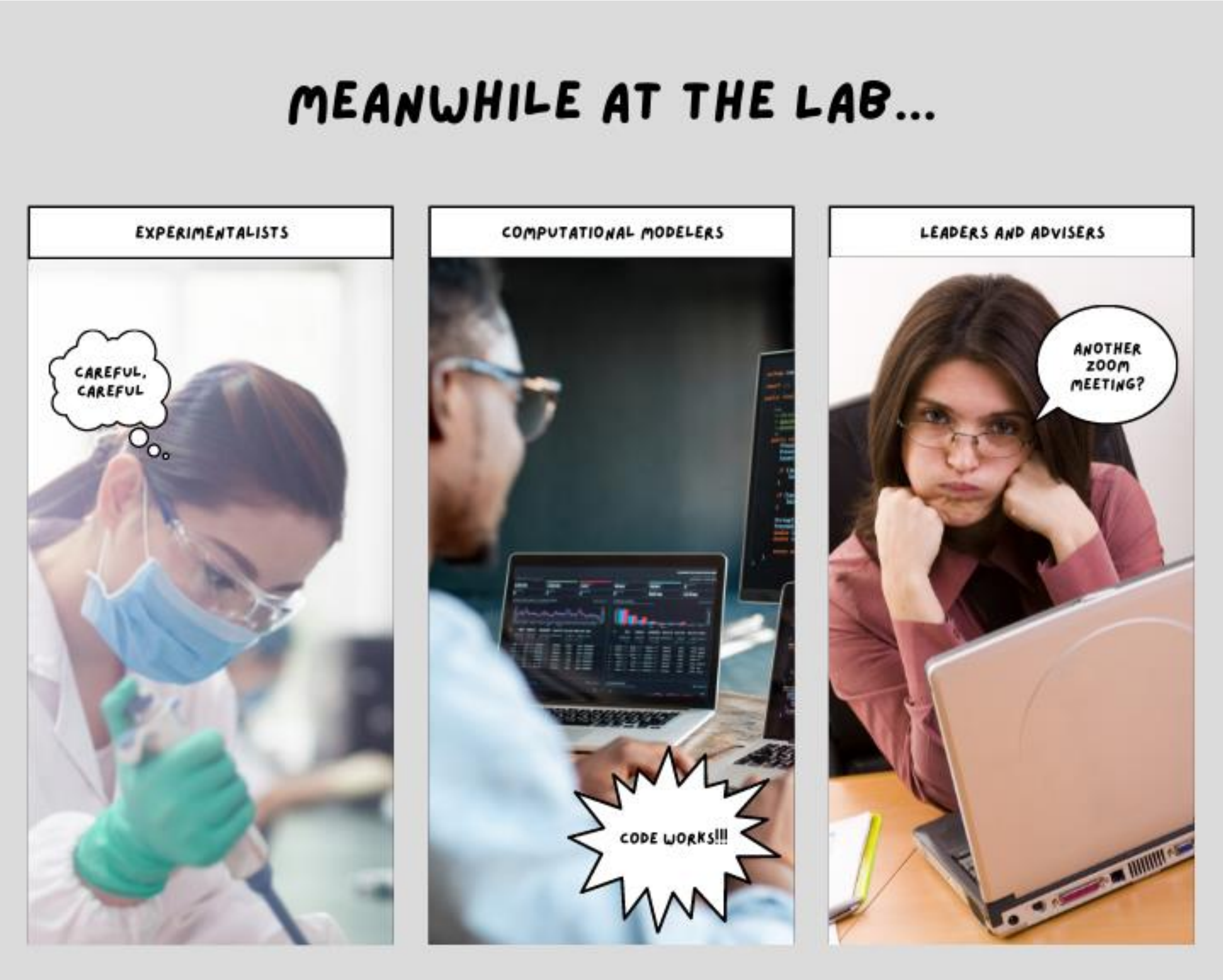
SCIENCE IN THE TIME OF COVID GRAPHIC ART CONTEST

As part of the 2021 EFRC-Hub-CMS-CCS Principal Investigators’ Meeting, the Department of Energy’s Office of Basic Energy Sciences (DOE BES) is sponsoring a Science in the Time of Covid Contest. Following the BES tradition, during each meeting there is an optional contest designed to educate, inspire, and entertain an intelligent but not expert audience about the extraordinary science, innovation, and people in the Energy Frontier Research Centers (EFRC), Energy Innovation Hubs, and Computational Materials and Chemical Sciences (CMS/CCS) Projects. Since early 2020, the Covid-19 pandemic has profoundly impacted all aspects of our lives, including how science is done. The Science in the Time of Covid Contest is an opportunity to capture with graphic art how the scientific endeavor has changed. The graphic art could be a cartoon, photograph, collage, drawing, or any other medium that can be displayed in a static image. Winning graphic art, selected by a panel of illustrious judges, will be announced at the Principal Investigators' Meeting on **October 18, 2021 at 4:15pm**.

The 15 submissions available at https://www.energyfrontier.us/science-in-time-of-covid, and they are reproduced below and listed in alphabetical order of the EFRC Centers/Hubs/CCS/CMS.

CONTEST ENTRIES:

1. Meanwhile in the Lab...



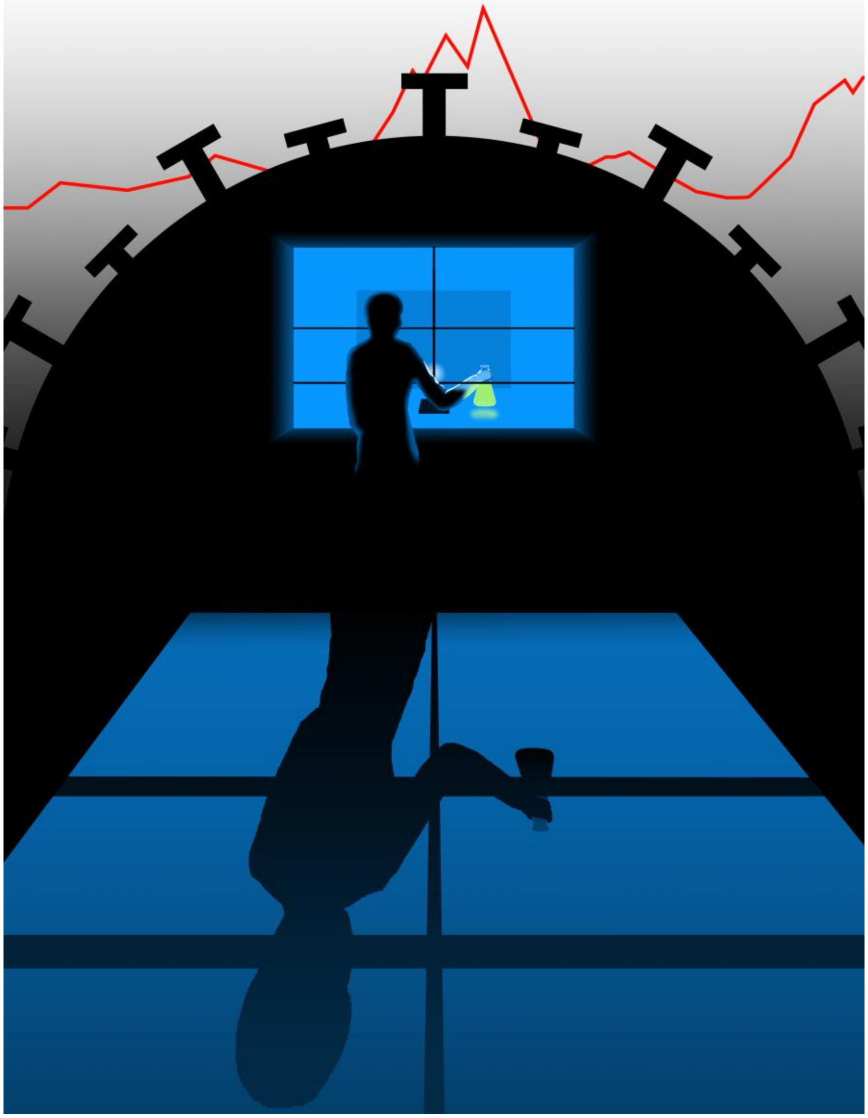
The COVID-19 pandemic has affected how scientists conduct research and meet deadlines. This graphic offers a glimpse into how these roles have changed.

Creators:
Steven Baksa, PhD Candidate

Graphic created by the Center for 3D Ferroelectric Microelectronics (3DFEM) EFRC for the Science in the Time of Covid Contest at the 2021 DOE EFRC-Hub-CMS-CSS Principal Investigators' Meeting.

EFRC Center: 3DFEM

2. The Light in the Cast Shadow



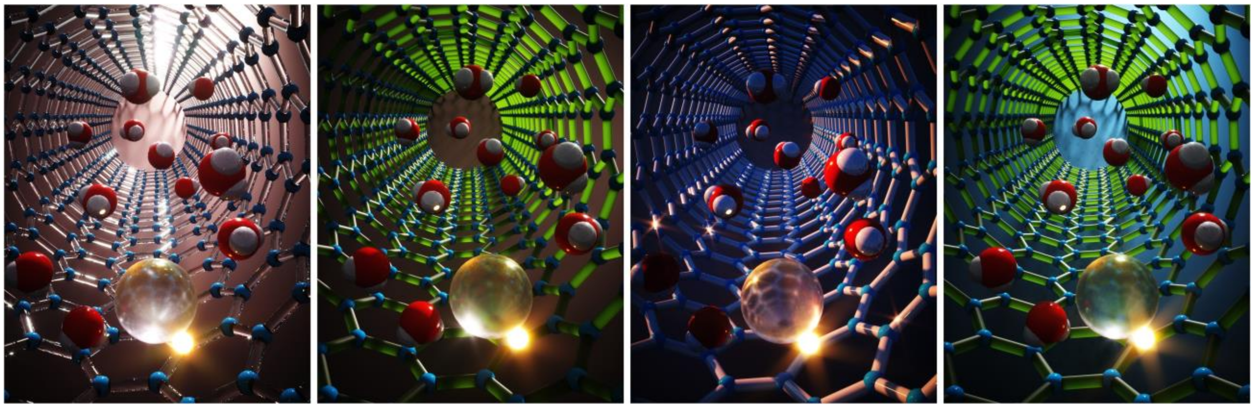
Even through the darkest parts of the pandemic so far, the efforts of science continue. The image depicts a scientist bathed in blue light, working with a florescent material, and in the shadow of Covid-19 and rising case numbers (new cases graph is based on data from the New York Times). The pursuit of knowledge can act as a light in the darkness caused by the looming dread of Covid-19, even in isolation.

Creators:
Dr. Grace B. Panetti and Brittany P. Wilburn M.S.

Graphic created by the Bioinspired Light-Escalated Chemistry (BioLEC) EFRC for the Science in the Time of Covid Contest at the 2021 DOE EFRC-Hub-CMS-CSS Principal Investigators' Meeting.

EFRC Center: BioLEC

3. Flowing towards the Exit



Like ions and water molecules in a CNT, we drift towards the exit of our one-dimensional COVID existence.

Creators:
Illustration concept: T. A. Pham, F. Aydin (LLNL), A. D. Rigos (MIT). Illustration by Ella Maru Studios.

Graphic created by the Center for Enhanced Nanofluidic Transport (CENT) EFRC for the Science in the Time of Covid Contest at the 2021 DOE EFRC-Hub-CMS-CSS Principal Investigators' Meeting.

EFRC Center: CENT

4. Furthering Groundbreaking Research During a Pandemic

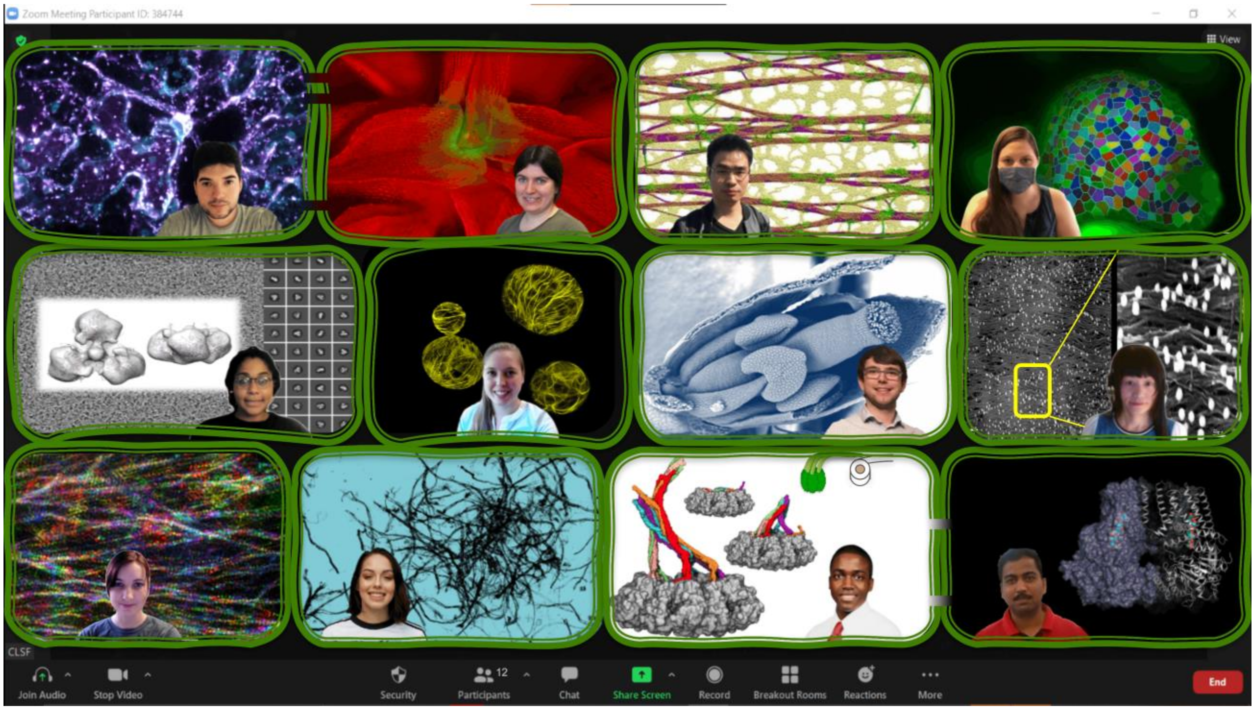
COVID-19 has impacted all of our lives in remarkably profound ways. Perhaps one of the most momentous changes has been in the way we conduct research and collaborate. This graphic is designed with that idea in mind, to inspire and remind us of the many hurdles we have faced and overcome in this difficult time.

Creators:
Samuel R. Bottum, PhD Candidate

Graphic created by the Center for Hybrid Approaches in Solar Energy to Liquid Fuels (CHASE) Hub for the Science in the Time of Covid Contest at the 2021 DOE EFRC-Hub-CMS-CSS Principal Investigators' Meeting.

Hub: CHASE

5. Open Cell Walls of Communication



This graphic portrays a dozen images arrayed as in a Zoom screen, with green plant cell walls surrounding early career researchers in CLSF. The background of each 'cell' is an image taken from the research performed by the corresponding individual during the time of COVID, representing diverse approaches such as cryo electron microscopy, coarse-grained and atomistic modeling, super-resolution fluorescence microscopy, genetic engineering, cell wall regeneration, nanogold labeling and SEM imaging. As a "Where's Waldo" Grand Challenge apropos of COVID, try to find the mask and the toilet paper.

Creators:
Sydney Duncombe, Sarah Kiemle, and Lynnicia Massenburg

Graphic created by the Center for Lignocellulose Structure and Formation (CLSF) EFRC for the Science in the Time of Covid Contest at the 2021 DOE EFRC-Hub-CMS-CSS Principal Investigators' Meeting.

EFRC Center: CLSF

6. Le Chatelier's Principle

We ideally research in a calm equilibrium state, which I imagine as a minima of free energy. In the time of covid our environment is being volatilely perturbed and torn apart while we try to find equilibrium in the lab. This work depicts a free energy graph shown in yellow with aspects of research represented by spheres that we try to juggle and keep in local minima during these perturbations.

Creators:
Amy Stegmann, PhD Candidate

Graphic created by the Center for the Science of Synthesis Across Scales (CSSAS) EFRC for the Science in the Time of Covid Contest at the 2021 DOE EFRC-Hub-CMS-CSS Principal Investigators' Meeting.

EFRC Center: CSSAS

7. MXene Discovery During COVID-19 Pandemic

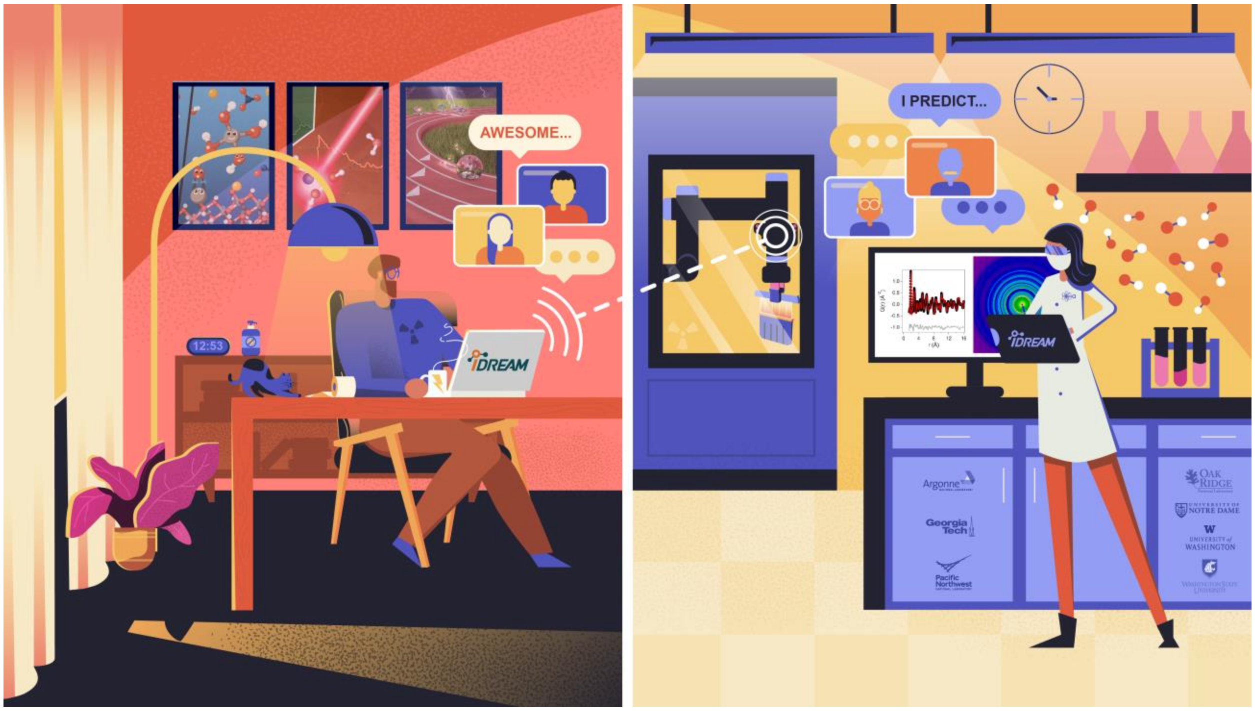
Pandemic has changed our daily lives in all aspects. University and scientific laboratories have not been an exemption to this. From complete shutdown in the beginning of the COVID-19 pandemic, to various limitations such as social distancing, wearing face masks and face shields (everyone knows about goggle fogs!), decreased personnel capacity in the lab, and online meetings, our labs at Drexel Nanomaterials group have faced many challenges. Despite all these, our MXene discovery journey has continued at an exceptional pace in this challenging times.

Creators:
Armin VahidMohammadi, Kyle Matthews, James Gravlin, Kateryna Shevchuk, Yury Gogotsi

Graphic created by the Fluid Interface Reactions, Structures and Transport Center (FIRST) EFRC for the Science in the Time of Covid Contest at the 2021 DOE EFRC-Hub-CMS-CSS Principal Investigators' Meeting.

EFRC Center: FIRST

8. IDREAM Shines a Long-Distance Light on Radioactive Waste Research



Teleworking from his home in Washington state, IDREAM EFRC postdoc Sebastian Mergelsberg operated the synchrotron's robotic arm 2,000 miles away at Argonne National Laboratory in Illinois. By pivoting to the virtual use of technology during COVID-19 travel restrictions, IDREAM researchers continue to build collaboration and discover insights into the chemical and physical makeup of the Hanford Site's legacy nuclear waste. This illustration by Stephanie King at Pacific Northwest National Laboratory captures the spirit of long-distance partnerships along with details about IDREAM and the pandemic experience.

Creators:

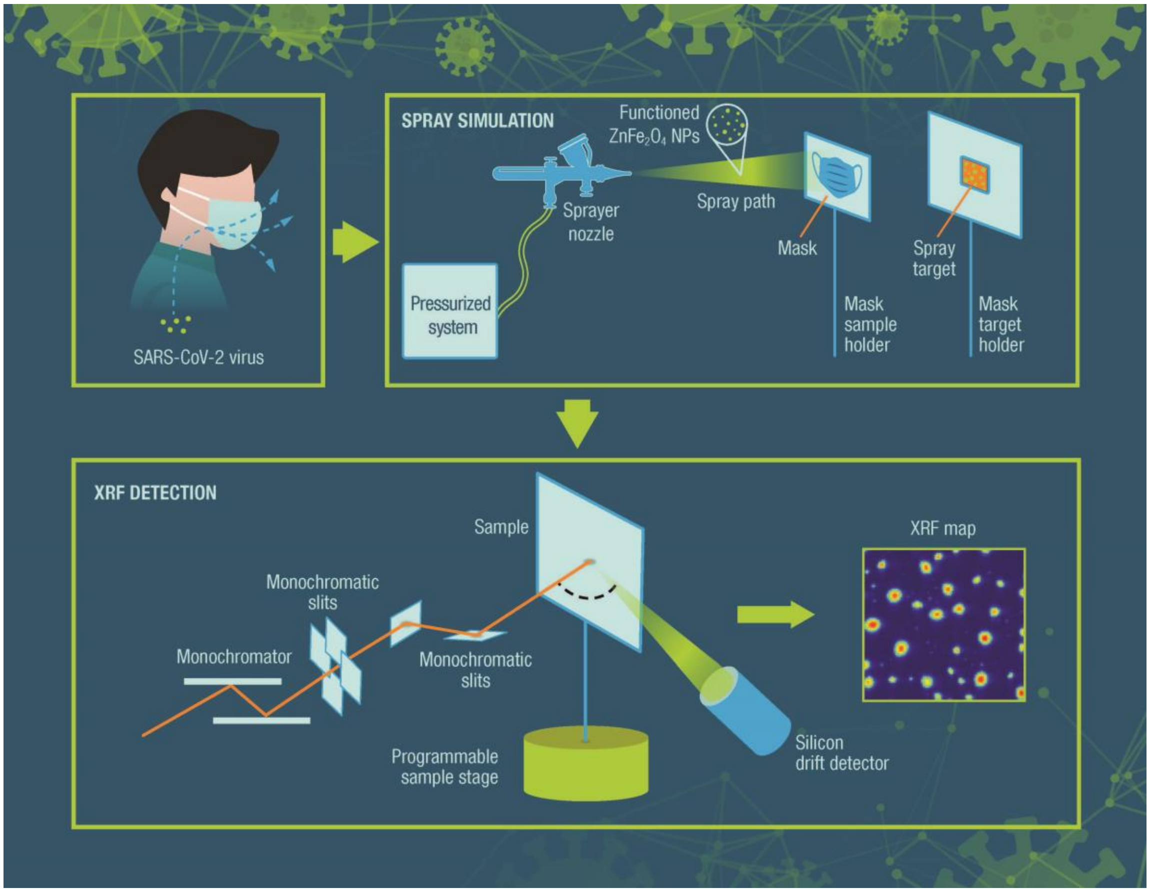
[1]Stephanie King, illustrator; [1]Sebastian Mergelsberg, geosciences postdoc; [1]Emily Nienhuis, materials scientist postdoc; [3]Yihui Wei, chemist grad student; [1,3]Carolyn Pearce, IDREAM EFRC director; [2,1]Xiaosong Li, IDREAM Early Career Network advisor; [3,1]Aurora Clark, IDREAM cross-cut lead.

[1]Pacific Northwest National Laboratory (PNNL), [2]University of Washington, [3]Washington State University

Graphic created by the Interfacial Dynamics in Radioactive Environments and Materials (IDREAM) EFRC for the Science in the Time of Covid Contest at the 2021 DOE EFRC-Hub-CMS-CSS Principal Investigators' Meeting.

EFRC Center: IDREAM

9. Synthesis and Characterization Science developed for Energy Storage has Broad Applicability Enabling Analysis of Virus Dispersion



Functionalized nanoparticles were synthesized to mimic the corona virus. These were suspended in artificial saliva and dispersed by aerosol onto N95 face masks. Synchrotron based x-ray fluorescence mapping effectively visualized the dispersion of the virus mimic on the masks.

Literature reference for the work: Chavis A. Stackhouse‡, Shan Yan‡, Lei Wang, Kim Kisslinger, Ryan Tappero, Ashley R. Head, Killian R. Tallman, Esther S. Takeuchi, David C. Bock*, Kenneth J. Takeuchi*, Amy C. Marschilok* "Characterization of Materials Used As Face Coverings for Respiratory Protection", *ACS Applied Materials and Interfaces*. DOI 10.1021/acsami.1c11200.

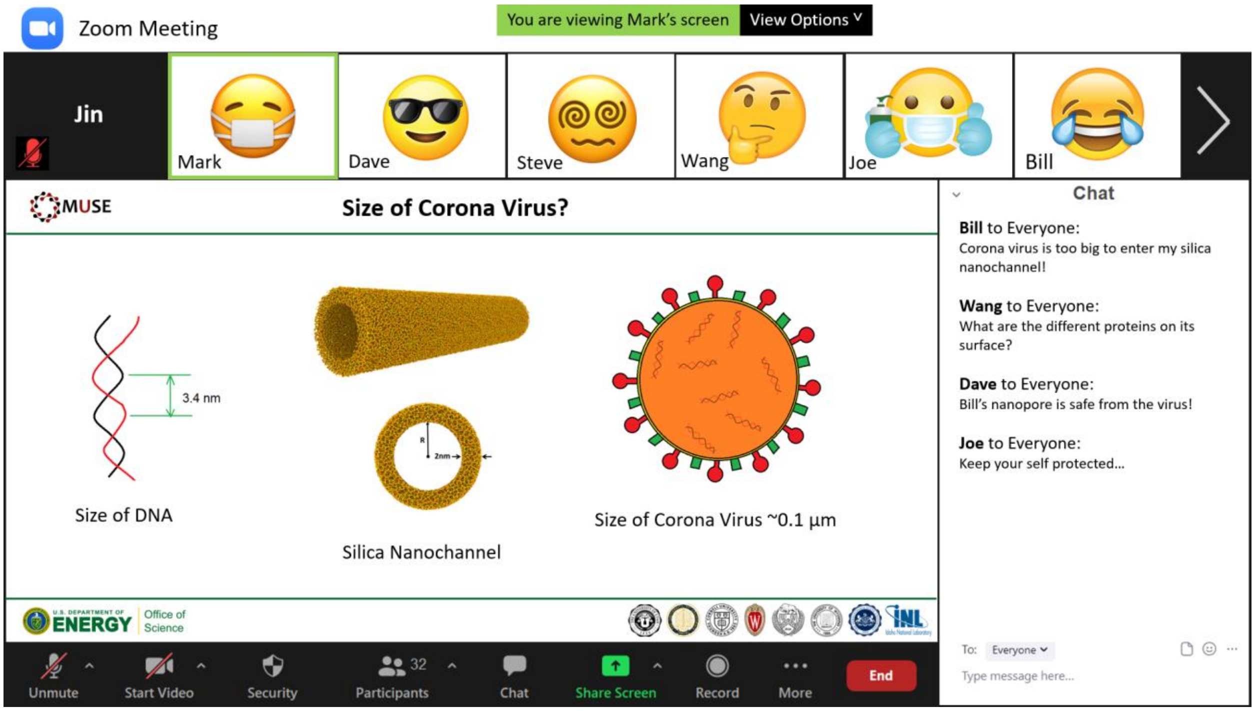
Creators:

Shan Yan,[1] Lei Wang,[2] David Bock,[2] Chavis Stackhouse,[2] Esther Takeuchi,[1,2] Kenneth Takeuchi,[1,2] Amy Marschilok,[1,2] Yelena Belyavina[2](graphic artist)
[1]Stony Brook University, [2]Brookhaven National Laboratory

Graphic created by the Center for Mesoscale Transport Properties (m2M/t) EFRC for the Science in the Time of Covid Contest at the 2021 DOE EFRC-Hub-CMS-CSS Principal Investigators' Meeting.

EFRC Center: m2Mt

10.Meeting



Bill to Everyone:
Corona virus is too big to enter my silica nanochannel!

Wang to Everyone:
What are the different proteins on its surface?

Dave to Everyone:
Bill's nanopore is safe from the virus!

Joe to Everyone:
Keep your self protected…

Muted, masked, cool, dazed, pondering, sterilized, laughing tears…, we all struggle to find our way through the nano-channels of our lives.

Creators:
Jiaqi Jin, Postdoctoral Researcher

Graphic created by the Multi-Scale Fluid-Solid Interactions in Architected and Natural Materials (MUSE) EFRC for the Science in the Time of Covid Contest at the 2021 DOE EFRC-Hub-CMS-CSS Principal Investigators' Meeting.

EFRC Center: MUSE

11. Precocious polymers

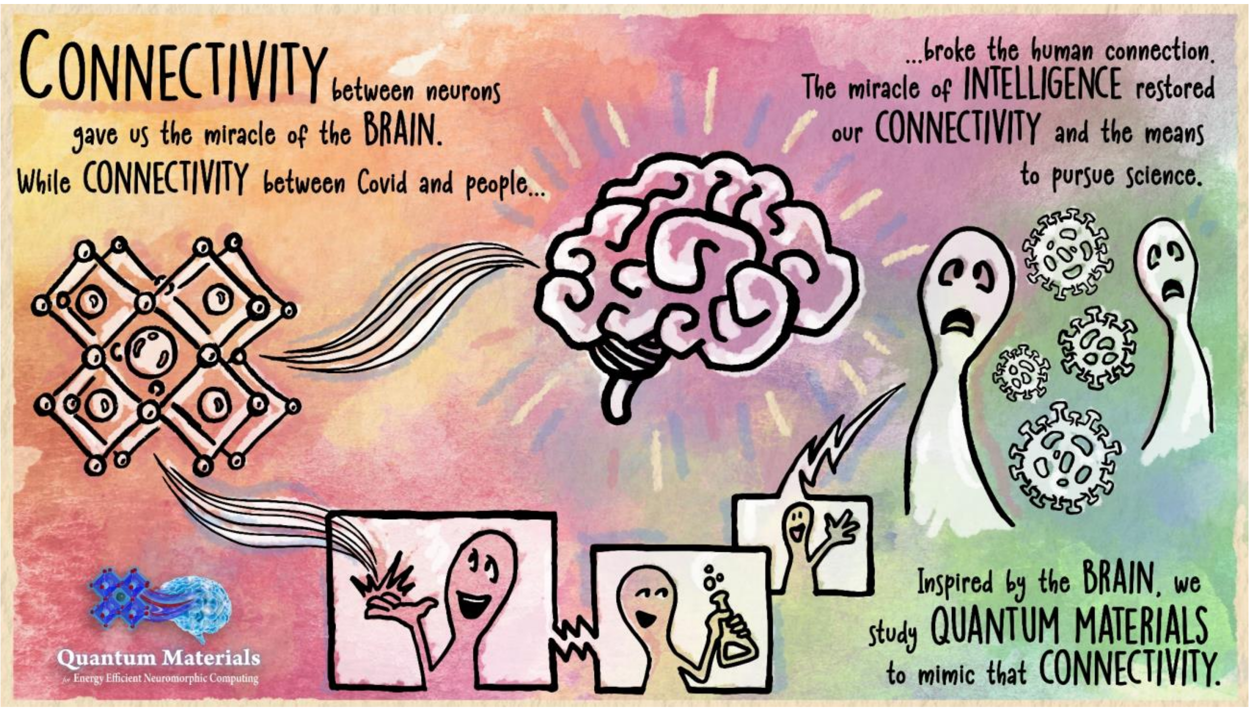
Here is an image of a polynorbornene polymer functionalized with 12C-4 ether rings cast into a 90um tall microfluidic device. Both the top and bottom slide of the microfluidic device have a coating of silver creating a reflective cavity. As the solvent evaporates radially outward from the drop of polymer a unique pattern forms within the polymer post.

Creators:
Varun Hegde, Sam Warnock, University of California Santa Barbara

Graphic created by the Center for Materials for Water and Energy Systems (M-WET) EFRC for the Science in the Time of Covid Contest at the 2021 DOE EFRC-Hub-CMS-CSS Principal Investigators' Meeting.

EFRC Center: M-WET

12. Connectivity



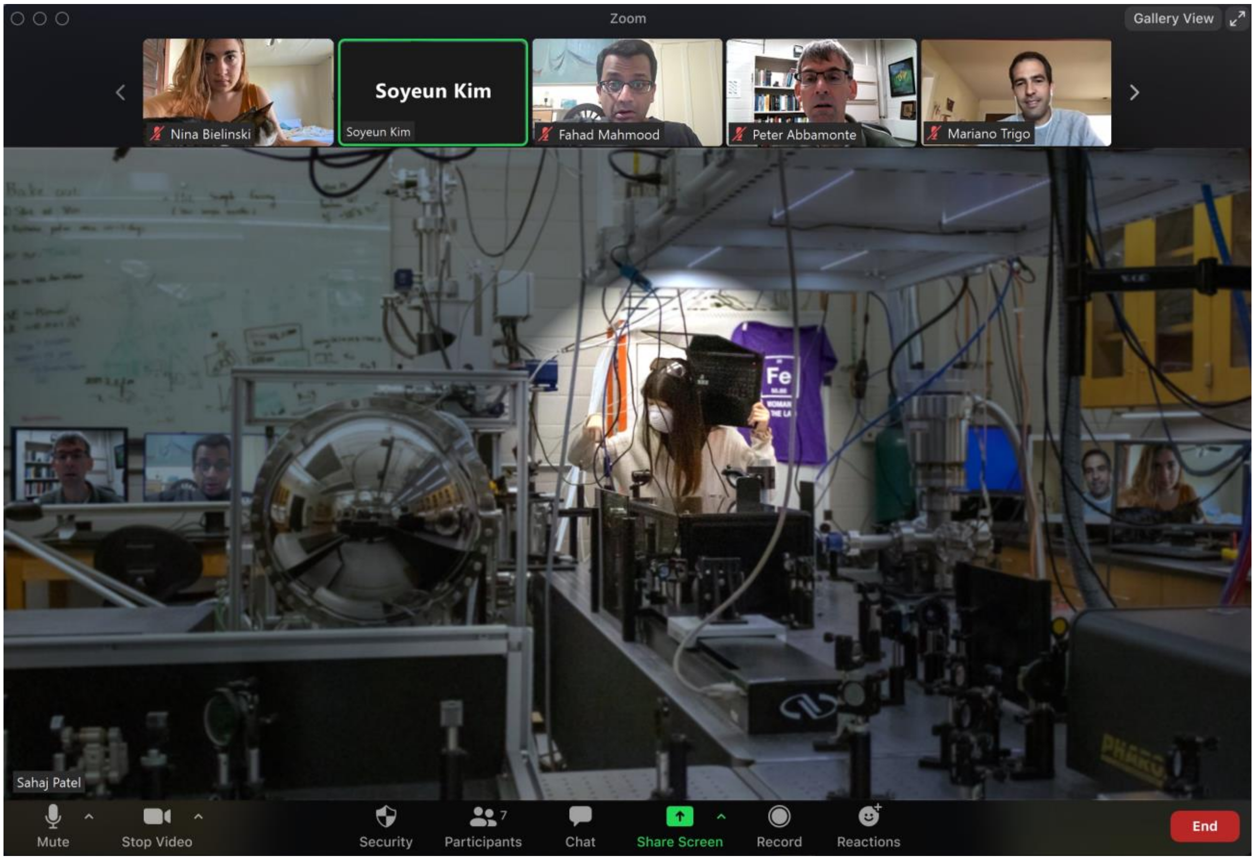
This graphic vignette takes a journey exploring how the brain's connectivity evolved into the miraculous thing that is intelligence. Facing the enormous challenges posed by the pandemic, science and technology provided the means to overcome the lack of face-to-face human connections. At Q-MEEN-C, we try to emulate the brain's connectivity, efficiency, and shear marvel, using quantum materials.

Creators:
Ivan Schuller, Alex Frano, Mario Rojas

Graphic created by the Quantum Materials for Energy Efficient Neuromorphic Computing (Q-MEEN-C) EFRC for the Science in the Time of Covid Contest at the 2021 DOE EFRC-Hub-CMS-CSS Principal Investigators' Meeting.

EFRC Center: Q-MEEN-C

13.Nevertheless she persisted (over Zoom)



QSQM postdoc Soyeun Kim discusses the photoemission measurement procedure at the University of Illinois as graduate student Nina Bielinski, Illinois PIs Fahad Mahmood and Peter Abbamonte, and SLAC PI Mariano Trigo Zoom in. Picture taken by undergraduate student Sahaj Patel (from a distance greater than 6 ft).

Creators:
Soyeun Kim, Nina Bielinski, Sahaj Patel, Fahad Mahmood, Peter Abbamonte (University of Illinois), Mariano Trigo (SLAC National Accelerator Lab)

Graphic created by the Quantum Sensing and Quantum Materials (QSQM) EFRC for the Science in the Time of Covid Contest at the 2021 DOE EFRC-Hub-CMS-CSS Principal Investigators' Meeting.

EFRC Center: QSQM

14. The year of fogged glasses, recluse behavior, and zoom fatigue: a montage

We have all been challenged in different ways during the COVID pandemic. Whether we do experiments in the lab, work on our computers at home, or zoom with our research groups, we inevitably have lived through similar experiences. Capturing snapshots of our collective lives in a humorous manner is our attempt to commemorate this time through art.

Creators:
Kira Wyckoff and Muna Saber

Graphic created by the Center for Synthetic Control Across Length-scales for Advancing Rechargeables (SCALAR) EFRC for the Science in the Time of Covid Contest at the 2021 DOE EFRC-Hub-CMS-CSS Principal Investigators' Meeting.

EFRC Center: SCALAR

15. Innovation and Collaboration: Ultra Materials for a Resilient, Smart Electricity Grid

Since the center's inception during Covid, ULTRA has worked to ensure the health and progress of our team and research. It has taken innovation and collaboration to navigate research and science through such unprecedented circumstances. With the support and connection of everyone, ULTRA has been able to find new ways to successfully further science in the time of Covid.

Creators:
Lisa Molloy, Subhajit Ghosh, Erick Guzman, and Yongjie Zou

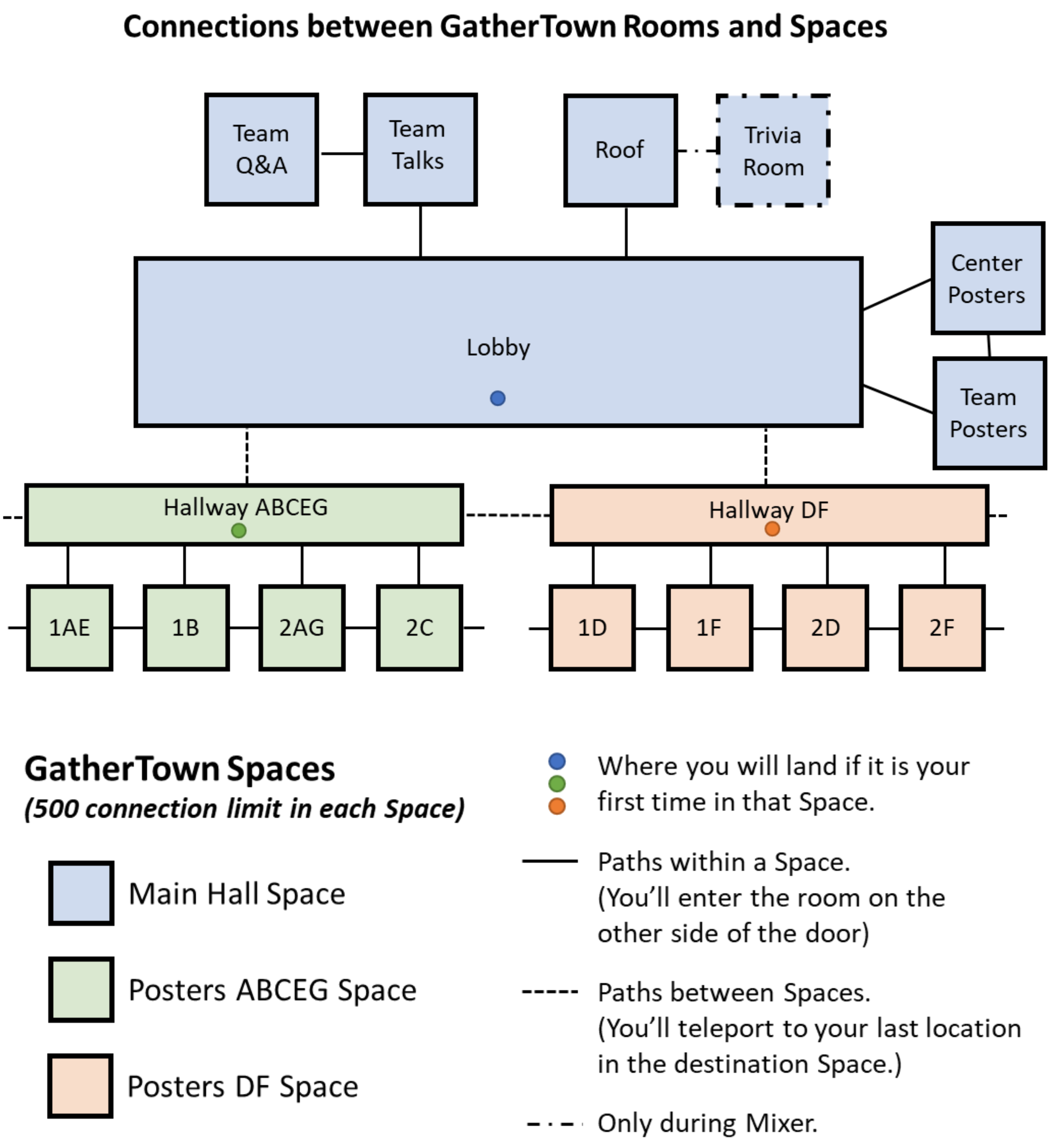
Graphic created by the Ultra Materials for a Resilient, Smart Electricity Grid (ULTRA) EFRC for the Science in the Time of Covid Contest at the 2021 DOE EFRC-Hub-CMS-CSS Principal Investigators' Meeting.

EFRC Center: ULTRA

GATHERTOWN MAPS

You may click on any square on the maps to navigate to the area map in this document. Use **Alt** + ← to navigate back to the previous location in the document.

OVERVIEW MAP



Connections between GatherTown Rooms and Spaces

GatherTown Spaces

(500 connection limit in each Space)

🟦 Main Hall Space

🟩 Posters ABCEG Space

🟧 Posters DF Space

● Where you will land if it is your first time in that Space.

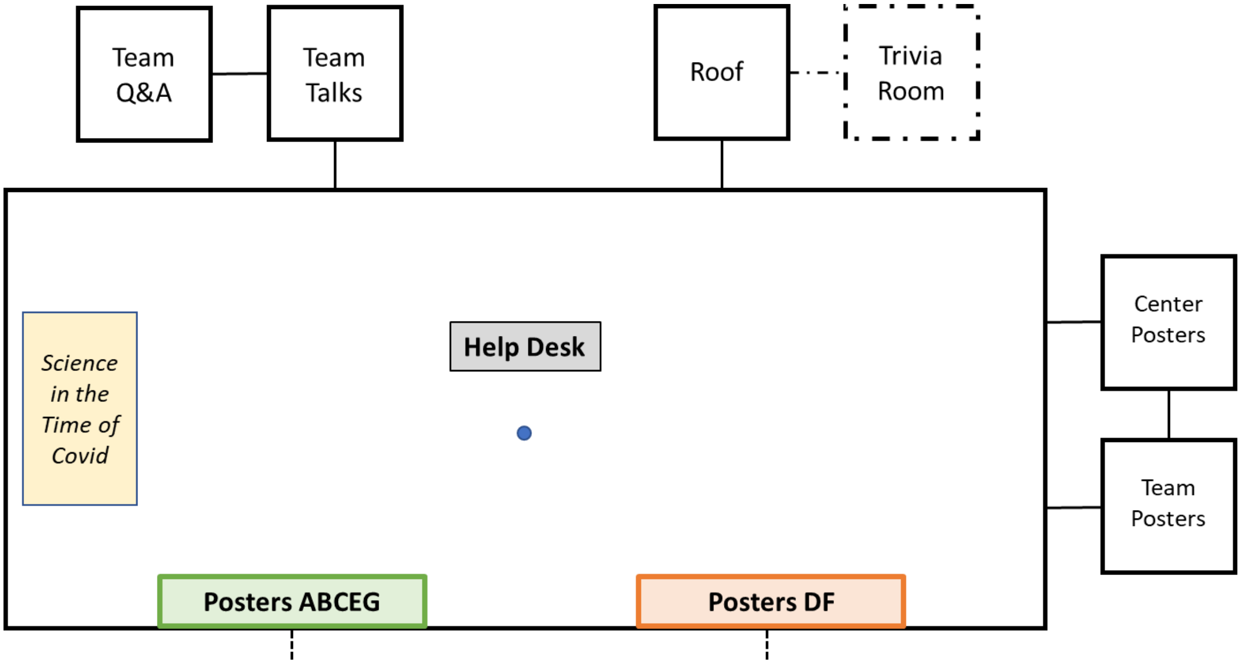
—— Paths within a Space. (You'll enter the room on the other side of the door)

----- Paths between Spaces. (You'll teleport to your last location in the destination Space.)

– · – Only during Mixer.

GatherTown Maps

Main Hall Space



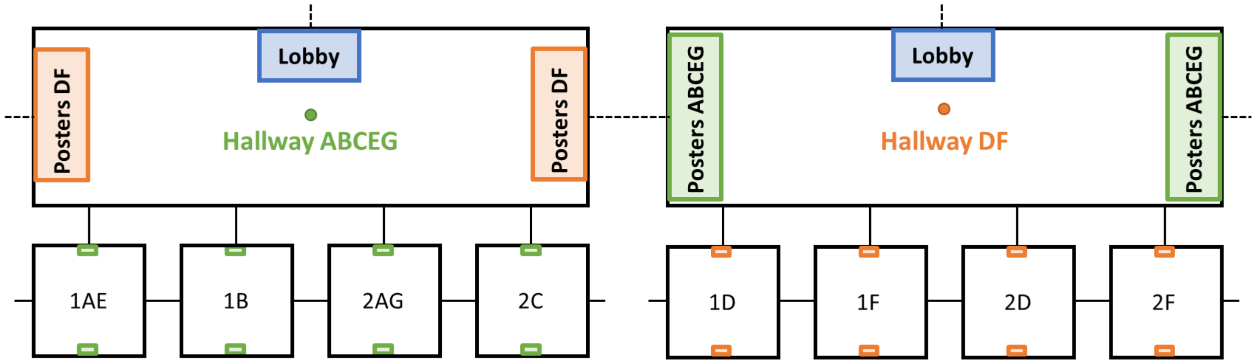
Doors to other rooms within the Main Hall Space

Doors to Posters ABCEG Space

Doors to Posters DF Space

● Starting location in the Main Hall GatherTown Space

Poster Hallways



Doors to other rooms within the Main Hall Space

Doors to Posters ABCEG Space

Doors to Posters DF Space

—— Paths within a Space.
(You'll enter the room on the other side of the door)

----- Two-way paths between Spaces.
(You'll teleport to your last location in the destination Space.)

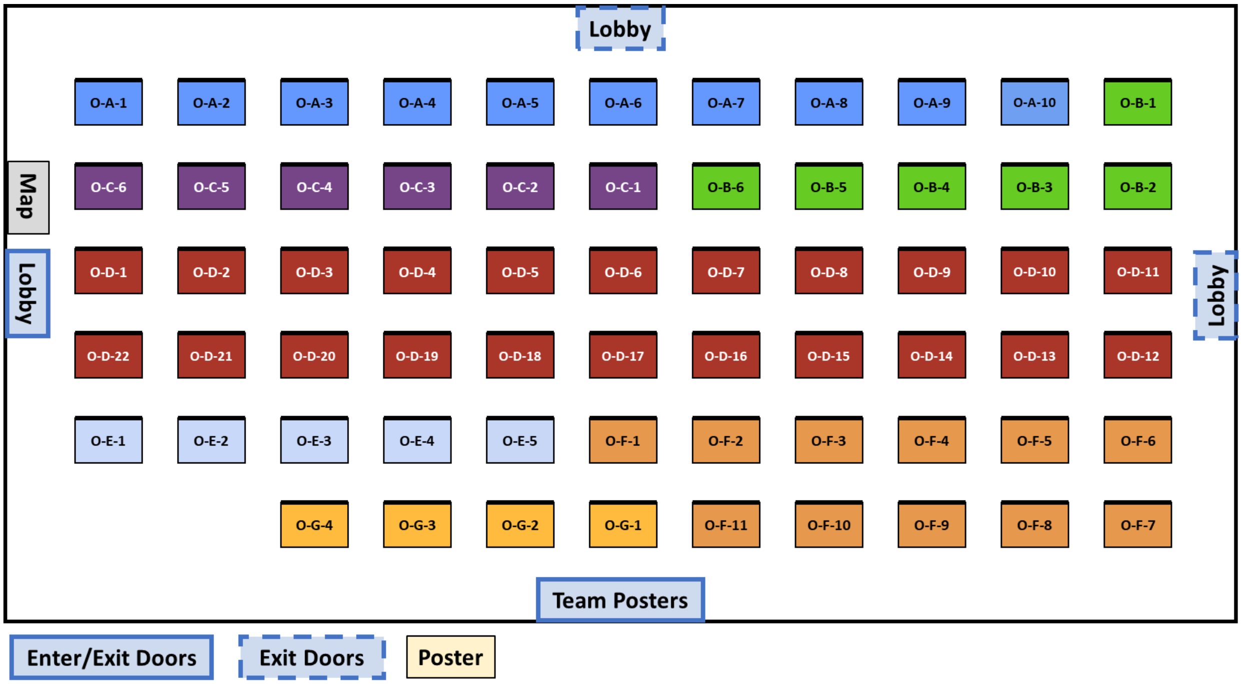
When teleporting into a GatherTown Space

- ● Where you will land if it is your first time in the destination Space.
- ● Otherwise, you will land at your last location in the destination Space.

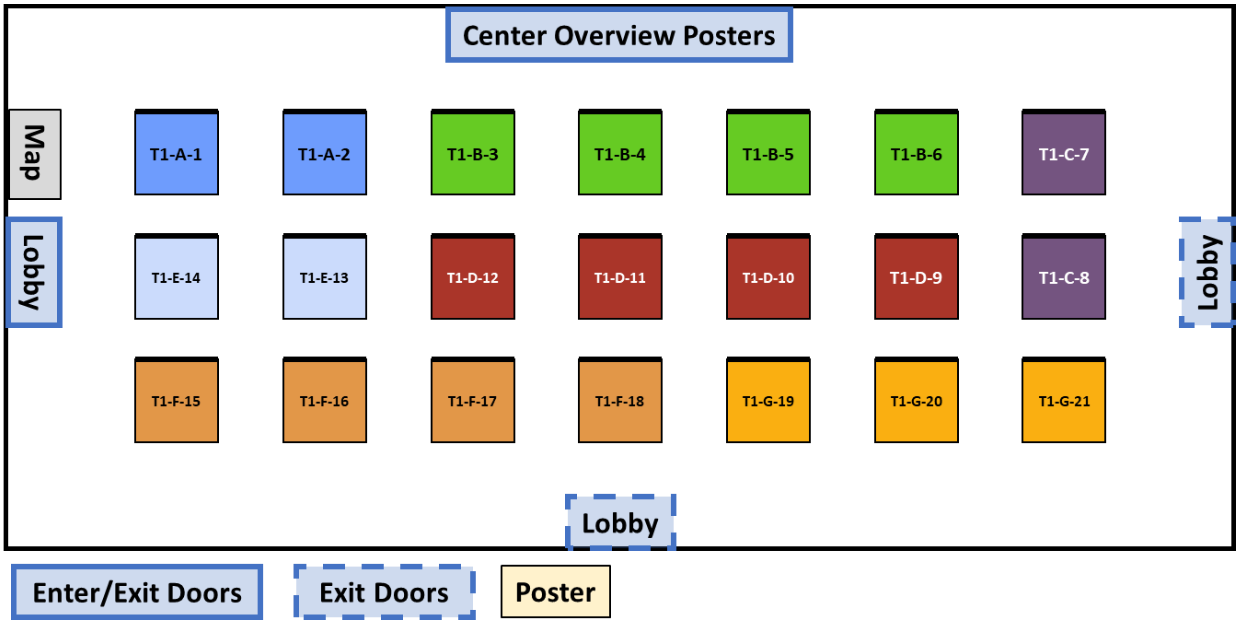
CENTER OVERVIEW POSTER MAP

Color Legend

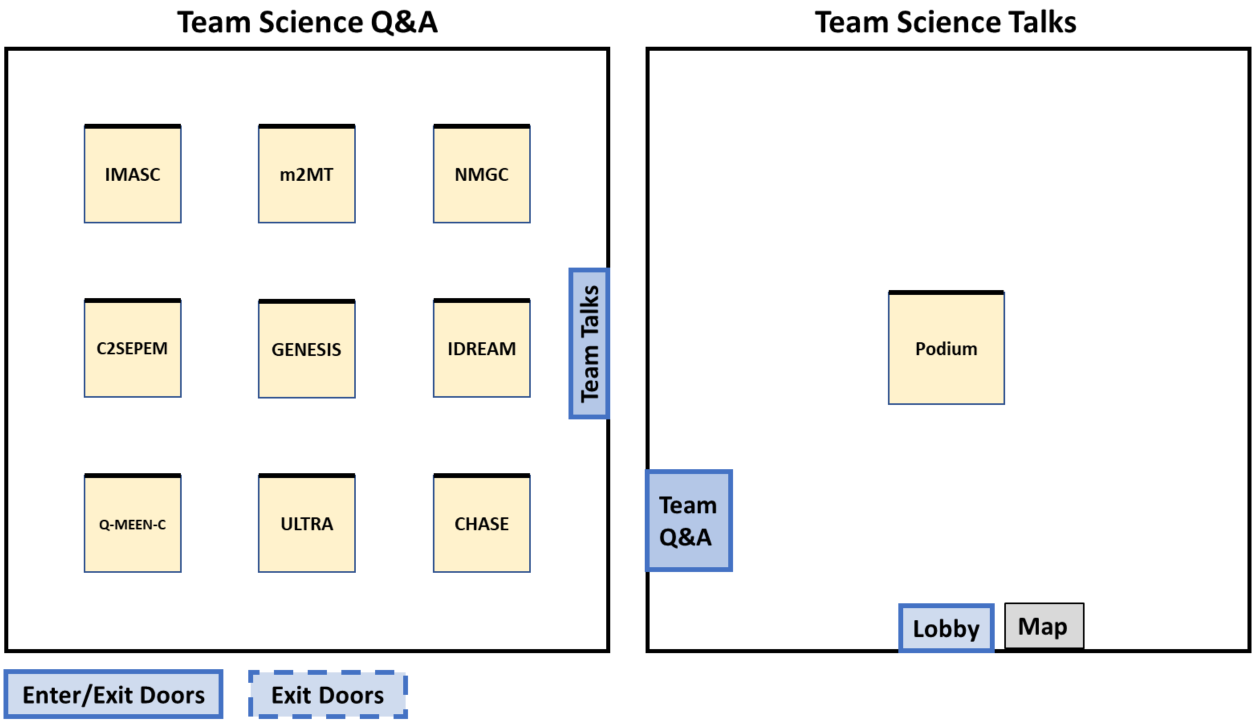
- ● A. Catalysis and Polymer Science
- ● B. Energy Storage
- ● C. Energy-Water
- ● D. Materials/Chemistry by Design and Synthesis
- ○ E. Nuclear Science
- ● F. Quantum Science and Microelectronics
- ● G. Solar Energy



TEAM SCIENCE POSTER MAP



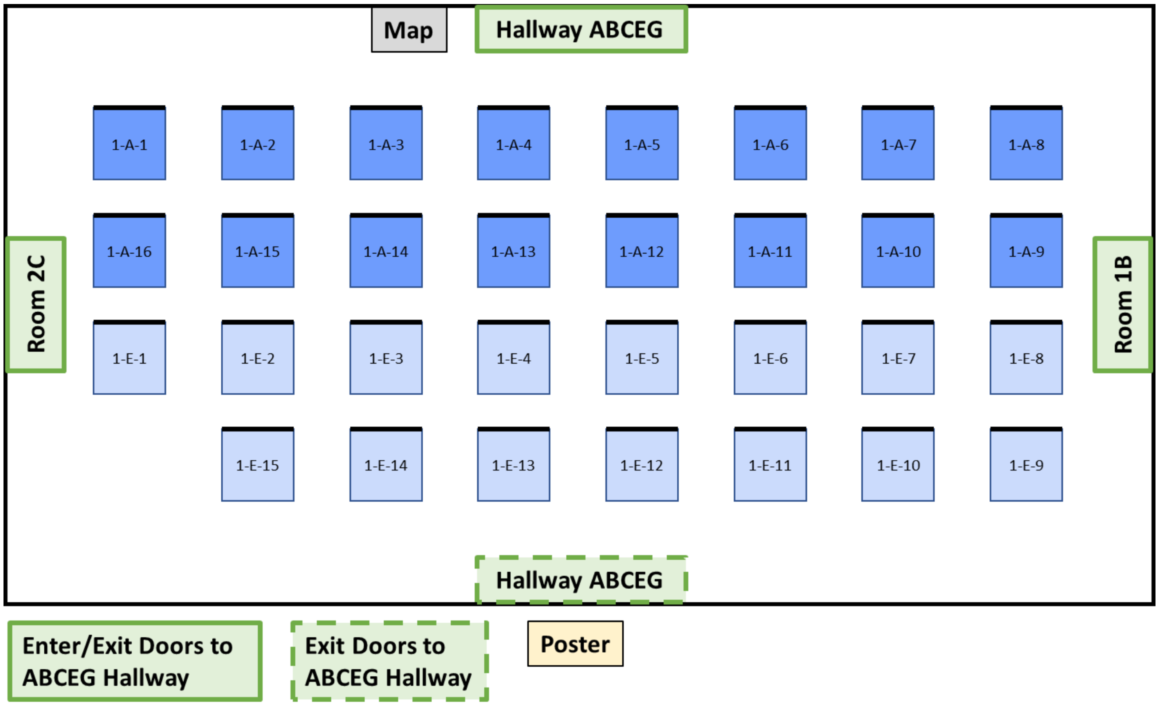
TEAM SCIENCE TALK AND Q&A MAP



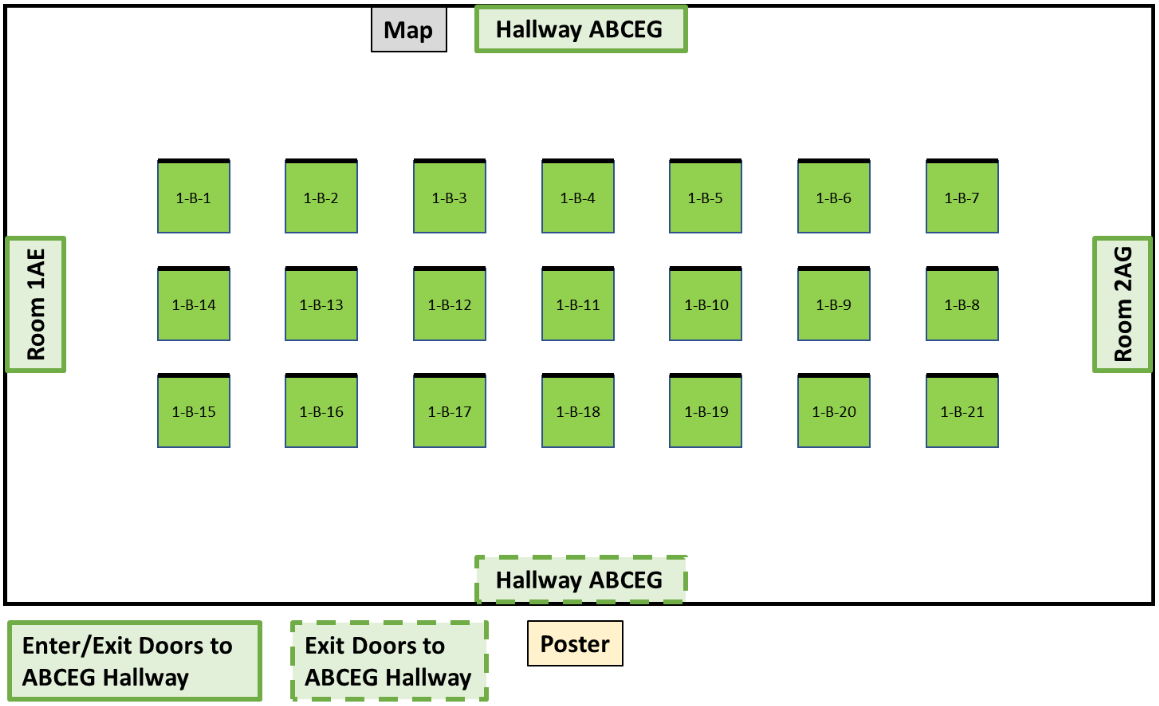
POSTER SESSION MAPS

You may click on any poster square on the maps to read the full abstract. Use **Alt** + ← to navigate back to the previous location in the document.

Room 1AE

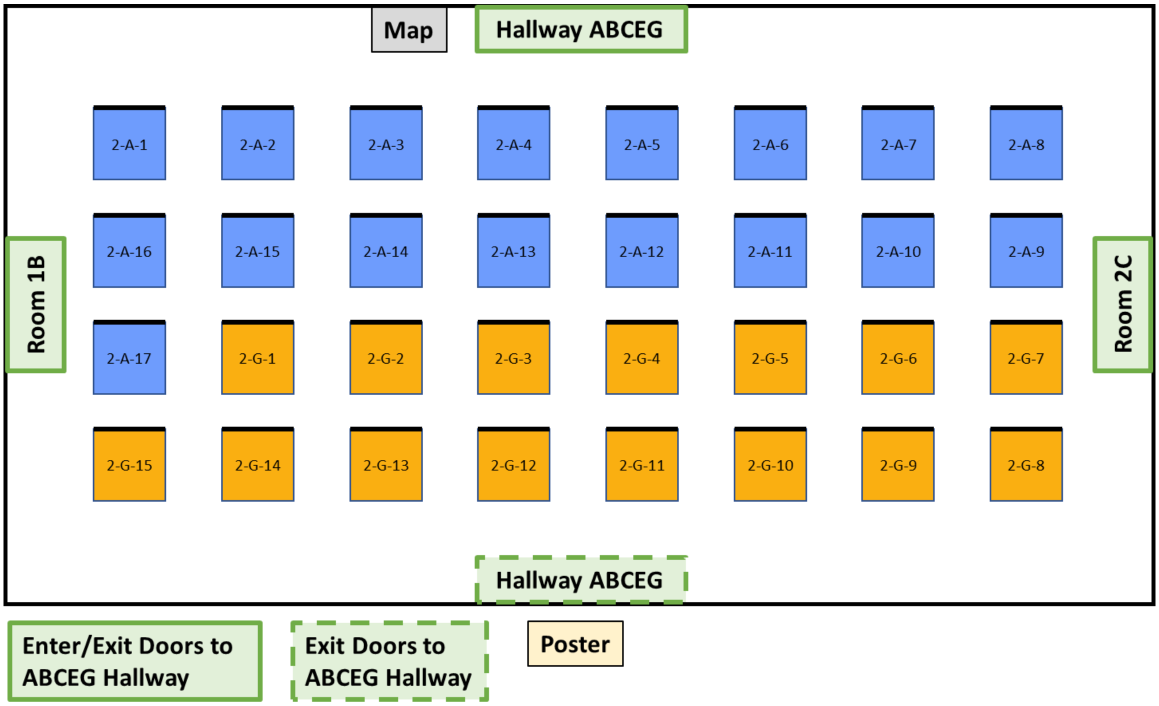


Room 1B

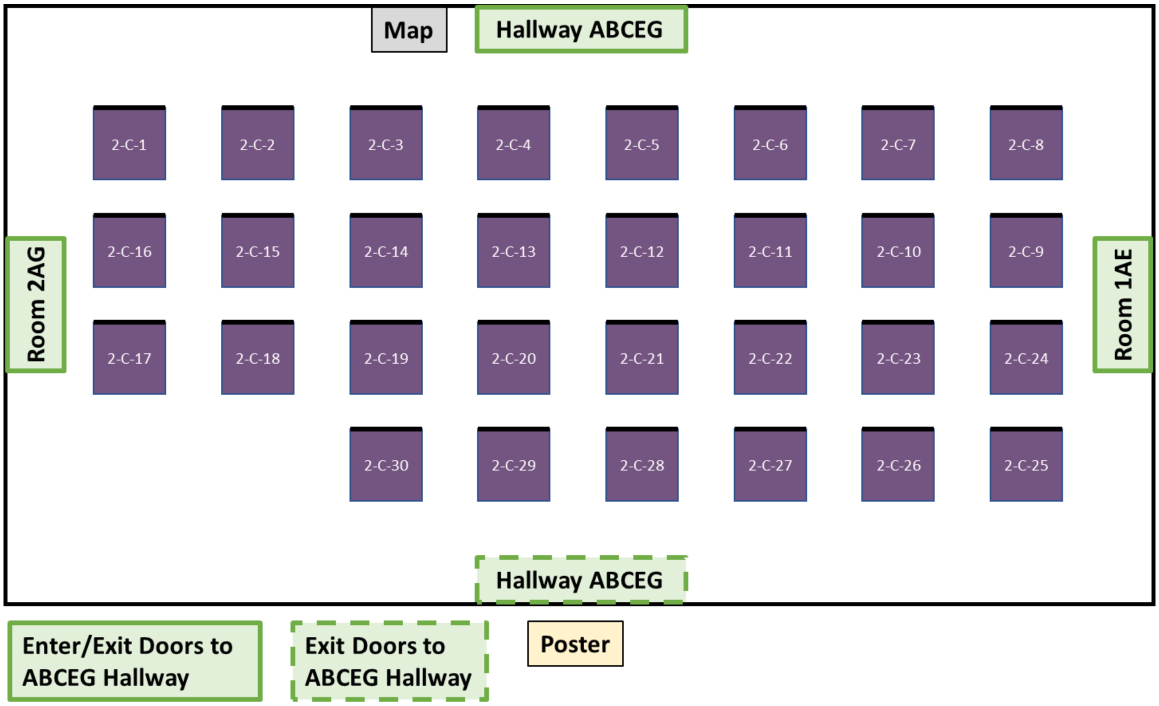


You may click on any poster square on the maps to read the full abstract. Use **Alt** + ← to navigate back to the previous location in the document.

Room 2AG

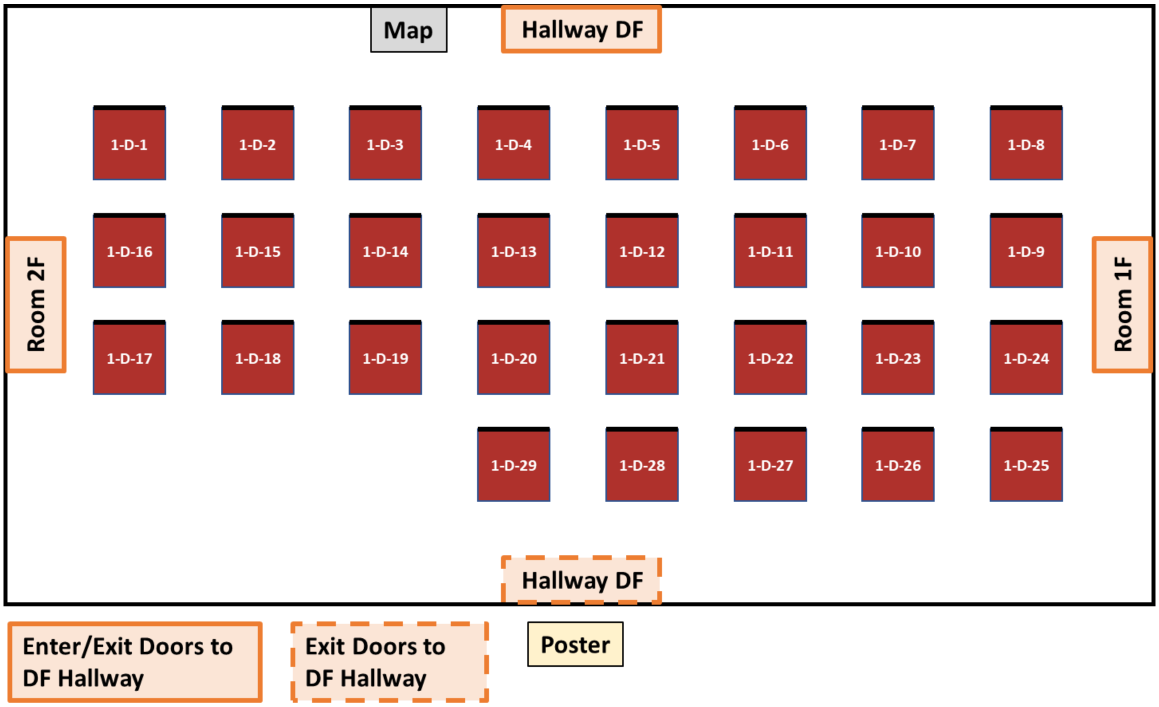


Room 2C

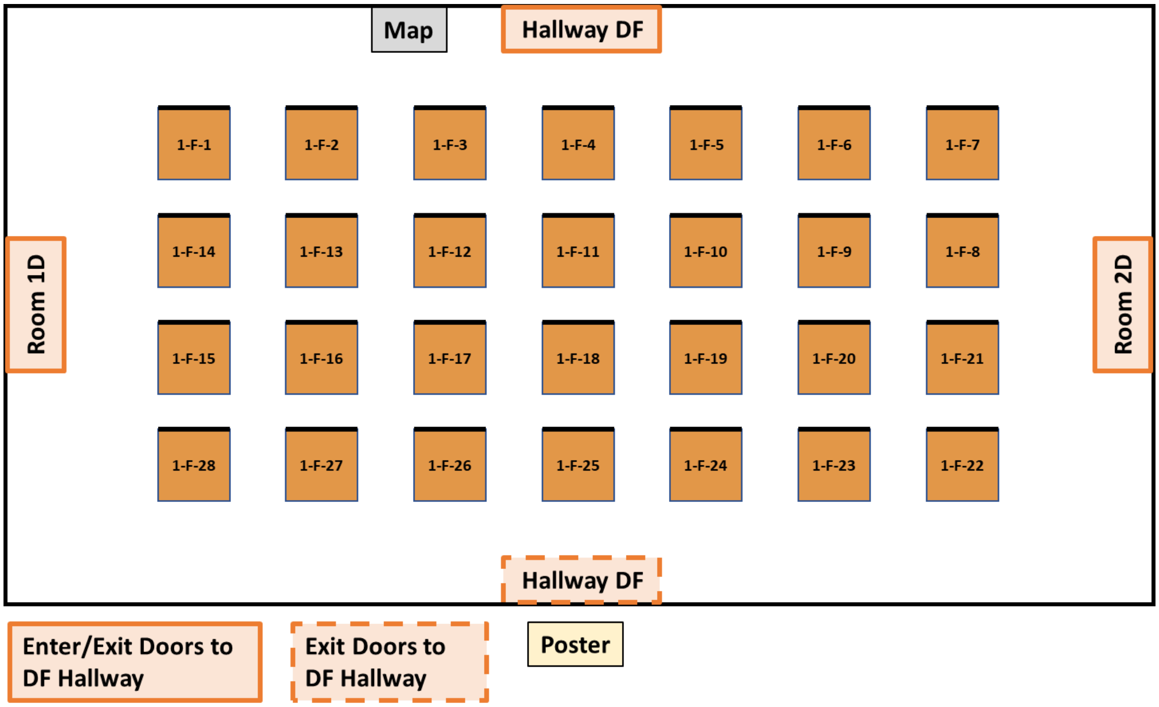


You may click on any poster square on the maps to read the full abstract. Use **Alt** + ← to navigate back to the previous location in the document.

Room 1D

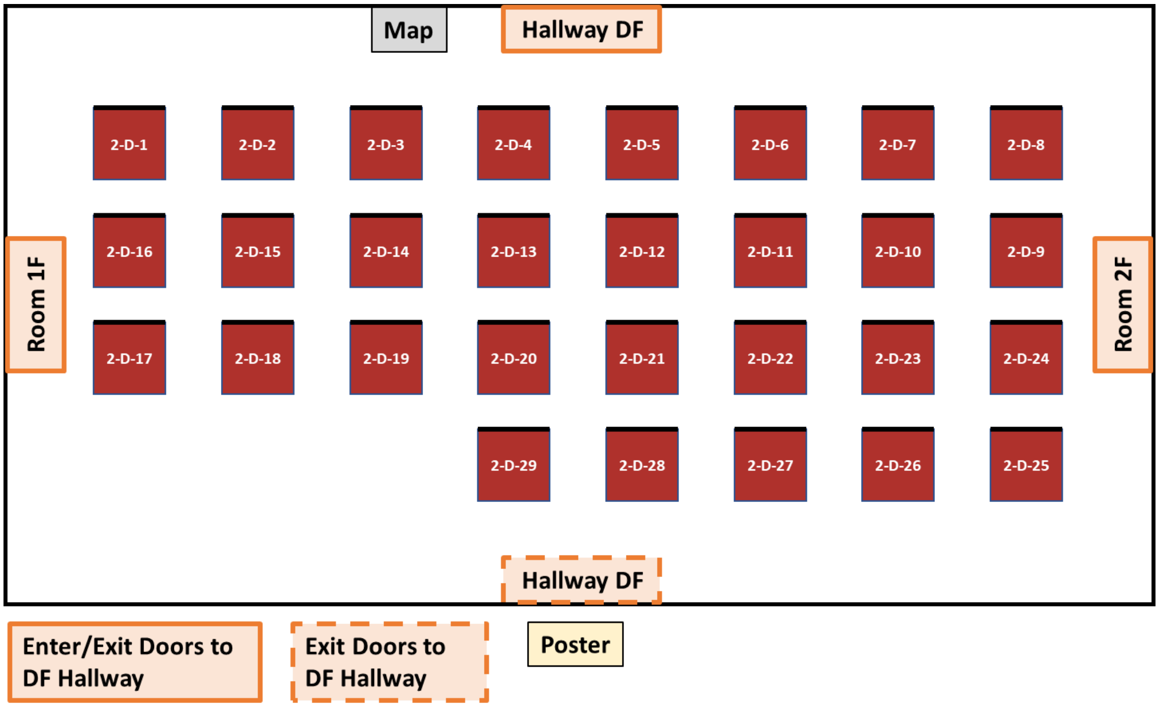


Room 1F

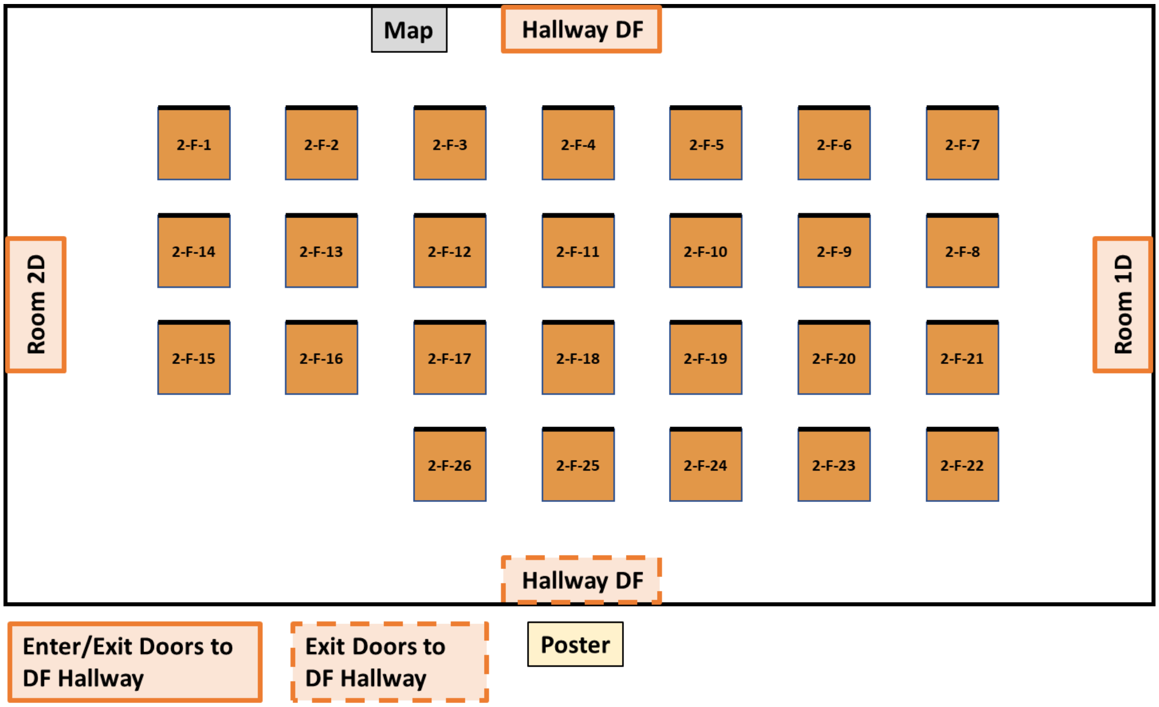


You may click on any poster square on the maps to read the full abstract. Use **Alt** + ← to navigate back to the previous location in the document.

Room 2D



Room 2F



CENTER OVERVIEW POSTER SESSION (ROOM: *CENTER OVERVIEW POSTERS*)

A. CATALYSIS AND POLYMER SCIENCE

O-A-1: [EFRC – ICOUP] INSTITUTE FOR COOPERATIVE UPCYCLING OF PLASTICS

Mahdi Abu-Omar[1], Geoffrey W. Coates[2], Massimiliano Delferro[3], Andreas Heyden[4], Wenyu Huang[5], Anne M. LaPointe[2], Byeongdu Lee[3], Erik Luijten[6], Frédéric A. Perras[5], Baron Peters[7], Kenneth R. Poeppelmeier[6], Aaron D. Sadow[5], Susannah L. Scott[1]

[1]University of California, Santa Barbara; [2]Cornell University; [3]Argonne National Laboratory; [4]University of South Carolina; [5]Ames Laboratory (lead institution); [6]Northwestern University; [7]University of Illinois at Urbana-Champaign

The iCOUP EFRC team will create fundamental principles that enable upcycling of used polyolefins (POs). Upcycling is defined as the selective conversion into products with higher economic value than the virgin materials. The iCOUP Scientific Mission is to uncover macromolecular and catalytic phenomena at the interface of molecular-scale chemistry and mesoscale materials science to enable upcycling of energy-rich plastics. **URL:** https://www.ameslab.gov/institute-for-cooperative-upcycling-of-plastics-icoup

O-A-2: [EFRC – CPI] CENTER FOR PLASTICS INNOVATION

LaShanda T.J. Korley[1], Thomas H. Epps, III[1], Michael C. Berg[1], Peng Bai[2], Mark A. Blenner[1], Stavros Caratzoulas[1], William Chen[1], Juan J. de Pablo[3], Hui Fang[1], Raymond J. Gorte[4], Laure V. Kayser[1], Aditya M. Kunjapur[1], Daeyeon Lee[4], Raul F. Lobo[1], Michael E. Mackay[1], Joshua K. Michener[5], Eleftherios T. Papoutsakis[1], Kevin V. Solomon[1], Dionisios G. Vlachos[1], Mary P. Watson[1]

[1]University of Delaware (lead institution); [2]University of Massachusetts Amherst; [3]University of Chicago; [4]University of Pennsylvania; [5]Oak Ridge National Laboratory

The mission of *CPI* is to develop catalytic and functionalization approaches and fundamental tools applicable to the upcycling of polymer plastics waste, with a strategic focus on enabling mixed-stream transformations from varied material form factors. More information and news about *CPI* can be found at www.cpi.udel.edu.

O-A-3: [CCS – ECC] EXASCALE CATALYTIC CHEMISTRY

Habib N. Najm[1], Khachik Sargsyan[1], Kyungjoo Kim[1], C. Franklin Goldsmith[2], Richard H. West[3], Eric J. Bylaska[4], David H. Bross[5], Branko Ruscic[5], Cosmin Safta[1], Judit Zádor[1]

[1]Sandia National Laboratories (lead institution); [2]Brown University; [3]Northeastern University; [4]Pacific Northwest National Laboratory; [5]Argonne National Laboratory

The ECC project's goal is to create a computational framework that accelerates the characterization of coupled heterogeneous/gas-phase reactions and reaction mechanisms with relevance to catalytic conversion of hydrocarbons, oxygenates, and small molecules. We capitalize on recent improvements in theoretical chemistry combined with improved mathematical software for solving complex problems integrating exascale-size supercomputers to develop a uniquely powerful chemical computational toolset for the research community. We have three major thrusts of the research that we conduct: Automated reaction path exploration on multidimensional potential energy surfaces., Automated reaction mechanism generation for heterogeneous catalysis, and Advanced thermochemistry database. https://ecc-project.sandia.gov/

O-A-4: [EFRC – CCEI] CATALYSIS CENTER FOR ENERGY INNOVATION

Omar Abdelrahman[1], Eric Bloch[2], Anibal Boscoboinik[3], Stavros Caratzoulas[2], Jingguang Chen[3,4], Phillip Christopher[5], Paul Dauenhauer[6], Mark Davis[7], Wei Fan[1], Anatoly Frenkel[3,8], Raymond Gorte[9], Song-I Han[5], Marianthi Ierapetritou[2], Yan Jin[2], Diongxia Liu[10], Raul Lobo[2], Marat Orasov[2], Susannah Scott[5], Dong Su[8], Christopher Murray[9], Michael Tsapatsis[11], Julia Valla[12], Dionisios G. Vlachos[2], Lynn Walker[13], Donald Watson[2]

[1]University of Massachusetts, Amherst; [2]University of Delaware (lead institution); [3]Brookhaven National Laboratory; [4]Columbia University; [5]University of California, Santa Barbara; [6]University of Minnesota; [7]California Institute of Technology; [8]Stony Brook University; [9]University of Pennsylvania; [10]University of Maryland College Park; [11]Johns Hopkins University; [12]University of Connecticut; [13]Carnegie Mellon

The mission of the Catalysis Center for Energy Innovation is to develop innovative heterogeneous catalytic technologies to transform lignocellulosic biomass into fuels, chemicals and advanced materials. **URL:** https://ccei.udel.edu/

O-A-5: [EFRC – ICDC] Inorganometallic Catalyst Design Center

Laura Gagliardi[1], John Anderson[1], Aditya Bhan[2], Donald M. Camaioni[3], Karena W. Chapman[5], Massimiliano Delferro[4], Omar K. Farha[6], Bruce Gates[7], Rachel B. Getman[8], Oliver Y. Gutiérrez[3], Joseph T. Hupp[6], Heather J. Kulik[9], Johannes A. Lercher[3,4], Connie C. Lu[2], Alex B. Martinson[4], Justin M. Notestein[6], R. Lee Penn[2], Donald G. Truhlar[2]

[1]University of Chicago; [2]University of Minnesota (lead institution); [3]Pacific Northwest National Laboratory; [4]Argonne National Laboratory; [5]Stony Brook University; [6]Northwestern University; [7]University of California, Davis; [8]Clemson University; [9]Massachusetts Institute of Technology; [10]Technische Universität München

The mission of the Inorganometallic Catalyst Design Center (ICDC) is to computationally guide the discovery of a new class of energy-science-relevant catalytic materials and understand the underlying structure-function relationships that lead to further catalyst discovery.
URL: http://icdc.umn.edu/

O-A-6: [EFRC – IMASC] Integrated Mesoscale Architectures for Sustainable Catalysis

Joanna Aizenberg[1], Juergen Biener[2], Anibal A. Boscoboinik[3], Anatoly I. Frenkel[3,4], Cynthia M. Friend[1], Boris Kozinsky[1], Robert J. Madix[1], Matthew M. Montemore[5], Philippe Sautet[6], Dario J. Stacchiola[3], Eric A. Stach[7], E. Charles H. Sykes[8], Jason F. Weaver[9]

[1]Harvard University (lead institution); [2]Lawrence Livermore National Laboratory; [3]Brookhaven National Laboratory; [4]Stony Brook University; [5]Tulane University; [6]University of California, Los Angeles; [7]University of Pennsylvania; [8]Tufts University; [9]University of Florida

The mission of IMASC is to develop the ability to improve catalytic selectivity by quantitatively scaling from model studies to catalytic conditions using advanced experiment and theory. **URL:** https://efrc.harvard.edu/

O-A-7: [CCS – SPARC-X] Simulation Package for Ab-Initio Real-Space Calculations

Qimen Xu[1], Abhiraj Sharma[1], Hua Huang[1], Benjamin Comer[1], Xiangyun Lei[1], Xin Jing[1], Shushree J. Sahoo[1], Edmond Chow[1], Andrew J Medford[1], John E Pask[2], Phanish Suryanarayana[1]

[1]Georgia Institute of Technology (lead Institution); [2]Lawrence Livermore National Laboratory

We present SPARC: Simulation Package for Ab-initio Real-space Calculations. SPARC can perform Kohn-Sham density functional theory calculations for isolated systems such as molecules as well as extended systems such as crystals and surfaces, in both static and dynamic settings. It is straightforward to install/use and highly competitive with state-of-the-art planewave codes, demonstrating comparable performance on a small number of processors and increasing advantages as the number of processors grows. Notably, SPARC brings solution times down to a few seconds for systems with O(100-500) atoms on large-scale parallel computers, outperforming planewave counterparts by an order of magnitude and more. We discuss application of SPARC to the study of how the surface properties and band structure of rutile titania (TiO_2) nanoparticles converge with particle size, while employing both semilocal and nonlocal density functionals. We also discuss the development of machine learned models in SPARC using featurization schemes that unite the electronic and atomistic structure descriptions.
URL: https://www.sparc-x.com/

O-A-8: [EFRC – CME] Center for Molecular Electrocatalysis

Aaron Appel[1], R. Morris Bullock[1], Brandi Cossairt[2], Sharon Hammes-Schiffer[3], Karthish Manthiram[4], James Mayer[3], Simone Raugei[1], Thatcher Root[5], Shannon Stahl[5], Yogi Surendranath[4], Eric Wiedner[1]

[1]Pacific Northwest National Laboratory (lead institution); [2]University of Washington; [3]Yale University; [4]Massachusetts Institute of Technology; [5]University of Wisconsin – Madison

Our scientific mission is to establish the fundamental principles needed for efficient interconversion of electrical energy and chemical bonds through precise control of electron and proton transfers. **URL:** https://efrc.pnnl.gov/cme/

O-A-9: [EFRC - BioLEC] Bio-Inspired Light-Escalated Chemistry

Gregory D. Scholes[1], Gabriela S. Schlau-Cohen[2], Matthew Bird[3], Felix N. Castellano[4], Paul J. Chirik[1], Abigail G. Doyle[5], Todd K. Hyster[6], Robert R. Knowles[1], David W. C. MacMillan[1], James K. McCusker[7], Ana L. Moore[8], Thomas A. Moore[8], Barry P. Rand[1], Garry Rumbles[9]

[1]Princeton University (lead institution); [2]Massachusetts Institute of Technology (MIT); [3]Brookhaven National Laboratory; [4]North Carolina State University; [5]University of California, Los Angeles; [6]Cornell University; [7]Michigan State University; [8]Arizona State University; [9]National Renewable Energy Laboratory (NREL)

The Bioinspired Light-Escalated Chemistry (BioLEC) Energy Frontier Research Center (EFRC) mission is inspired by the way in which photosynthesis combines the energy of two or more photons to perform chemistry that is unlikely at equilibrium. See biolec.princeton.edu for more information.

O-A-10: [CCS - BEAST] Beyond-DFT Electrochemistry with Accelerated and Solvated Techniques

Ravishankar Sundararaman,[1] Derek Vigil-Fowler,[2] Charles Musgrave,[3] Christopher Sutton,[4] Mauro Del Ben[5]

[1]Rensselaer Polytechnic Institute (lead institution); [2]National Renewable Energy Laboratory; [3]University of Colorado Boulder; [4]University of South Carolina; [5]Lawrence Berkeley National Laboratory

Electrochemical reactions are key to decarbonizing the world economy, but progress in understanding electrochemical systems and designing electrocatalysts is often hindered by the diversity of experimental conditions and inaccuracy of simulations. Theoretical understanding of electrochemical reactions is impeded by 1) the lack of a universal framework that efficiently treats arbitrary electrolytes, solvents and applied potentials with sufficient detail and fidelity to realistically and accurately model electrochemical systems and 2) the deficiencies of density functional theory (DFT), the primary computational tool for reaction modeling, in describing charge transfer and reaction barriers. We aim to address both challenges by developing accurate and efficient, solvated beyond-DFT methods. The first ingredient in these methods are accurate atomic-scale electrolyte solvation models that capture the equilibrium effect of electrolyte in a single electronic structure calculation. The second ingredient is the incorporation of GW many-body perturbation theory and the random phase approximation (RPA) total energy, which are accurate methods beyond DFT, into solvated and grand-canonical techniques to make them practicable for electrochemistry including solvation and bias effects. Finally, in addition to optimizing these combined techniques for exascale computing, we will also make them more widely applicable using machine learning (ML) approaches trained to a beyond-DFT electrochemical database to make RPA-quality predictions at DFT cost. Together, the BEAST team will deliver exascale-ready solvated beyond-DFT methods and ML acceleration using an electrochemical database to make truly *ab initio* electrochemistry accessible and ubiquitous.

B. ENERGY STORAGE

O-B-1: [HUB – JCESR] JOINT CENTER FOR ENERGY STORAGE RESEARCH

George Crabtree[1,2], Venkat Srinivasan[1], Nitash Balsara[3,4], Jeff Moore[5], Kevin Zavadil[6]

[1]Argonne National Laboratory (lead institution); [2]University of Chicago; [3]University of California, Berkeley; [4]Lawrence Berkeley National Laboratory; [5]University of Illinois, Urbana-Champaign; [6]Sandia National Laboratories

JCESR (jcesr.org) strives to enable a diversity of batteries for a diversity of uses so that each technological application has a safe, cheap, and efficient energy storage option. With this vision we perform world-leading team research to understand the role of solvation and develop redox flow and multivalent ion technologies. We approach our mission with multidisciplinary and multimodal team research, developing and using innovative tools to understand, design, and build energy storage materials "from the bottom up" where each atom or molecule has a prescribed role in producing energy storage systems with targeted behavior.

O-B-2: [EFRC – M2M/T] CENTER FOR MESOSCALE TRANSPORT PROPERTIES

Esther S. Takeuchi[1], Lynden A. Archer[2], David C. Bock[3], Karen Chen-Wiegart[1], Marca Doeff[4], Ping Liu[3], Amy C. Marschilok[1,2], Ekaterina Pomerantseva[5], Altug S. Poyraz[6], Elsa Reichmanis[7], Kenneth J. Takeuchi[1], Feng Wang[3], Lei Wang[3], Alan C. West[8], Stanislaus Wong[1], Guihua Yu[9], Yimei Zhu[3]

[1]Stony Brook University (lead institution); [2]Cornell University; [3]Brookhaven National Laboratory; [4]Lawrence Berkeley National Laboratory; [5]Drexel University; [6]Kennesaw State University; [7]Lehigh University; [8]Columbia University; [9]University of Texas at Austin

The m2M/t mission is to build the scientific knowledge base necessary to enable future creation of scalable electrochemical energy storage systems with high energy, high power, and long life.

URL: https://www.stonybrook.edu/commcms/m2m/

O-B-3: [EFRC – SCALAR] SYNTHETIC CONTROL ACROSS LENGTH-SCALES

Bradley Chmelka[1], Xiangfeng Duan[2], Bruce S. Dunn[2], Jian Luo[3], Brent C. Melot[4], Thomas F. Miller III[5], Sri R. Narayan[4], Laurent Pilon[2], Philippe Sautet[2], Kimberly A. See[5], Rachel Segalman[1], Ram Seshadri[1], Alex Spokoyny[2], Barry C. Thompson[4], Sarah H. Tolbert[2], Anton Van der Ven[1], and Johanna Nelson Weker[6]

[1]University of California, Santa Barbara; [2]University of California, Los Angeles (lead institution); [3]University of California, San Diego; [4]University of Southern California; [5]California Institute of Technology; [6]SLAC National Accelerator Laboratory

The SCALAR mission is to take a holistic approach to the design of new functional materials that bridges the atomistic, nanometer, and macro length-scales in the quest to improve battery performance, leveraging molecular and solid-state synthetic methods, combined with solution phase self-assembly, to create new electrode materials that increase capacity, reduce losses, and improve reversibility in rechargeable batteries.

URL: http://www.chem.ucla.edu/SCALAR/

O-B-4: [EFRC – CABES] Center for Alkaline Based Energy Solutions

Héctor D. Abruña[1], Tomás Arias[1], Joel Brock[1], Peng Chen[1], Geoffrey Coates[1], Francis DiSalvo[1], Robert DiStasio[1], Jiye Fang[2], Emmanuel Giannelis[1], Lena Kourkoutis[1], Tom Mallouk[3], Manos Mavrikakis[4], David Muller[1], Paul F. Mutolo[1], Kevin Noonan[5], Piotr Zelenay[6], Bryan Pivovar[7], Sharon Hammes-Shiffer[8], Andrej Singer[1], Jin Suntivich[1]

[1]Cornell University (lead Institution); [2]Binghamton University; [3]University of Pennsylvania; [4]University of Wisconsin-Madison; [5]Carnegie Mellon University; [6]Los Alamos National Laboratory; [7]National Renewable Energy Laboratory; [8]Yale University

CABES' mission is to achieve a detailed understanding of the nature, structure, and dynamics of electrocatalysis in alkaline media.
URL: https://cabes.cornell.edu/

O-B-5: [EFRC-BEES] Break Through Electrolytes for Energy Storage

Robert F. Savinell[1], Rohan Akolkar[1], Burcu Gurkan[1], Edward Maginn[3], Thomas Zawodzinski[2], Ah-Hyung (Alissa) Park[4], Allen Bard[8], Clemens Burda[1], Tessa Calhoun[2], Mark Dadmun[2], Steven Greenbaum[5], Emily Pentzer[7], Joshua Sangoro[2], Mark Tuckerman[6], Miomir Vukmirovic[9], Jesse Wainright[1]

[1]Case Western Reserve University (lead institution); [2]University of Tennessee at Knoxville; [3]University of Notre Dame; [4]Columbia University; [5]Hunter College; [6]New York University; [7]Texas A&M University; [8]University of Texas at Austin; [9]Brookhaven National Lab

BEES mission is to develop an understanding of (i) structure-property relationships, (ii) transport mechanisms, (iii) interfacial electrode-electrolyte structure and its evolution, and (iv) electron and ion transfer reactions in deep eutectic solvents (DES) and soft nanoparticles (SNP), and (v) how these structures and properties can be tailored at the atomistic level to advance electrochemical performance in electrochemical energy storage systems.
BEES URL: https://engineering.case.edu/research/centers/breakthrough-electrolytes-for-energy-storage

O-B-6: [EFRC – FIRST] Fluid Interface Reactions, Structures and Transport

Sheng Dai[1], Nina Balke[1], Stephan Irle[1], Paul Kent[1], Shannon Mahurin[1], Eugene Mamontov[1], Robert Sacci[1], Alexei Sokolov[1], Raymond Unocic[1], Hsiu-Wen Wang[1], David Wesolowski[1], Veronica Augustyn[2], Peter Cummings[3], Takeshi Egami[4], Paul Fenter[5], Yury Gogotsi[6], De-en Jiang[7], Jianzhong Wu[7], Michael Naguib[8], Marek Pruski[9], Adri Van Duin[10]

[1]Oak Ridge National Laboratory (lead institution); [2]North Carolina State University; [3]Vanderbilt University; [4]University of Tennessee, Knoxville; [5]Argonne National Laboratory; [6]Drexel University; [7]University of California, Riverside; [8]Tulane University; [9]Ames Laboratory; [10]Penn State University

To achieve fundamental understanding and validated, predictive models of the atomistic origins of electrolyte and coupled electron transport under nanoconfinement that will enable transformative advances in capacitive electrical energy storage and other energy-relevant interfacial systems. **URL:** https://web.ornl.gov/sci/first/

C. Energy-Water

O-C-1: [EFRC – M-WET] The Center for Materials for Water and Energy Systems

Benny D. Freeman[1], Lynn Katz[1], Rachel Segalman[2], Mahdi Abu-Omar[2], Chris Bates[2], Ethan Crumlin[3], Michael Doherty[2], Glenn Fredrickson[2], Venkat Ganesan[1], Songi Han[2], Craig Hawker[2], Alex Hexemer[3], Manish Kumar[1], Desmond Lawler[1], Nate Lynd[1], Dylan McReynolds[3], Zak Page[1], Donald Paul[1], Mukul Sharma[1], M. Scott Shell[2], Todd Squires[2], Gregory Su[3], Tom Truskett[1], Cheng Wang[3], Michael Webber[1]

[1]The University of Texas at Austin (lead institution); [2]University of California, Santa Barbara; [3]Lawrence Berkeley National Laboratory

M-WET's mission is to discover and understand fundamental science to design new membrane materials, develop tools and knowledge to predict new materials' interactions with targeted solutes, inspired by the need to provide fit for purpose water from low quality water sources and recover valuable solutes with less energy. **URL:** https://mwet.utexas.edu/

O-C-2: [EFRC – AMEWS] Advanced Materials for Energy-Water Systems

Wei Chen[1], Seth B. Darling[1,2], Juan J. de Pablo[1,2], Jeffrey W. Elam[1], Giulia Galli[1,2], Harold H. Kung[3], Chong Liu[2], Alex B.F. Martinson[1], Karen L. Mulfort[1], Paul Nealey[1,2], George C. Schatz[3], Steven J. Sibener[2], Dmitri Talapin[1,2], David M. Tiede[1], Matthew V. Tirrell[1,2], Andrei Tokmakoff[2], Gregory A. Voth[2], Nestor J. Zaluzec[1]

[1]Argonne National Laboratory (lead institution); [2]University of Chicago; [3]Northwestern University

The mission of the Advanced Materials for Energy-Water Systems (AMEWS) Center is to understand and design water-solid interfaces to enable future advances in materials for efficient water treatment, focusing on adsorption, reactivity, and transport.
URL: http://www.anl.gov/amews

O-C-3: [EFRC – CMC-UF] Center for Mechanistic Control of Unconventional Formations

Anthony R. Kovscek[1], Vladimir Alvarado[2], Saman Aryana[2], John R. Bargar[3], Illenia Battiato[1], Sally M. Benson[1], Gordon E. Brown Jr.[1,3], Jennifer L. Druhan[4], Matthias Ihme[1], Kristian Jessen[5], Teresa E. Lehmann[2], Hamdi A. Tchelepi[1], Theo T. Tsotsis[5], Christopher Zahasky[6], Mark D. Zoback[1]

[1]Stanford University (lead institution); [2]University of Wyoming; [3]SLAC National Accelerator Laboratory; [4]Univeristy of Illinois Urbana Champaign; [5]University of Southern California; [6]University of Wisconsin

CMC-UF provides crosscutting knowledge to achieve mechanistic control over the various nonequilibrium physical and geochemical processes that occur in extreme geological environments such as shale, mudstones, and other tight rocks with nanoscale pores.
URL: https://efrc-shale.stanford.edu

O-C-4: [EFRC – MUSE] Multi-Scale Fluid-Solid Interactions in Architected and Natural Materials

Michael Bartl[1], Darryl Butt[1], Milind Deo[1], Greeshma Gadikota[2], Michael Hoepfner[1], Joshua Kane[3], John Kaszuba[4], Jaioyan Li[5], Jules Magda[1], John McLennan[1], Brian McPherson[1], Jan Miller[1], Swomitra Mohanty[1], Pania Newell[1], Bryony Richards[1], Subhash Risbud[6], James Sutherland[1], Adri van Duin[7], Ilya Zharov[1]
[1]University of Utah (lead institution); [2]Cornell University; [3]Idaho National Laboratory; [4]University of Wyoming; [5]University of Buffalo; [6]University of California-Davis; [7]Pennsylvania State University

The mission of MUSE is to develop a new fundamental understanding and models of the transport and interfacial properties of fluids confined by porous media by integrating multi-scale experimental and theoretical methods including state-of-the-art microscopy imaging, and validated multi-scale, physics-based modeling of hierarchical and natural nanostructured materials of varying levels of physical and chemical heterogeneities.
See efrcmuse.utah.edu for details on the team and peer reviewed publications.

O-C-5: [EFRC – CENT] Center for Enhanced Nanofluidic Transport

Michael Strano[1], YuHuang Wang[2], Aleksand Noy[3], Zuzanna Siwy[4], Mark Reed[5], Narayana Aluru[6], Martin Bazant[1], Daniel Blankschtein[1], John Cumings[2], Menachem Elimelech[5], John T. Fourkas[2], Heather Kulik[1], Arun Majumdar[7], Charles Martin[8], Tuan Anh Pham[3], Eric Schwegler[3]
[1]Massachusetts Institute of Technology (lead institution); [2]University of Maryland; [3]Lawrence Livermore National Laboratory; [4]University of California, Irvine; [5]Yale University; [6]University of Illinois at Urbana-Champaign; [7]Stanford University; [8]University of Florida

CENT (https://cent.mit.edu/) will address emerging and compelling gaps in our knowledge of fluid flow and molecular transport in single digit nanopores and establish the scientific foundation for developing transformative molecular separation technologies impacting the Water – Energy Nexus.

O-C-6: [CCS – CSI] CHEMISTRY IN SOLUTION AND AT INTERFACES

Emily A. Carter[1,2], Pablo G. Debenedetti[2], Weinan E[2], Marivi Fernandez-Serra[3], Michael L. Klein[4], Neepa Maitra[5], Spiridoula Matsika[4], Athanassios Z. Panagiotopoulos[2], Annabella Selloni[2], Frank Stillinger[2], Salvatore Torquato[2], Xifan Wu[4], Roberto Car[2]
[1]University of California, Los Angeles; [2]Princeton University (lead institution); [3]Stony Brook University; [4]Temple University; [5]Rutgers University-Newark

CSI unites PIs at five universities to meet the challenge of simulating molecular processes in water and its solutions with multi-scale methodologies. Key to this effort is the development of machine learning (ML) approaches that extend ab-initio molecular dynamics simulations to unprecedented size and time scales without loss of accuracy (http://chemlabs.princeton.edu/ccsc/).

A major accomplishment has been the development of the Deep Potential (DP) methodology, whereby a deep neural network trained on quantum mechanical (density functional theory (DFT)) data models the potential energy surface of a multi-atom system. DP makes possible molecular dynamics simulations of millions of atoms on timescales of tens to hundreds of nanoseconds on state-of-the-art multi-GPU platforms, like the Summit supercomputer at ORNL. For this achievement DP was awarded the 2020 Gordon Bell Prize of the Association of Computing Machinery (ACM). An extension of the scheme, called Deep Wannier (DW), models polarization and polarizability surfaces, needed for computing the vibrational spectra measured in experiments. A further extension, called Deep Potential-Long Range combines DP and DW to model long-range electrostatics effects crucial in many energy applications. Recently, ML has been used to generate approximate DFT functionals. Preliminary tests suggest that xc-diff, an ML-generated meta-GGA functional can be more accurate than SCAN, the gold standard at this level of theory. The algorithms and software developed at CSI have been used in the applications outlined in the technical posters of CSI. They include studies of water thermophysical properties, water solutions, water solutions at material interfaces, and electron transfer in solvated environments.

D. MATERIALS/CHEMISTRY BY DESIGN AND SYNTHESIS

O-D-1: [EFRC – CBES] CENTER FOR BIO-INSPIRED ENERGY SCIENCE

Samuel I. Stupp[1], Joanna Aizenberg[2], Anna Balazs[3], Kyle Bishop[4], Paul Chaikin[5], Danna Freedman[1], Sharon Glotzer[6], Erik Luijten[1], Chad Mirkin[1], Monica Olvera de la Cruz[1], George Schatz[1], Emily Weiss[1], George Whitesides[2]
[1]Northwestern University (lead institution); [2]Harvard University; [3]University of Pittsburgh; [4]Columbia University; [5]New York University; [6]University of Michigan

CBES

The mission of the Center for Bio-Inspired Energy Science is to develop the next frontier in soft materials by designing structures that emulate many of the properties we see in biological systems. **URL:** https://cbes.northwestern.edu/

O-D-2: [EFRC – CLSF] CENTER FOR LIGNOCELLULOSE STRUCTURE AND FORMATION

Daniel J. Cosgrove[1], Charles T. Anderson[1], Paul Dupree[2], Enrique D. Gomez[1], Esther W. Gomez[1], Ying Gu[1], Candace H. Haigler[3], Mei Hong[4], Seong H. Kim[1], James D. Kubicki[5], B. Tracy Nixon[1], Hugh O'Neill[6], Alison W. Roberts[7], Tuo Wang[8], Yaroslava G. Yingling[3], Jochen Zimmer[9]

[1]The Pennsylvania State University (lead institution); [2]University of Cambridge; [3]North Carolina State University; [4]Massachusetts Institute of Technology; [5]University of Texas El Paso; [6]Oak Ridge National Laboratory; [7]University of Rhode Island; [8]Louisiana State University; [9]University of Virginia

Our mission at the Center for Lignocellulose Structure and Formation (CLSF) is to develop a nano- to meso-scale understanding of cellulosic cell walls, the energy-rich structural material in plants, and the physical mechanisms of wall assembly, forming the foundation for new technologies in sustainable energy and novel biomaterials. **URL:** http://lignocellulose.org/

O-D-3: [CCS – HETCAT] DEVELOPMENT OF EXASCALE FOR HETEROGENEOUS AND INTERFACIAL CATALYSIS

Mark S. Gordon[1], James Evans[1], Theresa L. Windus[1], Laura Carrington[2], Sarom Leang[2], Ananta Tiwari[2], Daniel Crawford[3], Heike Jagode[4], Anthony Danalis[4], David Sherrill[5], Masha Sosonkina[6]

[1]Iowa State University; [2]EP Analytics; [3]Virginia Polytechnic Institute and State University; [4]University of Tennessee, Knoxville; [5]Georgia Institute of Technology; [6]Old Dominion University

Summary: We are developing accurate *ab initio* electronic structure methods that have greatly reduced scaling with system size, to facilitate the application of these methods to heterogeneous catalysis for reactions that are important to the Department of Energy. The catalysts of primary interest are mesoporous silica nanoparticles (MSN); however, the methods developed in the proposed research will be applicable to *all* catalysts, heterogeneous and homogeneous. The developed electronic structure methods are being interfaced with advanced methods in non-equilibrium statistical mechanics that will enable the study of diffusion processes in nanopores, as well as the chemical reactivity. Computational investigations of heterogeneous catalysis require the explicit incorporation of many thousands of atoms in the simulations. Consequently, such simulations require algorithms that are able to take effective advantage of pre-exascale and exascale computers that are expected to become available within the next five years. The electronic structure method development will focus on fragmentation methods, the development of new dataflow algorithms, the exploration of novel computer architectures that can potentially reduce the energy/power consumption without significant adverse effects on time-to-solution, the development of interoperability among three no-cost electronic structure programs, and the creation of a quantum chemistry data base (QCDB) that can be used by any electronic structure program, all enabled by machine and deep learning paradigms. **URL:** https://hetcat-ccs.github.io

O-D-4: [EFRC – UNCAGE-ME] The Center for Understanding & Control of Acid Gas-Induced Evolution of Materials for Energy

Krista Walton[1], Christopher Jones[1], David Sholl[1], Sankar Nair[1], Rampi Ramprasad[1], Zili Wu[2], Bobby Sumpter[2], Katharine Page[2], Susan Sinnott[3], JR Schmidt[4], Israel Wachs[5], Jonas Baltrusaitas[5], Sophia Hayes[6], Tina Nenoff[7], Jessica Rimsza[7], Dave Dixon[8], Ryan Lively[1]

[1]Georgia Institute of Technology (lead institution); [2]Oak Ridge National Laboratory; [3]Pennsylvania State University; [4]University of Wisconsin-Madison; [5]Lehigh University; [6]Washington University in St. Louis; [7]Sandia National Laboratories; [8]The University of Alabama

Mission Statement: To develop and harness a deep knowledge base in the characterization, prediction, and control of acid-gas interactions with a broad class of materials to accelerate materials discovery in acid gas separations, conversion, and utilization. **URL:** https://www.efrc.gatech.edu

O-D-5: [CCS – NMGC] Nanoporous Materials Genome Center

J. Ilja Siepmann[1], Jason D. Goodpaster[1], Sapna Sarupria[1], Donald G. Truhlar[1], Jingyun Ye[2], David S. Sholl[3], Randall Q. Snurr[4], Laura Gagliardi[5], Coray M. Colina[6], David C. Cantu[7], Alan Aspuru-Guzik[8], Christopher Knight[9], Álvaro Vazquez-Mayagoitia[9]

[1]University of Minnesota–Twin Cities (lead institution); [2]Clarkson University; [3]Georgia Institute of Technology; [4]Northwestern University; [5]University of Chicago; [6]University of Florida; [7]University of Nevada–Reno; [8]University of Toronto; [9]Argonne National Laboratory

The Nanoporous Materials Genome Center (NMGC) develops exascale-ready software, computational/ theoretical chemistry methods, and data-driven science approaches that enable (i) the de-novo design of functional nanoporous materials (NPMs) for chemical separation and catalysis tasks of increasing complexity, (ii) the discovery of the most promising functional NPMs from databases of synthesized and hypothetical framework structures and the optimization of process conditions for specific applications, and (iii) the microscopic-level understanding of the fundamental interactions underlying the function of NPMs. The NMGC constructs NPM models that extend beyond currently accessible crystalline and/or homogeneous chemical systems to include hierarchical architectures, composite materials, responsive frameworks, and materials containing defects or partial disorder. NMGC website: http://nmgc.umn.edu/

O-D-6: [CCS – FLOSIC] EFFICIENT DENSITY FUNCTIONAL CALCULATIONS WITHOUT SELF-INTERACTION

Koblar A. Jackson[1], Juan Peralta[1], G. Christou[2], J. Karl Johnson[3], T. Baruah[4], R. Zope[4], M.R. Pederson[4], A. Ruzsinszky[5], J.P. Perdew[5]

[1]Central Michigan University (lead institution); [2]University of Florida at Gainesville; [3]University of Pittsburgh; [4]The University of Texas at El Paso; [5]Temple University

The FLOSIC Center (https://flosic.org) was funded by the U.S. Department of Energy in September 2017 as one of several Computational Chemical Sciences Centers. The Center's research is aimed at developing improved first-principles, density functional theory (DFT) -based methods for computationally modeling molecules and materials at the atomic level. It combines thrusts in the areas of software development and theory to address applications in the remaining thrust areas of catalysis and molecular scale magnetism. The ultimate goal of the Center is to produce user-friendly open-source software that allows efficient and predictive modeling of materials without the unphysical effects of electron self-interaction, the major flaw present in existing DFT-based methods.

O-D-7: [CCS – SPEC] Scalable Predictive Methods for Excitations and Correlated Phenomena

Sotiris S. Xantheas[1], Edoardo Aprà[1], Anne Chaka[1], Wibe de Jong[2], Thom H. Dunning, Jr.[3], Niranjan Govind[1], So Hirata[4], Sriram Krishnamoorthy[1], Karol Kowalski[1], Xiaosong Li[3], John J. Rehr[3], Chao Yang[2], Dominika Zgid[5]

[1]Pacific Northwest National Laboratory (lead institution); [2]Lawrence Berkeley National Laboratory;
[3]University of Washington; [4]University of Illinois; [5]University of Michigan

The Center for Scalable, Predictive methods for Excitation and Correlated phenomena (SPEC, https://spec.labworks.org/home) aims at providing the capability to enable scientists to simulate excited states and excited state processes with unprecedented predictive power and orders-of-magnitude greater computational performance than current methods. Our efforts aspire to remove a major barrier to realizing discoveries from next-generation experiments at BES light sources and accelerate progress on Grand Challenges in fields such as solar energy capture, catalysis, and energy storage. Our multidisciplinary team consisting of domain scientists, computer scientists and applied mathematicians who are working towards coupling theoretical and computational breakthroughs to deliver scalable, open-source software libraries suitable for simulating realistic systems on extreme-scale leadership computing facilities.

O-D-8: [EFRC – IQM] INSTITUTE FOR QUANTUM MATTER

Collin L. Broholm[1], N. Peter Armitage[1], Robert J. Cava[2], Natalia Drichko[1], Seyed M. Koohpayeh[1], Yi Li[1], Tyrel M. McQueen[1], Satoru Nakatsuji[1], Predrag Nikolic[1], Brad Ramshaw[3], Nitin Samarth[4], Oleg Tchernyshyov[1], David Vanderbilt[5]

[1]Johns Hopkins University (lead institution); [2]Princeton University; [3]Cornell University; [4]Penn State University; [5]Rutgers University

IQM realizes revolutionary quantum materials and structures where quantum effects such as entanglement and coherence find collective macroscopic manifestations. We expose, understand, and control the corresponding physical properties and explore the potential for energy related applications.
URL: https://iqm.jhu.edu/

O-D-9: [EFRC – Q-MEEN-C] QUANTUM MATERIALS FOR ENERGY EFFICIENT NEUROMORPHIC COMPUTING

Amanda Petford-Long[1], Alex Frano[2], Andy Kent[3], Axel Hoffmann[4], Robert Dynes[2], Eric Fullerton[2], Julie Grollier[5], Giulia Galli[6], Ivan K. Schuller[2], Jonathan Schuller[7], Marcelo Rozenberg[6], Mark Stiles[8], Oleg Shpyrko[2], Shriram Ramanathan[9], Shyue Ping-Ong[2], Vitaly Lomakin[2], Yayoi Takamura[10], Yeshaiahu Fainman[2], Yimei Zhu[11]

[1]Northwestern University; [2]University of California San Diego (lead institution); [3]New York University; [4]University of Illinois Urbana-Champaign; [5]Centre National de la Recherche Scientifique; [6]University of Chicago; [7]University of California Santa Barbara; [8]National Institute of Standards and Technology; [9]Purdue University; [10]University of California Davis; [11]Brookhaven National Laboratory

The mission of Q-MEEN-C is to generate the quantum-materials-based foundation for the development of an energy-efficient, fault-tolerant computer that is inspired by the human brain (“neuromorphic”). Energy-efficient neuromorphic computing offers a potentially disruptive technological capability to process complex inputs and produce elegantly simple, useful outputs. The breakaway from the conventional technology, the Turing-von Neumann paradigm, requires the development of new types of bio-inspired devices with functionalities resembling those of the brain’s synapses, neurons, axons, and dendrites that can be used to construct machines with artificial intelligence capabilities. Q-MEEN-C’s approach to achieving this focuses on research in the domains of both Charge- and Spin-related phenomena in quantum materials.
URL: https://qmeenc.ucsd.edu/

O-D-10: [CMS – C2SEPEM] Center for Computational Study of Excited-State Phenomena in Energy Materials

Steven G. Louie[1,2], James R. Chelikowsky[3], Jack R. Deslippe[1], Naomi Ginsberg[1,2], Felipe H. da Jornada[4], Jeffrey B. Neaton[1,2], Daniel Neuhauser[5], Diana Y. Qiu[6], Eran Rabani[1,2], Feng Wang[1,2], Chao Yang[1]
[1]Lawrence Berkeley National Laboratory (lead institution); [2]University of California at Berkeley; [3]University of Texas at Austin; [4]Stanford University; [5]University of California at Los Angeles; [6]Yale University

The mission of the Center for Computational Study of Excited-State Phenomena in Energy Materials (C2SEPEM) is to develop and implement new theories, methods, algorithms, and computer codes to explain and predict excited-state phenomena in materials. C2SEPEM performs research on first-principles many-body perturbation theory and advanced algorithms, as well as their experimental validation and efficient implementation to high performance computers. Studies on quasiparticle excitations, optical spectra, trion and bi-exciton formation, exciton-exciton interactions, nonlinear optical processes, time-dependent phenomena, and more are carried out for bulk and reduced-dimensional systems. These phenomena are particularly important in processes of energy conversion, transport and storage. Existing *ab initio* methods and software, especially for multiple-particle correlated excitations and time-dependent electron phenomena incorporating essential electron-electron interactions, have however been under explored and hence limiting their studies in real materials. The work at C2SEPEM (through a team of physical scientists, applied mathematicians and computational scientists) aims to fill this gap. In addition to expanding the frontiers of knowledge, an end product will be an integrated open-source software package, BerkeleyGW and associated codes, with capabilities (utilizing current petascale and future exascale high performance computers) to predict and understand a variety of excited-state phenomena from first principles. The research, based on equilibrium and nonequilibrium interacting multi-particle Green's function approaches, are validated via spectroscopic and other excited-state experiments. Software with new functionalities are regularly released to the community. **URL:** https://c2sepem.lbl.gov/

O-D-11: [CMS – QMC-HAMM] High accuracy multiscale models from quantum Monte Carlo

David Ceperley[1], Lucas K. Wagner[1], Elif Ertekin[1], Harley T. Johnson[1], Matt Turk[1], Andriy Nevidomskyy[2]
[1]University of Illinois Urbana-Champaign (lead institution); [2]Rice University

The state of the art in creating mesoscopic models starting from the microscopic behavior is based on density functional theory (DFT) calculations. In recent years, modern machine learning techniques have been able to reproduce potential energy surfaces from standard DFT functionals to a very high accuracy; the accuracy of the potential energy surfaces is often limited by the underlying DFT data. In quantum materials such as twisted bilayer graphene, effective electron interactions and weak van der Waals interactions can be critical to their behavior, which DFT does not treat accurately. Similarly, the phase diagram of hydrogen at high pressures and temperatures depends sensitively on the energy difference between very different phases, which are hard to treat with simple off-the-shelf electronic structure techniques.

To improve the quality of data on which mesoscopic models are based, it is necessary to move beyond density functional theory and to base mesoscopic models on more accurate microscopic calculations. The QMC-HAMM project uses quantum Monte Carlo (QMC) techniques to compute the properties of materials very accurately. Multiscale models are then derived based on these accurate calculations, using software and data to glue highly accurate QMC calculations to lattice-scale and continuum models of materials. In this poster, we will give an overview of the software and data ecosystem we are creating to accurately model and understand hydrogen and twisted 2D materials. **URL:** https://qmc-hamm.github.io

O-D-12: [CCS – PsiXC] From Wave Functions to Exchange Correlation for Large-Scale Electronic Structure

Bikash Kanungo, Khoi Dang, Vikram Gavini, Paul M. Zimmerman
University of Michigan

The two most widely used *ab initio* strategies for chemical and materials simulations are wave function and density functional theories (WFT, DFT). These methods were developed along parallel, but fundamentally different pathways. Among their differences are limits in applicability: WFT can be tuned to arbitrary accuracy, but scales poorly, while DFT is highly scalable, but strategies to obtain further accuracy are ambiguous. This project seeks to better intertwine WFT and DFT by creating new mechanisms for WFT to inform the design of more accurate DFT functionals, and for the resultant DFT to improve the computational efficiency of WFT.

This poster introduces two key components of this effort and describes how they will be combined into a synergistic strategy to improve both the scalability and the accuracy of first principles simulations. First, finite element methods — which provide a systematic and complete basis set—are used alongside a density inversion algorithm to convert electron densities into accurate exchange-correlation potentials. Second, new algorithms for full configuration interaction will give WFT benchmark results for challenging, strongly correlated models. The two components—when used together—will facilitate the training of new density functionals using the exact 3D exchange-correlation potential. The new functionals are aimed at capturing strong correlation effects using the DFT ansatz, with the goal of achieving WFT-like accuracy.

O-D-13: [CSM – EPW] Toward Exascale Computing of Electron-Phonon Couplings For Finite-Temperature Materials Design

Feliciano Giustino[1], Emmanouil Kioupakis[2]
[1]The University of Texas at Austin (lead institution); [2]University of Michigan at Ann Arbor

Functional materials for energy, electronics, and lighting operate at a finite, nonzero temperature. However, since finite-temperature calculations are challenging, most computational approaches to materials modeling and design focus on zero-temperature properties. For example, while high-throughput calculations of total energies at zero temperature are commonplace, screening materials for temperature-dependent properties such as electrical conductivity or luminescence quantum yield is currently beyond reach. Our mission is to enhance the technological and societal impact of computational materials design by enabling exascale calculations of materials properties at finite temperature. We are primarily interested in designer materials for post-Moore electronics, solar photovoltaics, and energy-efficient lighting. To realize this mission, we develop new first-principles theoretical and computational methods for calculating electron-phonon interactions and phonon-assisted quantum processes with predictive accuracy, for example temperature-dependent band structures, carrier mobilities and conductivities, and temperature-dependent optical phenomena such as light scattering, absorption, and luminescence. The backbone of the project is the EPW code, a leading open-source software for the study of electron-phonon interactions and materials properties at finite temperature. In this project we are expanding the functionality of EPW, enhancing its parallel scaling efficiency, and broadly engaging users and developers. Our progress is shared in real time with the community, using a transparent development model based on a continuous integration and deployment pipeline, and the software is released periodically under the GPL open-source license. The landing page of the project and code website, epw-code.org, contains information for a general audience. The subdomain docs.epw-code.org offers detailed documentation, benchmarks, and citation stats, and the subdomain forum.epw-code.org hosts a popular user form maintained by the team.

O-D-14: [CMS – MICCoM] Midwest Integrated Center for computational Materials

G. Galli[1,2], M. Chan[1], J. J. de Pablo[1,2], A. Ferguson[1], M. Govoni[1,2,] F. Gygi[3], J. Heremans[1], D. Talapin[1,2], J. K. Whitmer[4]
[1]Argonne National Laboratory (lead institution); [2]University of Chicago; [3]University of California Davis; [4]University of Notre Dame

The Midwest Integrated Center for Computational Materials, MICCoM (http://miccom-center.org/) develops and disseminates interoperable computational tools – open-source software, data, simulation methods, and validation procedures – that enable the community to simulate and predict properties of functional materials for energy conversion, and solid-state materials for quantum information science. The center is focused on the prediction of properties of heterogeneous systems composed of atomistic and nanoscale building blocks; the emphasis is placed on understanding and characterizing defects and interfaces, and on predicting finite-temperature spectroscopic and coherence properties. To predict the properties of heterogeneous systems, the center develops first principles electronic-structure methods, coupled to appropriate dynamical descriptions of matter and advanced sampling techniques, so as to capture all the relevant length and time scales of importance to materials design. Here we describe recent progress in coupling classical and quantum codes for the description of matter at the atomistic and molecular scales, together with their use to solve problems for molecules and condensed systems, including the study of chemical reactions at surfaces, aqueous interfaces, nanostructured materials, and solid-state qubits.

O-D-15: [CMS – COMSCOPE] CENTER FOR COMPUTATIONAL MATERIAL SPECTROSCOPY AND DESIGN

Gabi Kotliar[1,2], Sangkook Choi[1], Andrey Kuteopov[1], Corey Melnick[1], Robert Konik[1], Mark Dean[1], Cedomir Petrovic[1], Martha Greenblatt[2], Kristjan Haule[2], Kipton Barros[3], Manish Parashar[4], Yong-Xin Yao[5], Gia-Wei Chern[6]

[1]Brookhaven National Laboratory (lead institution); [2]Rutgers University; [3]Los Alamos National Laboratory; [4]University of Utah; [5]Ames National Laboratory; [6]University of Virginia

Strongly correlated materials hold out a promise of serving as the foundation of revolutionary technologies ranging from energy transmission systems to superior thermoelectric devices. But understanding the properties and functionalities of these materials is difficult as standard analytical tools are not well suited to their study. The aim of our DOE BES Computational Materials Science Center, Comscope, is to design and produce methodologies and a computational platform that will do for strongly correlated materials what DFT has done for less correlated systems. Our ultimate vision sees a scientist being able to predict the properties of a correlated material in an ab initio theoretical framework without experimental input. The tools that Comscope is building are predicated on combining dynamical mean field theory (DMFT) with first principles input and are developed to work on a range of computational platforms running the gamut from desktop workstations to leadership class machines. In advancing this vision, *Comscope* supports three code packages. The first of these, *Comsuite*, focuses on cases where correlations are primarily local, implementing three flavors of dynamical mean field theory in order of increasing computational complexity: LDA+RISB, LDA+DMFT, and GW+DMFT. The second Green's function based code is *FlapwMBPT*.

FlapwMBPT not only provides a means to understand the effects of non-local interactions in correlated materials, it also serves as the platform on which *Comsuite* is built. The third package, *EDRIXS*, enables XAS and RIXS computations, and represents *Comscope's* history of activities at NSLS-II.

URL: https://www.bnl.gov/cmpmsd/FlapwMBPT/

O-D-16: [CCS – QUESTC] HIERARCHICAL, SCALABLE GREEN'S FUNCTION MODELING OF CHEMISTRY AT INTERFACES

Mark van Schilfgaarde[1], Jao VandeLagemaat[1], Matt Beard[1], Ross Larsen[1], Mai-Ahn[1], Dimitar Pashov[2]
[1]National Renewable Energy Laboratories (lead institution); [2]King's College, London

This project's mission is to formulate a new, high-fidelity many-body Green's function implementation of electronic structure, called QuestC, aimed at nanostructured molecular systems. QuestC will be built around a reformulation of the Questaal electronic structure code (www.questaal.org) designed for systems in the thermodynamic limit. Through the use of Green's functions rather than the more traditional wave functions, our aim is to create a theoretical chemistry code package that can accurately address larger scale systems without the assumptions commonly made to be able to reach the many-atom scale. Green's function methods also naturally yield two-particle response functions, enabling the theory to probe excitations, in particular charge and spin susceptibilities.

As a Green's function based many-body theory, Questaal straddles density-functional and wave function based methods in accuracy and computational cost and, because it selects its own optimal reference point, offers exceptionally high fidelity compared to other Green's function methods. We will combine the Green's function approach with Questaal's short-ranged basis sets, the near-sightedness principle, and embedding techniques to provide an intuitive and chemically natural path for favorable scaling with system size without having to resort to lower-accuracy methods. These advantages will make it an ideal platform to address molecular systems or chemical systems with mixed boundary conditions, in particular molecular adsorbates interacting with low-dimensional and nanoscale systems for catalysis that are difficult to address with existing methods. By exploiting the short ranged nature of the one-particle basis QuestC will be designed with low-order scaling and heterogeneous parallelism suitable for current and future high-performance computing platforms.

As target applications we will study (1) the roles of defects, dopants and edges in promising nanostructured molecular systems used in solar photochemistry and (2) how the interplay between molecular and extended systems controls excited states, charge and spin transport in organic/inorganic hybrid 2D metal halides. These systems are of current interest to BES as they are actively researched in NREL's Solar Photochemistry core program and in its CHOISE EFRC and they are important systems for future photocatalytic, electrocatalytic and photonic devices.

O-D-17: [CCS – NGMD] AB INITIO MOLECULAR DYNAMICS BEYOND DENSITY FUNCTIONAL THEORY

Thomas F. Miller III[1], Frederick R. Manby[2], Garnet Kin-Lic Chan[1]
[1]California Institute of Technology (lead institution); [2]University of Bristol

We are pursuing theoretical innovations that include coupling highly correlated system wavefunction methods with DFT environments, transferable machine-learning methods for electronic structure, and non-adiabatic dynamics methods based on the path-integral framework.
URL: https://ccs-psi.org/

O-D-18: [EFRC – GENESIS] GENESIS: A Next Generation Synthesis Center

John B. Parise[1], Karena W. Chapman[1], Peter Khalifah[1], Simon L. Billinge[2], Peter J. Chupas[1,3], Kristin A. Persson[4], Gerbrand Ceder[4], Gabriel Veith[5], Brian Phillips[1], James Neilson[6], Katsuyo Thornton[7], Eric Dooryhee[8], Ping Liu[9], Jack Simonson[10]

[1]Stony Brook University (lead institution); [2]Columbia University; [3]Associated Universities Inc.; [4]Lawrence Berkeley National Laboratory; [5]Oak Ridge National Laboratory; [6] Colorado State University; [7] University of Michigan;[8]Brookhaven National Laboratory; [9] University of California, San Diego; [10]Farmingdale State College

GENESIS' mission is to develop a new paradigm for synthesis that accelerates the discovery of materials, by understanding how key structural and chemical transformations during synthesis are governed by the synthesis variables (https://www.stonybrook.edu/genesis/).

O-D-19: [EFRC – CSSAS] The Center For The Science of Synthesis Across Scales

François Baneyx[1], James J. De Yoreo[1, 2], Christopher J. Mundy[1,2], Jim Pfaendtner[1, 2], Lilo Pozzo[1], David Ginger[1], David Baker[1], Chun-Long Chen[1, 2], Brandi Cossairt[1], Andrew Ferguson[3], Samson A. Jenekhe[1], Sergei V. Kalinin[4], F. Akif Tezcan[5]

[1]University of Washington (lead institution); [2]Pacific Northwest National Laboratory; [3]University of Chicago; [4]Oak Ridge National Laboratory; [5]University of California – San Diego

We aim to harness the complex functionality of hierarchical materials by mastering the design of high-information-content building blocks that predictively self-assemble into responsive, reconfigurable, self-healing materials, and direct the formation and organization of inorganic components. **URL:** www.cssas-efrc.com

O-D-20: [EFRC – CHWM] Center for Hierarchical Waste Form Materials

Amoroso Jake[1], Besmann Theodore[2], Brinkman Kyle[3], Grandjean Agnès[4], DiPrete David[1], Hu Shenyang[5], Misture Scott[6], Phillpot Simon[7], Shustova Natalia[2], Wang Lumin[8], Was Gary[8], Hans-Conrad zur Loye[2]

[1]Savannah River National Laboratory; [2]University of South Carolina (lead institution); [3]Clemson University; [4]Commissariat à l'Energie Atomique (CEA); Pacific Northwest National [5]Laboratory; [6]Alfred University; [7]University of Florida; [8]University of Michigan

To combine experiment and modeling to develop the chemistry and structure motifs needed to create hierarchical materials that effectively immobilize nuclear waste in persistent architectures

URL: https://chwm.sc.edu

O-D-21: [EFRC – WASTEPD] CENTER FOR PERFORMANCE AND DESIGN OF NUCLEAR WASTE FORMS AND CONTAINERS

Gerald S. Frankel[1], Jincheng Du[2], Stephane Gin[3], Seong H. Kim[4], Jie Lian[5], Joseph V. Ryan[6], James E. Saal[7], John R. Scully[8], John D. Vienna[6], Jianwei Wang[9], Wolfgang Windl[1]

[1]The Ohio State University (lead institution); [2]University of North Texas; [3]Commissariat à l'énergie atomique et aux énergies alternatives (CEA); [4]Pennsylvania State University; [5]Rensselaer Polytechnic Institute; [6]Pacific Northwest National Laboratory; [7]Citrine Informatics; [8]University of Virginia; [9]Louisiana State University

The Center for Performance and Design of Nuclear Waste Forms and Containers (WastePD) is an EFRC comprising a focused scientific effort to understand the details of and commonalities in the aqueous corrosion mechanisms of glass, ceramics, and metals. The mission of WastePD is to understand the fundamental mechanisms of waste form degradation, and to apply that understanding to develop approaches for the design of new waste forms with improved performance. **URL:** https://efrc.osu.edu/

O-D-22: [EFRC – TETI] CENTER FOR THERMAL ENERGY TRANSPORT UNDER IRRADIATION

David Hurley[1], Jian Gan[1], Michael Manley[2], Anter El-Azab[3], Marat Khafizov[4], Krzysztof Gofryk[1], Mukesh Bachlav[1], Michael Benson[1], Lingfeng He[1], Zilong Hua[1], Matthew Mann[5], Chris Marianetti[6], Janelle Wharry[3], Chao Jiang[1], Miaomiao Jin[7], Madhab Neupane[8]

[1]Idaho National Laboratory (Lead Institution); [2]Oak Ridge National Laboratory; [3]Purdue University; [4]The Ohio State University; [5]Airforce Research Laboratory; [6]Columbia University; [7]Pennsylvania State University; [8]University of Central Florida

Mission Statement: To provide the foundational work necessary to accurately model and ultimately control electron- and phonon-mediated thermal transport in 5f-electron materials in extreme irradiation environments.
URL: https://teti.inl.gov/SitePages/Home.aspx

E. NUCLEAR SCIENCE

O-E-1: [EFRC – FUTURE] FUNDAMENTAL UNDERSTANDING OF TRANSPORT UNDER REACTOR EXTREMES

Mark Asta[1], Laurent Capolungo[2], Daniel Edwards[3], Sabrina Hadinoto[2], Edward Holby[2], Peter Hosemann[1], Djamel Kaoumi[4], Tiffany Kaspar[3], Aaron Kohnert[2], Nan Li[2], Digby Macdonald[1], Andrew Minor[1], Raluca Scarlat[1], Daniel Schreiber[3], John Scully[5], Farida Selim[6], Steven Spurgeon[3], Sandra Taylor[3], Blas Uberuaga[2], Yongqiang Wang[2]

[1]University of California, Berkeley; [2]Los Alamos National Laboratory (lead institution); [3]Pacific Northwest National Laboratory; [4]North Carolina State University; [5]University of Virginia; [6]Bowling Green State University

Mission Statement: To understand how the coupled extremes of irradiation and corrosion work in concert to modify the evolution of materials by coupling experiments and modeling that target fundamental mechanisms. **Website:** www.lanl.gov/projects/future

O-E-2: [EFRC – MSEE] MOLTEN SALTS IN EXTREME ENVIRONMENTS

James F. Wishart[1], Simon M. Pimblott[2], Shannon M. Mahurin[3], Yu-chen Karen Chen-Wiegart[1,4], Eric Dooryhee[1], Anatoly I. Frenkel[1,4], Simerjeet K. Gill[1], Benjamin Ocko[1], Kotaro Sasaki[1], Ruchi Gakhar[2], Lingfeng He[2], Gregory Horne[2], Vyacheslav Bryantsev[3], Sheng Dai[3], Alexander Ivanov[3], Claudio J. Margulis[5], Jay A. LaVerne[6], Edward. J. Maginn[6]

[1]Brookhaven National Laboratory (lead institution); [2]Idaho National Laboratory; [3]Oak Ridge National Laboratory; [4]Stony Brook University; [5]The University of Iowa; [6]The University of Notre Dame

MSEE's mission is to provide fundamental and predictive understanding, based in atomistic/molecular level descriptions, of molten salt bulk and interfacial chemistry, including the effects of solutes, impurities and radiation, that will underpin molten salt reactor technology.
URL: https://www.bnl.gov/moltensalts/

O-E-3: [EFRC – IDREAM] INTERFACIAL DYNAMICS IN RADIOACTIVE ENVIRONMENTS AND MATERIALS

Carolyn I. Pearce[1,2], Gregory K. Schenter[1,2], Lawrence A. Anovitz[3], Aurora E. Clark[2,1], Jaehun Chun[1], James J. De Yoreo[1,4], Gregory A. Kimmel[1], Jay A. La Verne[5], Xiaosong Li[4,1], Emily T. Nienhuis[1], Thomas M. Orlando[6], Kevin M. Rosso[1], Andrew G. Stack[3], Linda Young[7], Zheming Wang[1,2], Xin Zhang[1]

[1]Pacific Northwest National Laboratory (lead institution); [2]Washington State University; [3]Oak Ridge National Laboratory; [4]University of Washington; [5]University of Notre Dame; [6]Georgia Institute of Technology; [7]Argonne National Laboratory

The scientific mission of ***IDREAM*** is to master fundamental interfacial chemistry in complex environments characterized by extremes in alkalinity and low-water activity and chemical phenomena driven far from equilibrium by ionizing radiation.

O-E-4: [CCS – NEREST] NUMERICALLY-EXACT RELATIVISTIC MANY-BODY ELECTRONIC STRUCTURE THEORY

Edward F Valeev[1], Robert J Harrison[2], Deborah A Penchoff[3]

[1]Virginia Tech (lead institution); [2]Stony Brook University; [3]University of Tennessee

CCS Center "Numerically-Exact Relativistic many-body Electronic Structure Theory" (NEREST) innovates novel techniques for simulating the relativistic many-body electronic structure with rigorous control of the numerical errors necessary for predictive description of structures, energetics, and spectra of heavy-element compounds. To achieve these goals the traditional Gaussian atomic-orbital technology in favor of adaptive multiresolution real-space numerical representations pioneered by the Center members to represent both low-energy and high-energy spinors. The nearly numerically exact description of relativistic electrons in heavy-element-containing molecules will permit crucial benchmarking of the traditional Gaussian-based (and other) numerical technologies in the context of chemistries and spectroscopy of heavy-element compounds.

O-E-5: [EFRC – CAST] CENTER FOR ACTINIDE SCIENCE & TECHNOLOGY

Thomas E. Albrecht-Schoenzart, Ryan E. Baumbach

Florida State University

The mission of CAST is to advance our understanding of how electronic structure and bonding influence the chemical and physical properties of heavy elements that lead to the development of game-changing nuclear technologies that improve energy security, environmental remediation, and train the next generation of nuclear scientists. **URL:** https://cast.magnet.fsu.edu/

F. Quantum Science and Microelectronics

O-F-1: [EFRC – ULTRA] Ultra Materials for a Resilient, Smart Electricity Grid

Robert J. Nemanich[1], Stephen Goodnick[1], Fernando Ponce[1], Marco Saraniti[1], Arunima Singh[1], David J. Smith[1], Yuji Zhao[1], Debdeep Jena[2], H. Grace Xing,[2] Timothy Grotjohn[3], Jack Flicker[4], Robert Kaplar[4], Srabanti Chowdhury[5], Mary Ellen Zvanut[6], Martin Kuball[7], Alexander Balandin[8], Richard Wilson[8]

[1]Arizona State University (lead institution); [2]Cornell University; [3]Michigan State University; [4]Sandia National Laboratory; [5]Stanford University; [6]University of Alabama Birmingham; [7]University of Bristol; [8]University of California-Riverside

The mission of the Ultra Materials for a Resilient, Smart Electricity Grid (EFRC) (https://ultracenter.asu.edu/) is to understand fundamental phenomena in ultra-wide band gap (UWBG) materials – including synthesis, defect and impurity incorporation, electronic structure at interfaces, the interaction of electrons and phonons at high fields to achieve extreme electrical properties, and phonon phenomena that affect thermal transport. We will establish a Future Grid Co-Design Ecosystem enabling communication across all levels of the science and technology.

O-F-2: [EFRC – 3DFeM] Center for Three Dimensional Ferroelectric Microelectronics

Susan Trolier-McKinstry[1], Nasim Alem[1], Thomas Beechem[2], Ismaila Dabo[1], Saptarshi Das[1], Giovanni Esteves[3], Venkatraman Gopalan[1], Michael David Henry[3], Jon Ihlefeld[4], Thomas Jackson[1], Steven Jesse[5], Sergei Kalinin[5], Kyle Kelley[5], Qi Li[1], Ying Liu[1], Jon-Paul Maria[1], Vijay Narayanan[1], Kai Ni[6], Shashank Priya[1], Shriram Ramanathan[2], Andrew Rappe[7], Joan Redwing[1], Abhronil Sengupta[1]

[1]The Pennsylvania State University (lead institution); [2]Purdue University; [3]Sandia National Laboratories; [4]University of Virginia; [5]Oak Ridge National Laboratory; [6]Rochester Institute of Technology; [7]University of Pennsylvania

MISSION: 3DFeM will exploit the 3rd dimension in microelectronics for functions beyond interconnects by incorporating low-power, non-volatile ferroelectric memory. Ferroelectric materials and new devices will be co-designed, integrated reliably, and densely interconnected with logic to enable low-power, 3D non-von Neumann computation.
Website: https://pennstateoffice365.sharepoint.com/sites/3DFeMSite

O-F-3: [CMS – COMMS] Computational Mesoscale Materials Science

Long-Qing Chen, Ismaila Dabo, Roman Engel-Herbert, Venkatraman Gopalan, Jinchao Xu
Penn State University (lead institution)

The mission of COMMS, a DOE Computational Materials Science (CMS) Center, is to advance the basic mesoscale science of quantum and functional materials and to accelerate their insertion into devices. Its central goal is to further theory, algorithms, exascale computation, and software development for mesoscale quantum and functional materials. The main objectives of the proposed program are to (1) explore and understand the thermodynamic stability of mesoscale structures and their responses to external thermal, mechanical, electric, and magnetic stimuli, (2) develop mesoscale computational models and innovative numerical algorithms to expand these algorithms towards exascale computations, and (3) implement these ideas into a corresponding software for understanding, discovering and manipulating emergent mesoscale architectures and phenomena in quantum and functional materials, and (4) experimentally validate and refine the theory and computational tools using atom-resolution materials synthesis in tandem with cutting-edge quantum characterization methods. A key outcome of the proposed project is an experimentally validated software package, **Q-POP**, for understanding and predicting the mesoscale structure evolution of quantum and functional materials.
URL: https://www.mri.psu.edu/computational-mesoscale-materials-science

O-F-4: [CMS – CPSFM] Center for Predictive Simulations of Functional Materials

Anouar Benali[1], M. Chandler Bennett[2], Anand Bhattacharya[1], Raymond Clay[3], P. Ganesh[2], Olle G. Heinonen[1], Paul R.C. Kent[2], Jaron T. Krogel[2], Ho Nyung Lee[2], Ye Luo[1], Lubos Mitas[4], Brenda Rubenstein[5], Hyeondeok Shin[1], Luke Shulenburger[3]
[1]Argonne National Laboratory; [2]Oak Ridge National Laboratory (lead Institution); [3]Sandia National Laboratories; [4]North Carolina State University; [5]Brown University

CPSFM

The Center for Predictive Simulation of Functional Materials develops, applies, validates, and disseminates parameter-free methods, open source codes, and scientific data to predict and explain the properties of functional materials for energy applications. The Center aims to quantitatively predict, analyze, and eventually design functional and quantum materials with tailored properties that will accelerate new materials development and bring enabling and essential clarity to our modeling and understanding of these materials. The Center develops *robust*, *convergent*, and *generally applicable* electronic structure methods that properly and predictively capture the physics of these materials, primarily using external parameter free Quantum Monte Carlo (QMC) methods in the open source QMCPACK code to achieve this goal. These methods will take full advantage of the upcoming Exascale supercomputers, and strongly complement today's more empirical approaches.
URL: https://cpsfm.ornl.gov/

O-F-5: [EFRC – NPQC] CENTER FOR NOVEL PATHWAYS TO QUANTUM COHERENCE IN MATERIALS

James G. Analytis[1,2], David D. Awschalom[3,4], Dmitri N. Basov[5], Ania C. Bleszynski Jayich[6], Stefano Cabrini[1], Aashish A. Clerk[3,4], Michael F. Crommie[1,2], Giulia Galli[3,4], Supratik Guha[3,4], F. Joseph Heremans[3], Martin Holt[3], Alessandra Lanzara[1,2], Joel E. Moore[1,2], Jeffrey B. Neaton[1,2], Jiwoong Park[3,4], Eli Rotenberg[1], Feng Wang[1,2], Alexander Weber-Bargioni[1], Chao Yang[1], Norman Y. Yao[1,2], Xufeng Zhang[3]

[1]Lawrence Berkeley National Laboratory (lead institution); [2]University of California, Berkeley; [3]Argonne National Laboratory; [4]University of Chicago; [5]Columbia University; [6]University of California, Santa Barbara

The mission of this EFRC is to expand dramatically our understanding and control of coherence in solids by building on recent discoveries in quantum materials along with advances in experimental and computational techniques. [npqc.lbl.gov]

O-F-6: [EFRC – QSQM] QUANTUM SENSING AND QUANTUM MATERIALS

Peter Abbamonte[1], Barry Bradlyn[1], Tai Chiang[1], Thomas Devereaux[2], Ben Feldman[2], Taylor Hughes[1], Angela Kou[1], Vidya Madhavan[1], Nadya Mason[1], Kathryn Moler[2], Dirk Morr[3], Philip Phillips[1], David Reis[2], Zhi-Xun Shen[2], Mariano Trigo[2], Dale Van Harlingen[1], Fahad Mahmood[1], Daniel Shoemaker[1]

[1]University of Illinois, Urbana-Champaign (lead institution); [2]SLAC Linear Accelerator Laboratory; [3]University of Illinois, Chicago

The mission of the QSQM (iquist.illinois.edu/programs/qsqm) is to develop three new quantum sensing techniques—scanning qubit microscopy, two-electron Einstein-Podolsky-Rosen (EPR) spectroscopy, and nonlinear x-ray optics—and use them to study local and nonlocal quantum observables in quantum materials, particularly exotic superconductors, topological crystalline insulators, and strange metals.

O-F-7: [EFRC – CMQT] CENTER FOR MOLECULAR QUANTUM TRANSDUCTION

Michael R. Wasielewski[1], Michael E. Flatté[2], Danna E. Freedman[3], Gregory D. Fuchs[4], Randall E. Goldsmith[5], Mark C. Hersam[1], Ezekiel Johnston-Halperin[6], Matthew D. Krzyaniak[1], Nathalie P. de Leon[7], Jeffrey R. Long[8], Xuedan Ma[1], George C. Schatz[1], Nathaniel P. Stern[1], Roel Tempelaar[1], Emily A. Weiss[1], Joel Yuen-Zhou[9]

[1]Northwestern University (lead institution); [2]University of Iowa; [3]Massachusetts Institute of Technology; [4]Cornell University; [5]University of Wisconsin-Madison; [6]Ohio State University; [7]Princeton University; [8]University of California – Berkeley; [9]University of California – San Diego

The mission of the CMQT is to develop the fundamental scientific understanding needed to carry out quantum-to-quantum transduction through a bottom up synthetic approach which imparts atomistic precision to quantum systems. **URL:** https://cmqt.org

O-F-8: [EFRC – PRO-QM] PROGRAMMABLE QUANTUM MATERIALS

D.N. Basov[1], Ana Asenjo-Garcia[1], Cory Dean[1], James Hone[1], James Shuck[1], Michal Lipson[1], Andrew Millis[1], Abhay Pasupathy[1], Xavier Roy[1], Xiaoyang Zhu[1], David Cobden[2], Daniel Gamelin[2], Jiun-haw Chu[2], Di Xiao[2], Xiaodong Xu[2], Matt Yankowitz[2], Valentina Bisogni[3], Abhay Pasupathy[3]

[1]Columbia University (lead institution); [2]University of Washington; [3]Brookhaven National Laboratory

Mission statement: to discover, characterize, and deploy new forms of quantum matter controllable by gating, light, magnetic proximity, and nano-mechanical manipulation. **URL:** https://quantum-materials.columbia.edu

O-F-9: [EFRC – CATS] Center for the Advancement of Topological Semimetals

Anand Bhattacharya[1], Anton Burkov[2], Paul Canfield[3,4], Olle Heinonen[1], Jennifer Hoffman[5], Pablo Jarillo-Herrero[6], Samuel Jiang[1], Adam Kaminski[3,4], Qiong Ma, Ross McDonald[8], Robert McQueeney[3,4], Peter Orth[3,4], Susanne Stemmer[9], Toni Taylor[8], Ashvin Vishwanath[5], Linlin Wang[3], Dmitry Yarotski[8], Jianxin Zhu[8]
[1]Argonne National Laboratory; [2]University of Waterloo; [3]Ames Laboratory (lead institution); *[4]Iowa State University; [5]Harvard University; [6]Massachusetts Institute of Technology; [7]Boston College; [8]Los Alamos National Laboratory; [9]University of California – Santa Barbara*

CATS' mission is to understand and discover new quantum phenomena and functionality in topological materials with a particular focus on topological semimetals (TSMs). CATS is organized into three crosscutting research thrusts to (1) predict, discover, and understand new bulk magnetic TSMs; (2) discover and control novel quantum states and functionality in thin films and heterostructures; and (3) investigate the dynamical manipulation of topological states. **URL:** http://cats.ameslab.gov

O-F-10: [EFRC – M^{2}QM] Molecular Magnets for Quantum Materials

Hai-Ping Cheng[1], Garnet Chan[2], George Christou[1], Arthur Hebard[1], Stephen Hill[3], Mark Pederson[4], Talat Rahman[5], John Stanton[1], Neil Sullivan[1], Samuel Trickey[1], Vivien Zapf[6], Xiaoguang Zhang[1], Xiao-Xiao Zhang[1]
[1]University of Florida (lead institution); [2]California Institute of Technology; [3]Florida State University; [4]University of Texas El Paso; [5]University of Central Florida; [6]Los Alamos National Laboratory

The goal of the Center for Molecular Magnetic Quantum Materials is to turn molecular magnets into quantum materials that are useful for both quantum information science and for quantum current conventional devices.
URL: https://efrc.ufl.edu/

O-F-11: [EFRC – PTL] Photonics at Thermodynamic Limits

Paul Alivisatos[1], Harry Atwater[2], Paul Braun[3], Mark Brongersma[4], Jennifer Dionne[4], Shanhui Fan[4], Naomi Ginsberg[5], Tony Heinz[4], Aaron Lindenberg[4], Prineha Narang[5], Ralph Nuzzo[6], Eran Rabani[1], Alberto Salleo[4], Eli Yablonovitch[1]
[1]University of California at Berkeley; [2]California Institute of Technology; [3]University of Illinois, Urbana-Champaign; [4]Stanford University (lead institution); [5]Harvard University; [6]University of Illinois Urbana-Champaign

The Photonics at Thermodynamic Limits (PTL) EFRC strives to achieve photonic operations at thermodynamic limits by controlling the flow of protons, electrons and phonons in atomically-architected materials, enabling entirely new energy conversion systems. **URL:** https://ptl.stanford.edu/

G. Solar Energy

O-G-1: [HUB – CHASE] Center for Hybrid Approaches in Solar Energy to Liquid Fuels

Jessica M. Anna[4], Joanna, M. Atkin[1], James F. Cahoon[1], Felix N. Castellano[5], Javier J. Concepcion[3], Jillian L. Dempsey[1], Carrie L. Donley[1], Jeffrey E. Dick[1], Mehmed Ertem[3], Zahra Fakhraai[4], Karen I. Goldberg[4], David C. Grills[3], Sharon Hammes-Schiffer[2], Nilay Hazari[2], Catherine M. Heyer[1], Patrick L. Holland[2], Elena Jakubikova[5], Yosuke Kanai[1], Tim Lian[6], Matthew R. Lockett[1], Rene Lopez[1], Paul A. Maggard[5], Thomas E. Mallouk[4], Gerald F. Manbeck[3], James M. Mayer[2], Gerald J. Meyer[1], Alexander J. M. Miller[1], Gregory N. Parsons[5], Dmitry E. Polyansky[3], Jose A. Rodriguez[1], Renato N. Sampaio[1], Eric A. Stach[4], Stephen J. Tereniak[1], Alexander Tropsha[1], Hailiang Wang[2]

[1]University of North Carolina at Chapel Hill (lead institution); [2]Yale University; [3]Brookhaven National Laboratory; [4]University of Pennsylvania; [5]North Carolina State University; [6]Emory University

The mission of the CHASE Hub is to develop the fundamental science necessary for the synthesis of hybrid photoelectrodes that generate storable liquid fuels using only the small molecules found in air as chemical feedstocks and sunlight as the sole energy source. Pairing the light-absorbing properties of semiconductor materials with the selective fuel-producing reactivity of molecular catalysts, CHASE is advancing a new paradigm of liquid solar fuels generation. This vast, mostly unexplored space at the intersection between molecular catalysts and heterogeneous materials presents unique opportunities for breakthroughs in photocatalyst durability and access to high-octane liquid fuels. **URL:** http://chase.unc.edu.

O-G-2: [Hub – LiSA] Liquid Sunlight Alliance

Harry A. Atwater[1,2], Theo Agapie[1,2], Marco Bernardi[1,2], Scott Cushing[1,2], William Goddard[1,2], John Gregoire[1,2], Joel Haber[1,2], Ryan Hadt[1,2], Jonas Peters[1,2], Kimberly See[1,2], Chengxiang Xiang[1,2], Peter Agbo[1,3], Joel Ager[1,3], Alexis Bell[1,3], Jason Cooper[1,3], Walter Drisdell[1,3], Naomi Ginsberg[1,3], Martin Head-Gordon[1,3], Frances Houle[1,3], Jeff Neaton[1,3], Kristin Persson[1,3], Francesca Toma[1,3], Lin-Wang Wang[1,3], Adam Weber[1,3], Peidong Yang[1,3], Junko Yano[1,3], Bill Tumas[1,4], Emily Warren[1,4], Wilson Smith[1,4], Adele Tamboli[1,4], Andriy Zakutayev[1,4], Nate Neale[1,4], Thomas Jaramillo[1,5], Frank Abild-Pedersen[1,5], Michal Bajdich[1,5], Amy Cordones-Hahn[1,5], Shane Ardo[1,6], Cliff Kubiak[1,7], Shannon Boettcher[1,8]

[1]Liquid Sunlight Alliance; [2]California Institute of Technology (lead institution); [3]Lawrence Berkeley National Laboratory; [4]National Renewable Energy Laboratory; [5]SLAC, National Accelerator Laboratory; [6]University of California, Irvine; [7]University of California, San Diego; [8]University of Oregon

The mission of the Liquid Sunlight Alliance (LiSA) is to establish the science principles by which durable coupled microenvironments can be co-designed to efficiently and selectively generate liquid fuels from sunlight, water, carbon dioxide, and nitrogen. These principles will guide the creation of microenvironment assemblies co-designed to harness diverse sunlight-driven phenomena with unprecedented catalytic selectivity, durability, and efficiency under a fluctuating solar resource, using pure or impure feedstocks. **URL:** http://liquidsunlightalliance.org

O-G-3: [CMS – NPNEQ] Center for Non-Perturbative Studies of Functional Materials under Nonequilibrium Conditions

Tadashi Ogitsu[1], Xavier Andrade[1], Alfredo A. Correa[1], Sangeeta Rajpurohit[2], Liang Tan[2], David Prendergast[2], Das Pemmaraju[3], Aaron M. Lindenberg[3,4]

[1]Lawrence Livermore national Laboratory (lead institution); [2]Lawrence Berkeley National Laboratory; [3]SLAC National Accelerator Laboratory; [4]Stanford University

Functional materials—materials that respond to external stimuli such as voltages, light, and magnetic fields to provide a useful function—are an important aspect of developing cutting-edge technologies. A key focus area within materials science is designing, synthesizing, and characterizing these materials to take full advantage of their capabilities. However, experiments testing the materials' reactions to strong stimuli often produce complex and convoluted data, making it difficult to fully understand the meaning of the results. Additional capabilities enabling direct control of the functional properties of materials in extreme conditions—and thus addressing the complex data—could ultimately transform materials science research and directly benefit future technologies. Advances in high-performance computing (HPC) have provided a platform to perform theoretical modeling at large scales and complexity using density functional theory and quantum molecular dynamics. Researchers then use these models to guide their experiments, taking advantage of advances in experimental techniques to analyze materials and confirm the theories. This experiment–theory approach has guided the development of the multi-disciplinary **Center for Non-Perturbative Studies of Functional Materials under Non-Equilibrium Conditions (NPNEQ)**. The center will focus on the development of scalable software, optimized for state-of-the-art HPC systems, to help interpret complex experimental data. Specifically, the software supports ab initio, non-perturbative studies of functional materials far from equilibrium, enabling predictive simulations to drive fundamental advances in areas such as non-equilibrium quantum materials, attosecond strong-field physics, and warm dense matter. Part of work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344.

Project Website: https://sc-programs.llnl.gov/basic-energy-science-at-llnl/npneq

O-G-4: [EFRC – CHOISE] Center for Hybrid Organic Inorganic Semiconductors for Energy

Matthew C. Beard[1], Joseph Berry[1], Jeffrey Blackburn[1], Volker Blum[2], Giulia Galli[3], Jinsong Huang[4], Yan Li[5], Joseph M. Luther[1], David B. Mitzi[2], Peter C. Sercel[6], Adrienne Stiff-Roberts[2], Michael Toney[7], Z. Valy Vardeny[5], Yanfa Yan[8], Yong Yan[9], Wei You[4], Kai Zhu[1]

[1]National Renewable Energy Laboratory (lead institution); [2]Duke University; [3]University of Chicago; [4]University of North Carolina, Chapel Hill; [5]University of Utah; [6]CHOISE; [7]University of Colorado, Boulder; [8]University of Toledo; [9]San Diego State University

CHOISE Mission: To enable unprecedented synthetic control over the emergent phenomena of spin, charge, and light-matter interactions, in tailored organic-inorganic perovskite-inspired systems for energy science.

URL: https://www.choise-efrc.org/

NO POSTER: [CCS – EXAQC] NOVEL TOOLKIT FOR HARNESSING THE POWER OF EXASCALE COMPUTING FOR CATALYST DESIGN

Anna Krylov[1], Shaama Mallikarjun Sharada[1]
[1]*University of Southern California (lead institution)*

The progress in computing hardware offers tantalizing promises for the advancement of technology and solving pressing societal needs. In chemistry, the ability to run large-scale predictive atomistic simulations can lead to real breakthroughs in photocatalysis and help solve such important problems as anthropogenic CO_2 utilization.

However, to take advantage of the existing and future hardware, the software stack needs to be developed. The team of two PIs from USC will be working on developing key software elements necessary to deploy state-of-the-art theoretical models on exascale. The proposed work includes developing electronic structure algorithms and software and employing them to study catalytic materials. The software will be massively parallelized and made ready for exascale architecture as well as for Cloud computing.

Specifically, we propose to develop tools that will harness the computational power of the next-generation computer architectures and workflow automation methods to carry out high-throughput studies of photochemical and plasmonic pathways for CO_2 reduction. We address the following key aspects: (i) Employ high-level ab initio methods capable of treating open-shell species and multiple electronic states, along with requisite properties enabled by state-of-the-art implementation exploiting cost-reduction techniques and parallelization. (ii) Harness full power of exascale computing to enable exploration of the nuclear degrees of freedom (dynamics, reaction pathways) and statistical sampling. (iii) Implement workflow automation routines, error-handling routines, and data-driven accelerators (such as database-accelerated dynamics and sampling) to enable high-throughput simulations and screening studies for these high-level methods. (iv) Apply these techniques to identify mechanisms of photoredox and plasmonic CO_2 reduction and establish protocols for catalyst design and discovery based on high-throughput screening and reinforcement learning methods.

GRADUATE STUDENT AND POSTDOCTORAL TEAM SCIENCE CONTEST

TEAM SCIENCE TALKS: TUESDAY, OCTOBER 19, 2021; *1:00 – 2:40* PM

(Room: *Team Science Talk,* Enter via GatherTown)

Student and Postdoc Team in orange; Speakers underlined

1:00 pm - 1:10 pm

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

1:11 pm - 1:21 pm

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

1:22 pm - 1:32 pm

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

1:33 pm - 1:43 pm

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

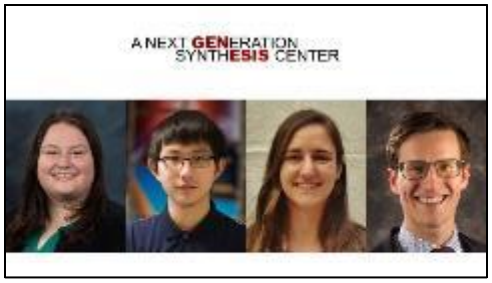

(from left) Zhenglu Li, Mit H. Naik, and Emma C. Regan

1:44 pm - 1:54 pm

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

1:55 pm - 2:05 pm

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

2:06 pm - 2:16 pm

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

2:17 pm - 2:27 pm

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

2:28 pm - 2:38 pm

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 Q&A: 2:40 – 3:00 pm

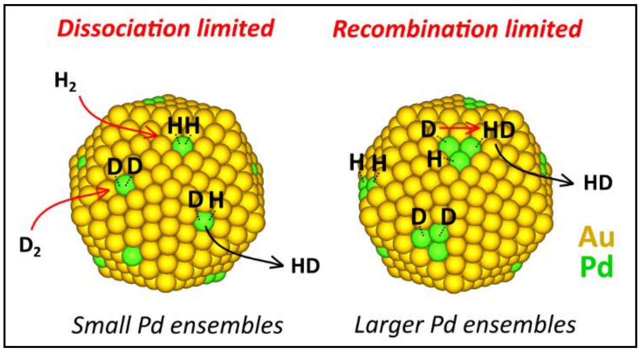
(Room: *Team Q&A,* Enter via GatherTown)

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

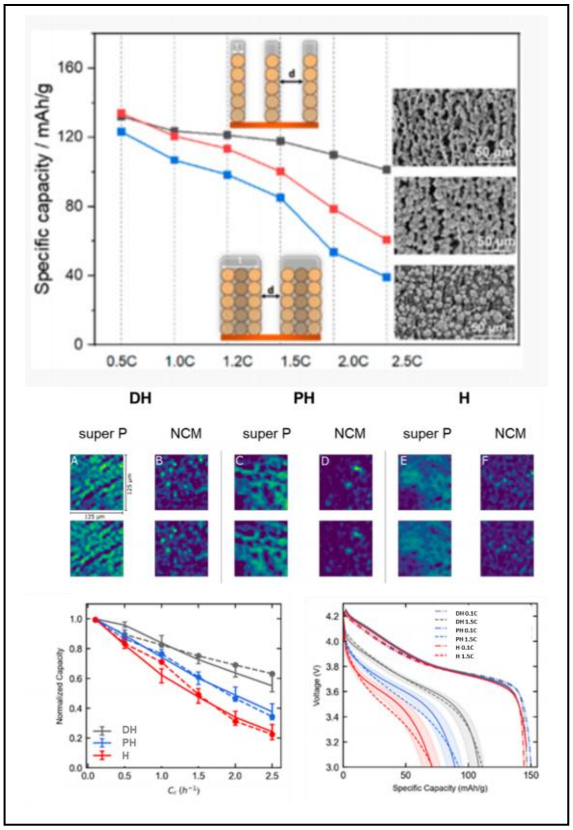
Dilute Pd-in-Au alloy catalysts are promising materials for selective hydrogenation catalysis and have been a focus of IMASC over the past years. Previous surface science studies have contributed mechanistic insight on the energetic aspect of hydrogen dissociation, migration and recombination on dilute 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.

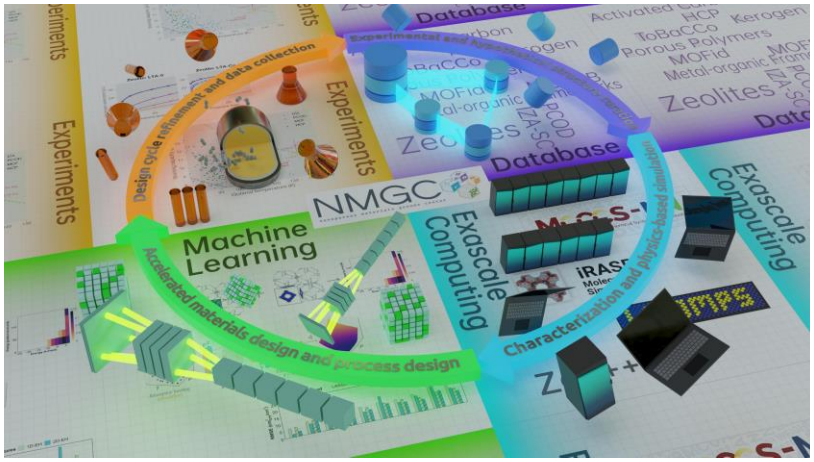
This study brought together expertise in electrode design and fabrication (UTA), detailed 3-dimensional characterization of the electrodes using confocal Raman microscopy paired with NMF analysis (SBU/BNL), and continuum modeling predicting the electrochemistry of the resultant electrodes (CU). The team 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).

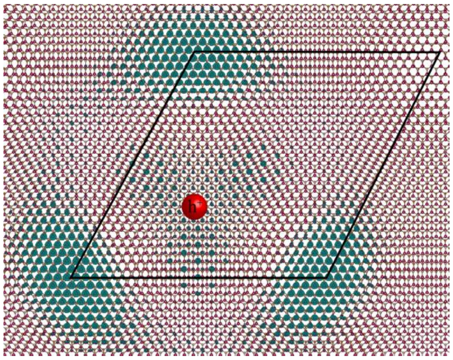


Fig. 1. Calculated electron density isosurface (4% of maximum) for a particular moiré exciton with the hole coordinate fixed at a point (red sphere), showing the charge-transfer character. The solid lines enclose the moiré primitive unit cell.

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.

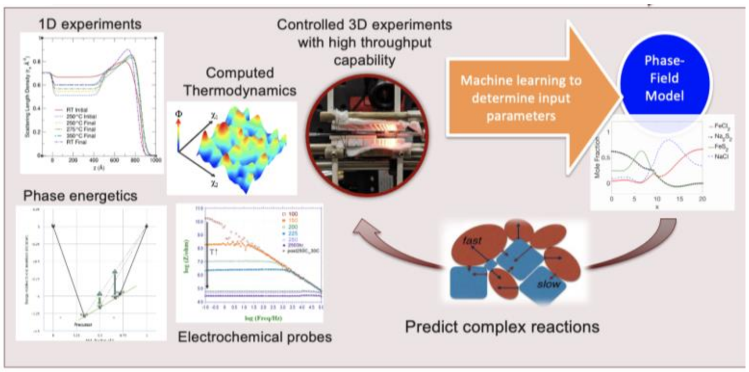


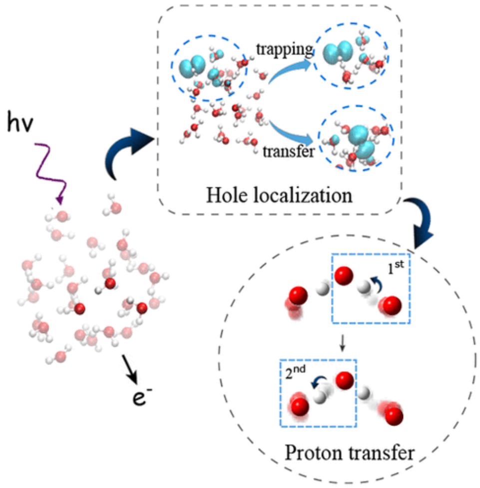
Fig. 1: A schematic of the collaborative effort in GENESIS EFRC, integrating theory, experiments, simulations, and machine learning to elucidate complex reaction pathways and enable control of synthesis.

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$_x$CoO$_{3-\delta}$ (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].

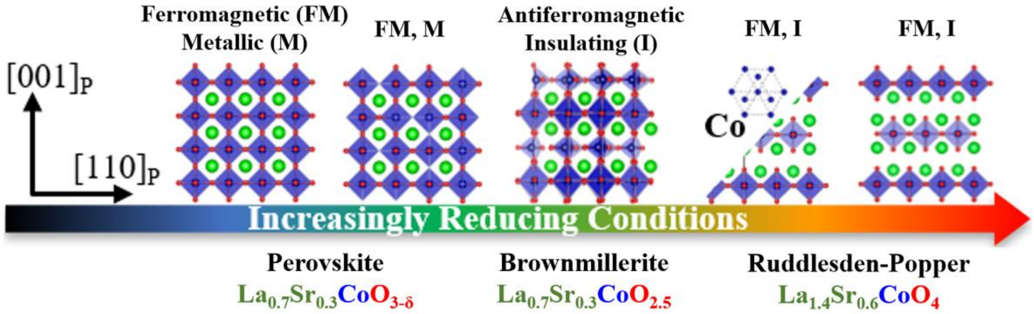


Figure 1 Crystal structure diagrams for the annealed LSCO films along with their associated magnetic and electrical properties.

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.

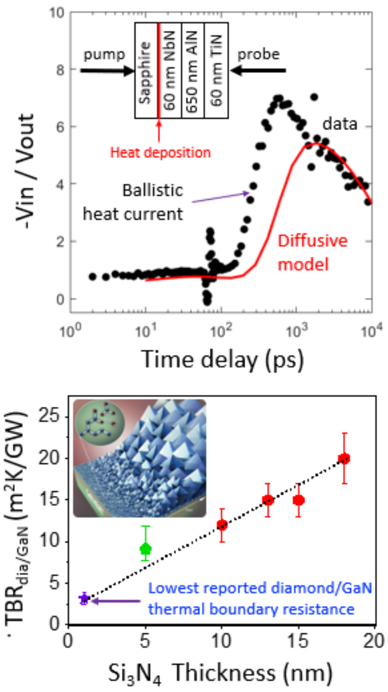
Contributions: I. Chiu performed the main experimental work involved in the study. S. Zhang conducted the first-principles calculations. I. Chiu and S. Zhang both contributed to the abstract writing and figure design.

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 C₂ 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

The reduction of CO to multi-carbon products on heterogenous copper electrocatalysts offers an environmentally 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.

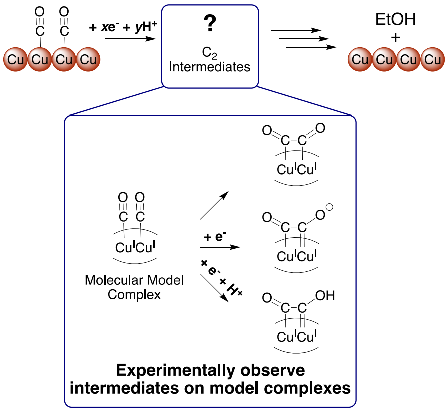


Figure 1: Molecular model complexes are used to investigate intermediates in CO reduction reaction.

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.

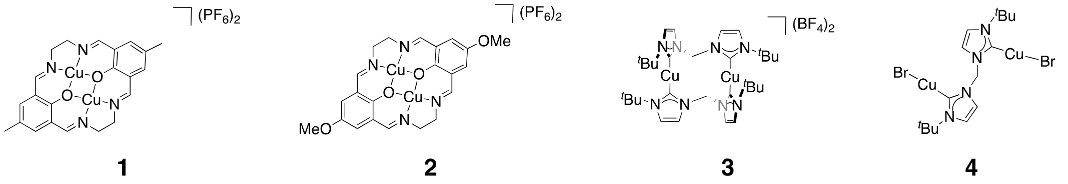


Figure 2: Complexes investigated as models for the copper surface.

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 ^{1}H 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.

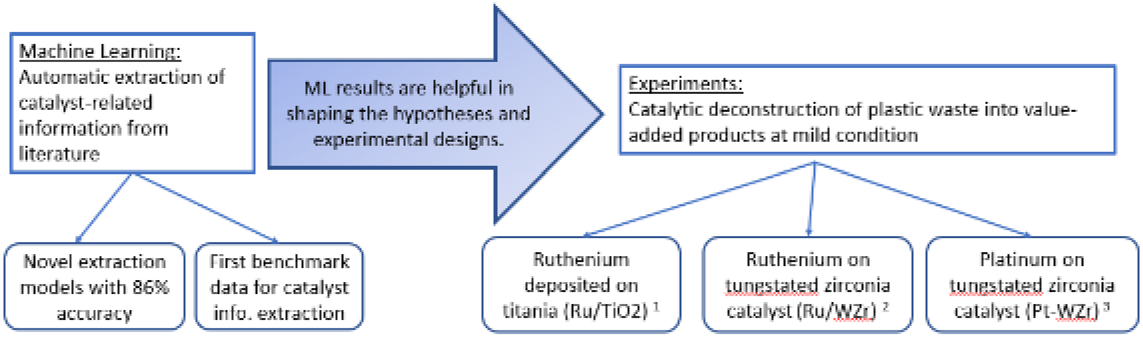
Contributions: This project was conceived by M.D., K.I.G., E.J., W.D.J., and T.E.M. W.D.J. synthesized model compounds and performed experimental studies. M.D. carried out all computational experiments. W.D.J. and M.D. prepared this abstract with input from all authors.

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.



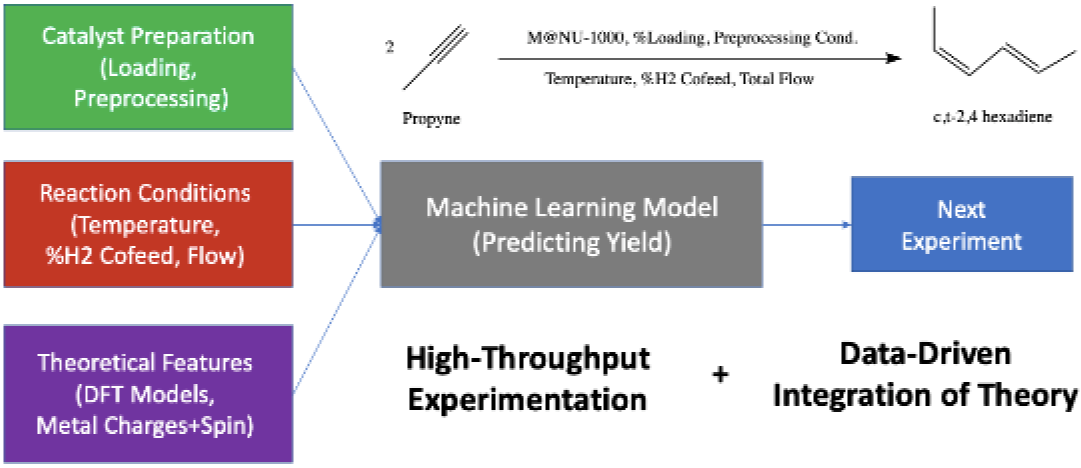
1. Kots, P. A.; Liu, S.; Vance, B. C.; Wang, C.; Sheehan, J. D.; Vlachos, D. G., Polypropylene Plastic Waste Conversion to Lubricants over Ru/TiO2 Catalysts. *ACS Catalysis* **2021,** *11* (13), 8104-8115.
2. Wang, C.; Xie, T.; Kots, P.; Vance, B.; Yu, K.; Kumar, P.; Fu, J.; Liu, S.; Tsilomelekis, G.; 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

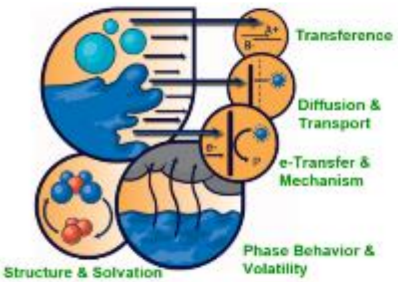


Fig 1. Target DES properties to be optimized for RFB

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.

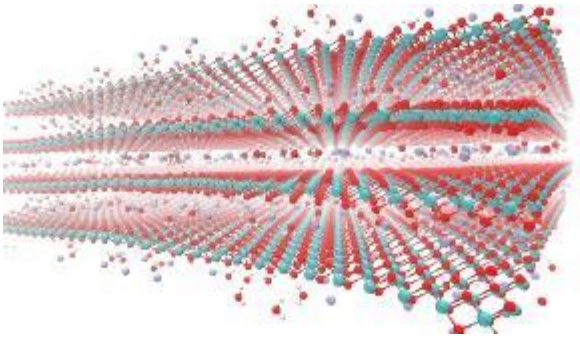


Figure 2. Structure of birnessite showing the hydrated interlayer environment responsible for the capacitive behavior in aqueous electrolytes. (blue: manganese, red: oxygen, white: hydrogen, lavender:

References

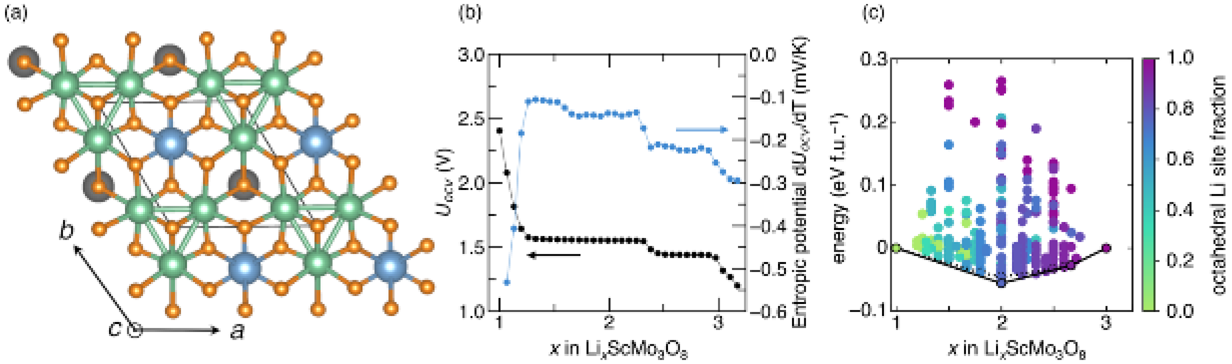
1. Boyd, S.; **Ganeshan, K.**; **Tsai, W.-Y.**; Wu, T.; **Saeed, S.**; Jiang, D.E.; Balke, N.; van Duin, A.C.T.; Augustyn, V. "Effects of Interlayer Confinement and Hydration on Capacitive Charge Storage in Birnessite." *Nature Mater.* DOI: 10.1038/s41563-021-01066-4.
2. **Saeed, S.**; **Fortunato, J.**; **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 $LiScMo_3O_8$

[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.

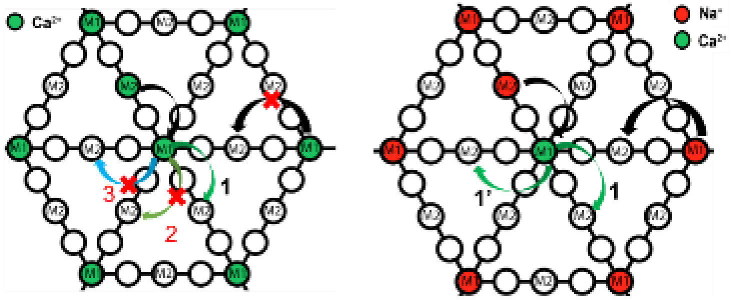


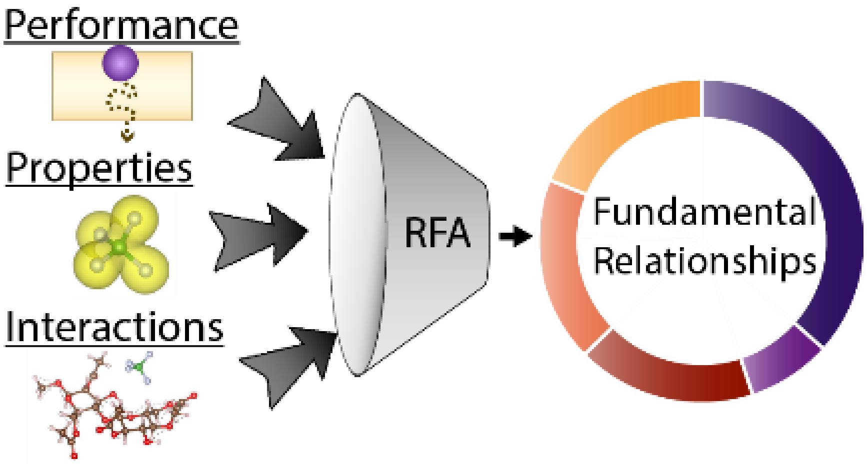
Figure 3: Schematic of diffusion pathways through NASICON framework comparing Ca^{2+}- vs. Na^+-assisted Ca^{2+} diffusion.

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.

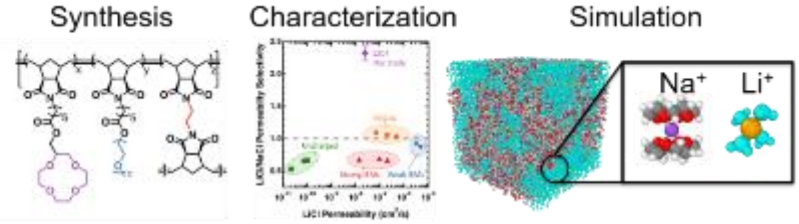


Contributions: C.L.R. and M.E. designed experimental research; C.L.R. performed experimental research; M.L. and H.J.K. designed and carried out computational and machine learning research.

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.

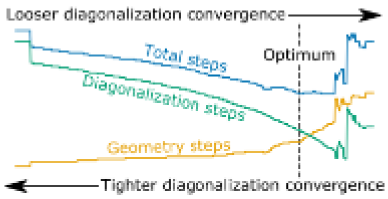
T1-D-9: APPLICATION OF A NOVEL SADDLE POINT OPTIMIZATION ALGORITHM ON SURFACE REACTIONS INVOLVING BIDENTATE ADSORBATES

[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.



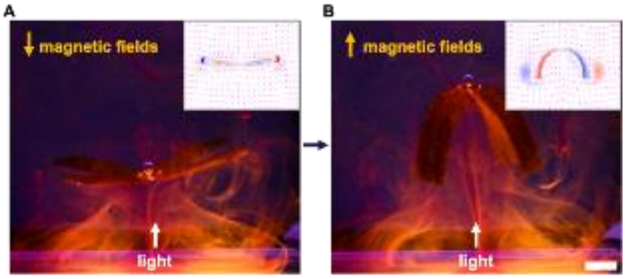
Refinement of saddle point geometries is the most computationally expensive step in the calculation of reaction rate constants under transition state theory. Commonly used saddle point optimization methods rely on iterative diagonalization of the Hessian matrix to identify the direction of lowest curvature. 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.

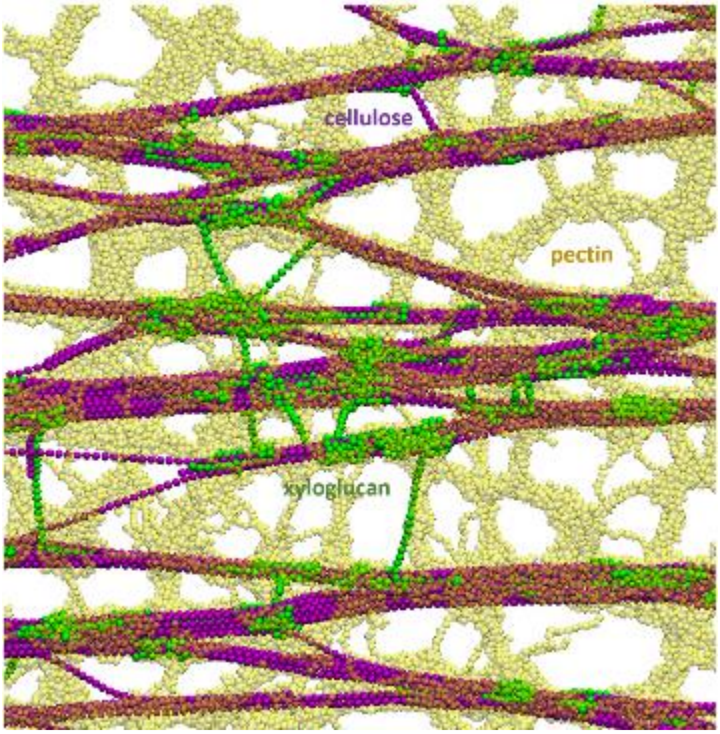
References: *Li, C., *et al*. Supramolecular-Covalent Hybrid Polymers for Light-Activated Mechanical Actuation *Nature Materials* **19,** 900 (2020); Li, C., *et al*. “Fast and programmable locomotion of hydrogel-metal hybrids under light and magnetic fields”. *Science Robotics* **5**, eabb9822 (2020); 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).

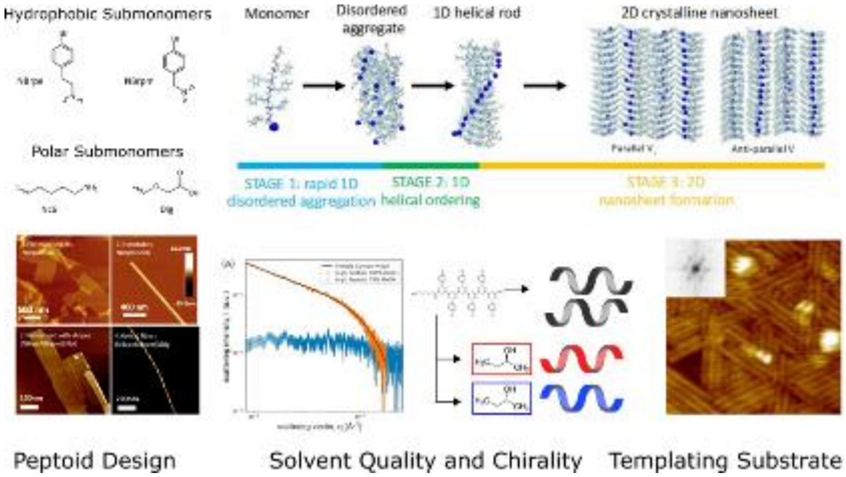
[2] Wilson, L. A., Deligey, F., Wang, T. & Cosgrove, D. J. Saccharide analysis of onion outer epidermal walls. *Biotechnol Biofuels* **14**, 66 (2021).

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.

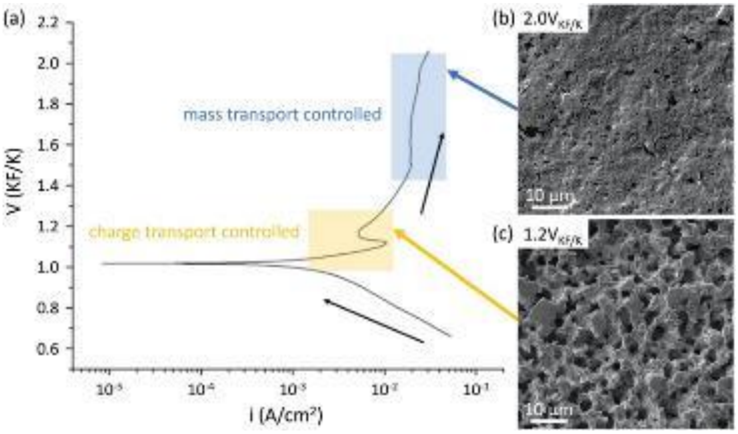


Figure 4. Electrochemical corrosion behavior of Cr in FLiNaK at 600°C: a) Potentiodynamic polarization plot; SEM of Cr surface hold at b) $2.0V_{KF/K}$ and c) $1.2V_{KF/K}$

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.

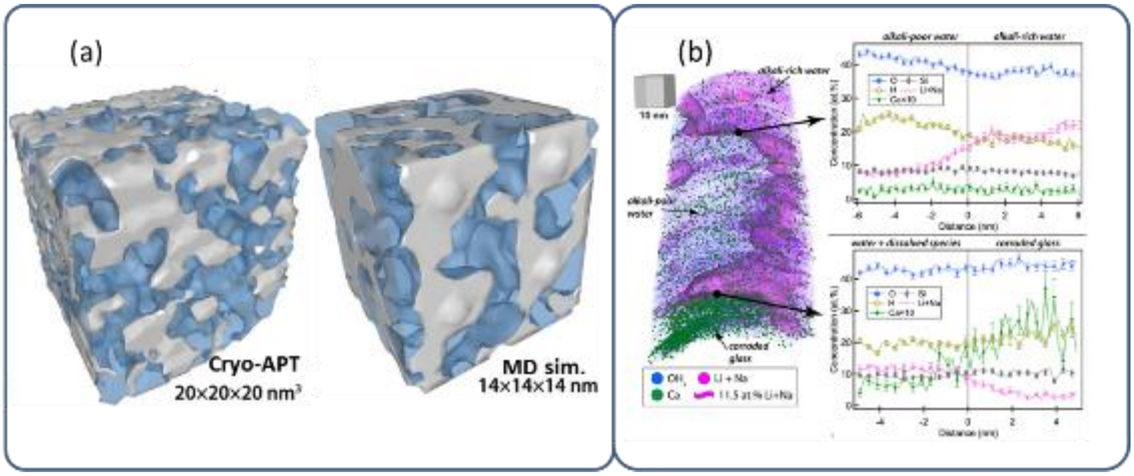
References: [1] Zhou, et al. Nature Comms 11 3430 (2020). [2] Liu et al. Nature Comms 12 3441 (2021).

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.

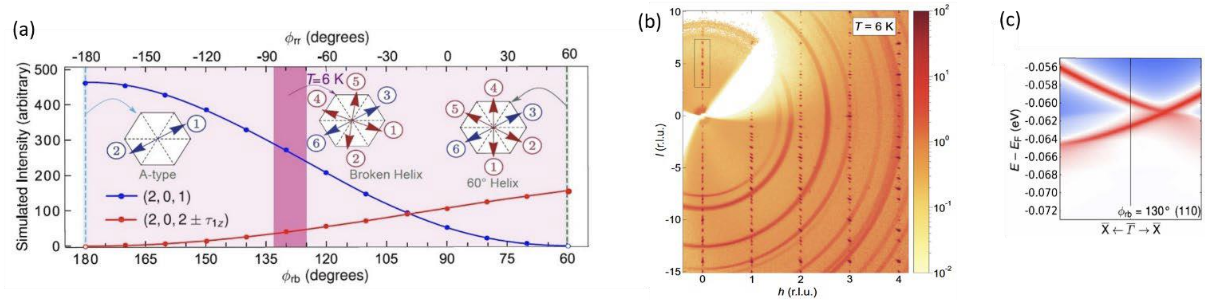
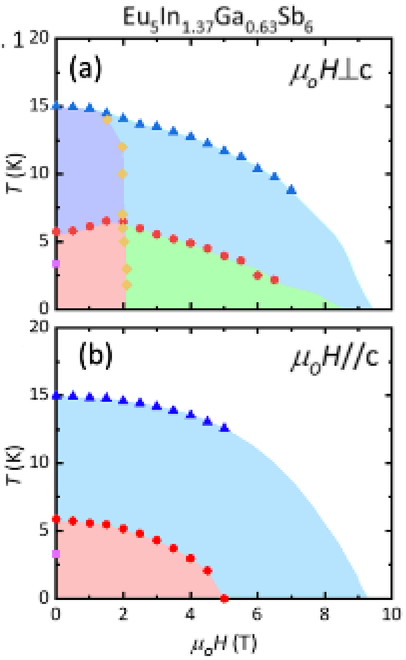


Figure. (a) Simulated neutron diffraction intensities for different turning angles continuously interpolates between different magnetic orders. (b) Neutron diffraction data in the broken-helix phase as measured on Corelli at the Spallation Neutron Source. (c) DFT calculation shows the Dirac cone in the (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

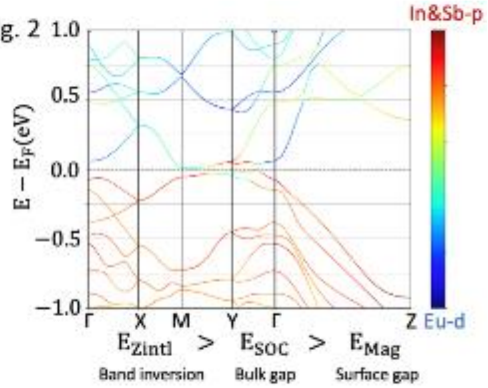
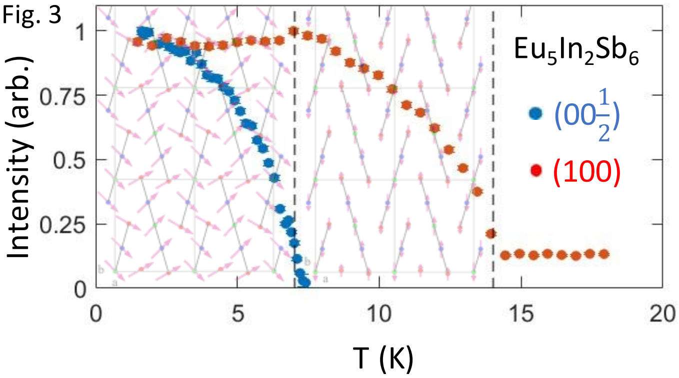


Fig. 3



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-MOSE₂ 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-MoSe₂ 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.

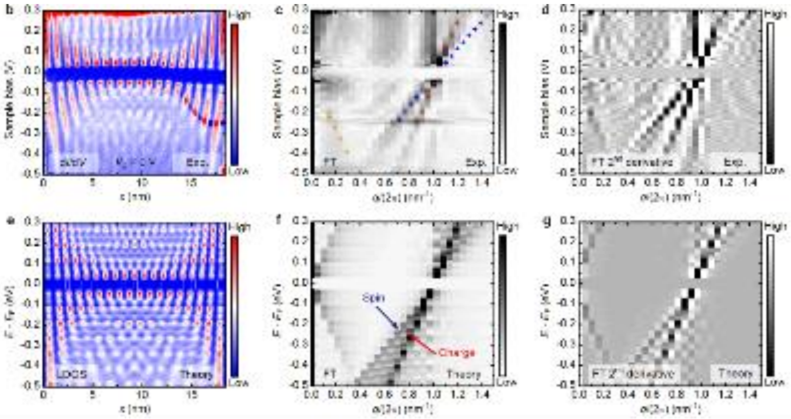


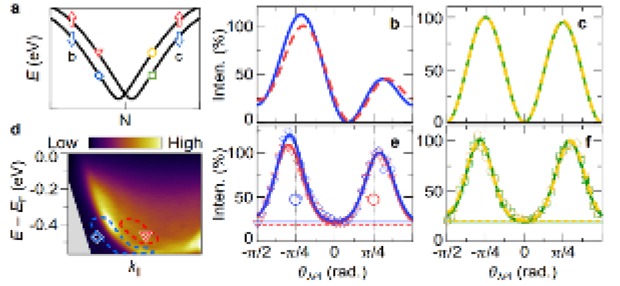
Figure 1. Experimental data (upper panel) and theoretical calculation (lower panel) of the charge density modulation and spin-charge separation in a MoSe₂ mirror twin boundary.

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 $(TaSe_4)_2I$

[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]
[1]University of Illinois at Urbana-Champaign; [2]Lawrence Berkeley National Laboratory

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, $(TaSe_4)_2I$. 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 $(TaSe_4)_2I$.



(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 $(TaSe_4)_2I$ 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, $(TaSe_4)_2I$ 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 $(TaSe_4)_2I$ 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.

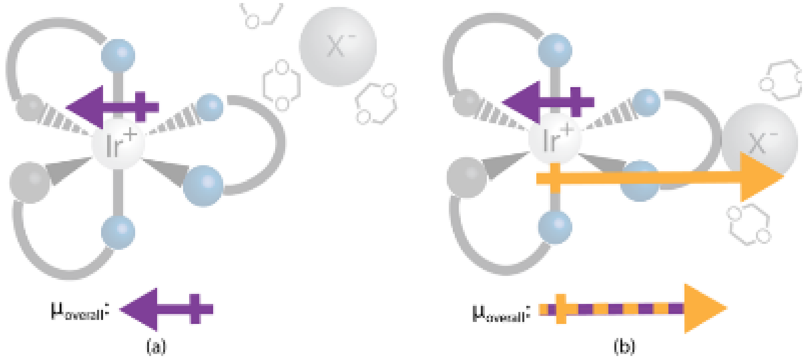
QSQM postdoc Dr. Soyeun Kim then preformed the helicity-dependent laser-based ARPES experiment to observe properties of a KW fermion. Since this experiment is (pseudo)spin-sensitive, it provides signatures of a KW fermion which acquires a spin texture from spin-orbit coupling. QSQM graduate student Robert 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 $(TaSe_4)_2I$. 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.



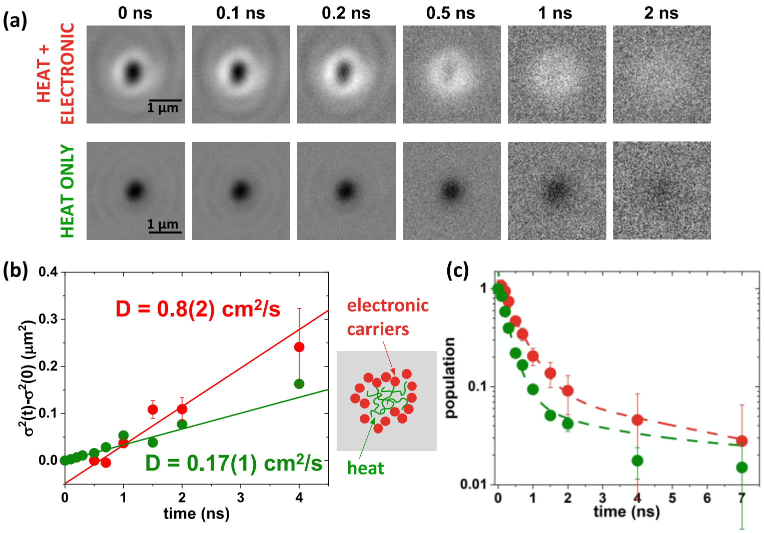
Contributions: J.D.E. designed and built the microwave experiment and wrote the dipolar relaxation simulation. N.S. performed Stern-Volmer quenching studies and quantum yield studies. A.Z. did the sample preparation, microwave measurements, and data analysis. H.H.R. synthesized the IrBArF complex and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

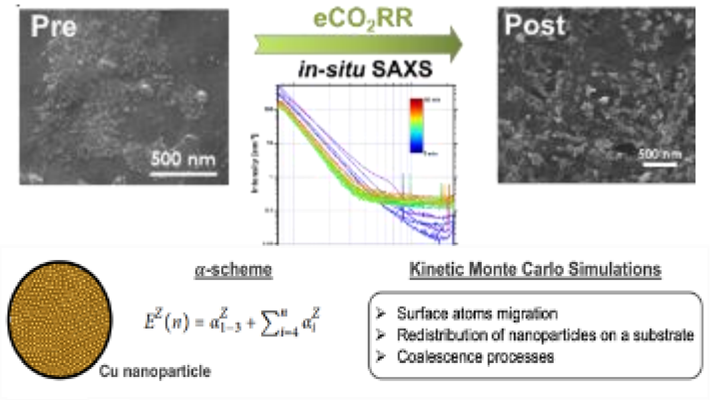


Figure 1. *a) Illustration of the morphological changes of Cu nanoparticles during CO_2RR observed by pre-and post-catalysis imaging, and* in situ *SAXS data. b) Schematic showing how the alpha parameters co-derived from machine learning and density functional theory predict energetics for modelling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

POSTER SESSION I: TUESDAY, OCTOBER 19, 2021; 11:00 – 1:00 PM

A. CATALYSIS AND POLYMER SCIENCE (ROOM: *1AE*)

1-A-1: SELECTIVE HYDROGENOLYSIS OF POLYOLEFINS TO MONODISPERSE LUBRICANTS USING PLATINUM ON STRONTIUM TITANATE NANOCUBOIDS

[EFRC – iCOUP] Ryan A. Hackler[1], Robert M. Kennedy[1], Kimaya Vyavhare[1], Gokhan Celik[1], Uddhav Kanbur[2], Ian Peczak[3], Ammal C. Salai[4], Andreas Heyden[4], Aaron D. Sadow[2], Kenneth R. Poeppelmeier[3], Ali Erdemir[5], Massimiliano Delferro[1]
[1]Argonne National Laboratory; [2]Ames Laboratory; [3]Northwestern University; [4]University of South Carolina; [5]Texas A&M University

Synthetic polymers are ubiquitous and critical to the function of modern life. However, the pervasiveness and volume of polymers has resulted in an enormous and growing amount of polymer waste, which has a long lifetime in the environment, and the current recycling infrastructure is unable to effectively process the waste. Here, we show that well-dispersed Pt nanoparticles supported on $SrTiO_3$ nanocuboids (with cube-on-cube epitaxy) by atomic layer deposition can convert pre- and post-consumer polyethylene (PE, 8,000 – 158,000 Da) into value-added high-quality liquids (HQLs) by hydrogenolysis at 170 psi H_2 and 300 °C under solvent-free conditions. Adsorption of PE on the catalytic surfaces plays a significant role in selective hydrogenolysis, as shown by catalytic, solid-state NMR of adsorbed ^{13}C-enriched PE, and density functional theory. We attribute the formation of uniform low dispersity products to a combination of preferential binding of high molecular weight PE on the catalyst surface and stronger adsorption of PE to Pt than to the $SrTiO_3$ support.

These uniform, low molecular weight products (c.a. 500 – 800 Da) also act as lubricants. Tribology tests, such as wear scar formation analysis and coefficient of friction measurements, show HQLs produced from high-density PE (HDPE), linear low-density PE (LLDPE), and packaging films performing superior to petroleum-based lubricants such as mineral oils (e.g. 44% reduction in wear scar volume). The HQLs also perform comparably to synthetic lubricants such as polyalphaolefins (PAOs) and can be blended such that a synergistic reduction in wear is observed, showcasing the efficacy of polyolefin hydrogenolysis to produce lubricants.

1-A-2: TWO-DIMENSIONAL PALLADIUM RAFTS CONFINED IN COPPER NANOSHEETS FOR SELECTIVE SEMIHYDROGENATION OF ACETYLENE

[EFRC – ICDC] Jian Liu[1], Siriluk Kanchanakungwankul[2], Donald G. Truhlar[2] and Joseph T. Hupp[1]
[1]Northwestern University; [2]University of Minnesota

The development of highly selective and active catalysts to catalyze industrially an important semihydrogenation reaction remains an open challenge. Herein, we designed and prepared the bimetallic Pd/Cu(111) catalyst with the Pd rafts confined in Cu nanosheet, which exhibits desirable catalytic performance towards acetylene semihydrogenation to ethylene with selectivity of > 90%. Theoretical studies validate that the Pd/Cu(111) catalysts can enhance the reaction activity by reducing the activation barriers of hydrogenation steps, and can improve the selectivity by weakening the binding of C2H4. The presence of Pd rafts confined in Cu nanosheets effectively successfully transforms Cu nanosheets which are nearly inert toward semihydrogenation of acetylene, into catalysts that are display high active and selectivity under mild reaction conditions. This work offers a well-defined Pd/Cu(111) model catalyst at nano-scale, bridging the pressure and materials gap between surface-science catalysis and real world catalysis.

1-A-3: CLOSING THE GAP BETWEEN MODEL ALKANE AND POLYOLEFIN HYDROCRACKING

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

Hydrocracking is an attractive method for valorization of waste polyolefins (PO) to valuable fuels and lubricants under mild processing conditions. Hydrocracking catalysts are bifunctional to enable specific mechanisms; metal sites (de)hydrogenate and acid sites break (crack) C-C bonds forming intermediates (i.e., olefins). Although hydrocracking mechanisms are well described for model short alkanes, it is unclear how these concepts translate to PO feedstocks, thus limiting widescale adoption. For example, macromolecule reactivity differs from alkanes due to slow transport and strong intermolecular interactions in the melt . This research aims to i) compare hydrocracking reactivity between polymers and small molecules and ii) establish a mechanistic framework for PO hydrocracking using basic descriptors to close the gap between model alkanes and polymers. Our results highlight that metal-to-acid site molar ratio (MAB) for various catalysts plays a significant role in low density polyethylene (LDPE) hydrocracking. Increasing MAB shifts the extractable product (C_1 – C_{35}) selectivity to heavier hydrocarbons, and the solid product selectivity to smaller polymer chains with increased branching. High MAB catalysts provide a pseudo-equilibrium between olefins and their associated paraffins over the metal sites, and acid-catalyzed β-scission becomes slow because of preferential wetting of the melt, leading to a relatively deep isomerization of the polymer. Analysis of solid residues using gel permeation chromatography (GPC) and nuclear magnetic resonance (NMR) identify the opportunities in hydrocracking to tune selectivity for valuable branched products. This work demonstrates the complexity of hydrocracking macromolecules that are inherent to 'real' plastics waste and outlines strategies for optimization toward valorization.

1-A-4: POLYETHYLENE UPCYCLING TO LONG-CHAIN ALKYLAROMATICS BY TANDEM HYDROGENOLYSIS/AROMATIZATION

[EFRC – iCOUP] Fan Zhang[1], Manhao Zeng[1], Ryan D. Yappert[2], Jiakai Sun[1], Yu-Hsuan Lee[1], Anne M. LaPointe[3], Baron Peters[2], Mahdi M. Abu-Omar[1], Susannah L. Scott[1]
[1]University of California, Santa Barbara; [2]University of Illinois, Urbana-Champaign; [3]Cornell University

Every year, 300 million tons of plastic is discarded as waste, creating a growing environmental burden. Existing mechanical recycling methods generate lower value materials, which makes these processes economically challenging. As part of the Institute for Cooperative Upcycling of Polymers (iCOUP), we are developing new chemical upcycling methods that aim to motivate better plastic recovery and reduce environmental impacts. Here, we report a tandem catalytic conversion of polyethylene (PE) by platinum supported on ⍰-alumina, which produces alkylaromatic liquids (~C_{30}) in high yield in the absence of solvent or hydrogen. These alkylaromatic products may find broad applications in surfactants, solvents, and refrigeration fluids. By coupling exothermic hydrogenolysis with endothermic aromatization, the overall reaction can proceed to high conversion even at a relatively low temperature (ca. 280 °C). A simple kinetic model was shown to describe the progress of the tandem reactions. The process was also shown to be successful in the conversion of different types of commercial grade PE (HDPE, LDPE). In addition, catalyst stability tests demonstrated longevity and multiple cycles of regeneration. Our current efforts focus on understanding the role of metal and support in the overall transformation, leading to better design of catalysts to achieve efficient depolymerization into high-value products.

1-A-5: CATALYZING THE PRODUCTION OF CONJUGATED DIENES FROM BIOMASS DERIVED CYCLIC ETHERS ON ZrO_2

[EFRC – CCEI] Yichen Ji[1], Sai Praneet Batchu[2], Ajibola Lawal[3], Stavros Caratzoulas[2], Raymond J. Gorte[1], Omar A. Abdelrahman[3]
[1]University of Pennsylvania; [2]University of Delaware; [3]University of Massachusetts, Amherst

Conjugated dienes are backbone monomers used in many industrial polymerization processes, mainly produced as byproducts of naphtha cracking. With the increasing shift towards shale gas feeds to naphtha cracking units, rich in C1-C3 compounds that will not produce dienes as a byproduct, on-purpose conjugated diene production becomes necessary. As part of the work in the Catalysis Center for Energy Innovation, we have discovered that ZrO_2 exhibited an excellent performance in the renewable production of conjugated dienes via the dehydra-decyclization of biomass-derived cyclic ethers. Catalytic activity over ZrO_2 is comparable to and more stable than previously reported, easily deactivated (due to the unsaturated hydrocarbons) catalysts, and the selectivity is above 90%. ZrO_2 is especially more favorable in producing conjugated dienes relative to other Brønsted or Lewis acid catalysts; the ratio of 1,3-pentadiene (conjugated):1,4-pentadiene (non-conjugated) from 2-methyltetrahydrofuran dehydration is more than an order of magnitude larger on ZrO_2 than on TiO_2 and Al_2O_3. Temperature programmed desorption has shown that both pentadienes are primary rather than diene isomerization products on each catalyst. Density-Functional Theory simulations of both tetrahydropyran and 2-methyltetrahydrofuran on ZrO_2 indicate reaction via a favorable, surface-intermediate transformation pathway, which leads to the high selectivity for conjugated diene products. By intentionally poisoning the active catalyst with sodium, we investigated the nature of the active sites that are responsible for the high selectivity to conjugated dienes on ZrO_2 and whose density is less than the Lewis acidic site density determined by isopropanol TPD.

1-A-6: MECHANISTIC INSIGHTS INTO CARBON-CARBON COUPLING ON NIAU AND PDAU SINGLE-ATOM ALLOYS

[EFRC – IMASC] Paul Kress[1], Romain Réocreux[2], Ryan Hannagan[1], Theodore Thuening[1], J. Anibal Boscoboinik[3], Michail Stamatakis[2], E. Charles H. Sykes[1]
[1]Tufts University; [2]University College, London; [3]Brookhaven National Laboratory

Carbon-carbon coupling is a ubiquitous step in many important chemical reactions and sp^3-sp^3 carbon-carbon coupling can be especially challenging to perform. We studied NiAu single-atom alloys (SAAs) and demonstrate the coupling of surface-bound methyl to selectively produce ethane. We find that the NiAu SAA is active for both low temperature C-I bond cleavage and selective sp^3-sp^3 carbon-carbon coupling of methyl groups. To gain more insight into the reaction mechanism *ab initio* kinetic Monte Carlo simulations were performed which included the effect of the iodine atom, which was previously considered a bystander species in coupling studies on PdAu SAAs. When considering the role of iodine in the system it is found that on NiAu SAAs, iodine atoms preferentially bind to the Ni site, leaving the methyl groups on Au, while on PdAu SAAs, the binding strength of methyl and iodine to Pd are more similar. Together, these data offer insight into the role of adsorbate and ligand effects that must be considered in SAA systems, specifically for sp^3-sp^3 carbon-carbon coupling reactions. The effect of iodine and methyl groups on the reaction pathway are discussed, as well as their binding strengths to the active site, and an analogy between this model single-site heterogenous catalyst and homogenous organometallic catalysts is made in which ligands must unbind from the active site in order for the reaction to proceed.

1-A-7: UIO-66-DERIVED MOF CATALYSTS FOR C-C COUPLING REACTIONS

[EFRC – ICDC] Saumil Chheda[1], Julian Schmid[2], Laura Löbbert[3], Ruixue Zhao[3], Thais Scott[4], Jian Zheng[2], Navneet Khetrapal[1], Carlo A. Gaggioli[1], Daniel King[4], Clara Lopez, Donald M. Camaioni[2], Oliver Y. Gutierrez[2], Ricardo Bermejo-Deval[3], Yue Liu[3], Roshan A. Patel[1], J. Ilja Siepmann[1], Matthew Neurock[1], Laura Gagliardi[4], and Johannes Lercher[2,3]
[1]University of Minnesota; [2]Pacific Northwest National Laboratory; [3]Technical University Munich; [4]University of Chicago

The catalytic C-C coupling of hydrocarbons is key to the production of valuable intermediates and fine chemicals. We have utilized the structural properties of Zr-based UiO-66 metal-organic framework (MOF) to design selective catalysts for important C-C coupling reactions. Our preparation strategies are based on the modulated synthesis of defect-containing MOFs and subsequent metalation through post-synthetic techniques. Using a combination of kinetic experiments, characterization, and computational tools we demonstrate UiO-66-based materials as effective catalysts for the aldol condensation of acetone and furfural, and for 1-butene dimerization to linear octenes.

We found that UiO-66 catalyst synthesized in presence of formic acid modulator offers low energy pathways for aldol condensation. Density functional theory (DFT) studies suggest that the reaction proceeds through a concerted base-catalyzed enol formation pathway. The computed activation energies and rate-determining steps agree well with the experimentally observed results.

We also investigated different single-atom transition metal catalysts (Ni, Co, Cu, and Cr) supported on UiO-66 for 1-butene dimerization. Our experimental findings and the DFT-computed free energy barriers indicate towards the Cossee-Arlmann reaction mechanism. The dimerization free energy barriers inversely correlate with the 1-butene adsorption free energies on different M^{2+}/UiO-66 catalysts with Ni^{2+}/UiO-66 as the most active catalyst investigated here

with C-C coupling as the rate-determining step. Ni^{2+}/UiO-66 also showed a remarkable selectivity towards desired linear octene products.
These studies manifest the advantageous structural properties of MOFs to perform C-C coupling reactions at cationic sites. This knowledge can be utilized to design selective MOF-based catalysts for C-C coupling reactions across various substrates.

1-A-8: DEPOLYMERIZATION OF HYDROXYLATED POLYMERS VIA LIGHT-DRIVEN C-C BOND CLEAVAGE

[EFRC – BioLEC] Suong T. Nguyen[1], Elizabeth A. McLoughlin[1], James H. Cox[1], Brett P. Fors[2], Robert R. Knowles[1]
[1]Princeton University; [2]Cornell University

The accumulation of persistent plastic waste in the environment is widely recognized as an ecological crisis. New chemical technologies are necessary both to upcycle existing plastic waste streams into high-value chemical feedstocks and to develop next-generation materials that are recyclable by design. In this poster, we will present a catalytic methodology for the depolymerization of the commercial phenoxy and epoxy resins as well as high molecular weight hydroxylated polyethylene derivatives upon visible light irradiation near ambient temperature. Proton-coupled electron transfer (PCET) activation of hydroxyl groups periodically spaced along the polymer backbone furnishes reactive alkoxy radicals that promote chain fragmentation through C–C bond *beta*-scission. Depolymerization produces well-defined and isolable product mixtures that are readily diversified to polycondensation monomers. In addition to controlling depolymerization, the hydroxyl group modulates the thermomechanical properties of these polyethylene derivatives, yielding myriad materials for diverse consumer applications. These results demonstrate a new approach to polymer upcycling based on light-driven C–C bond cleavage that has the potential to establish new links within a circular polymer economy and influence the development of new materials that are degradable by design.

1-A-9: DILUTE PD-IN-AU ALLOY RCT-SIO2 CATALYSTS FOR ENHANCED OXIDATIVE METHANOL COUPLING

[EFRC – IMASC] Amanda Filie[1], Tanya Shirman[1], Alexandre C. Foucher[2], Eric A. Stach[2], Michael Aizenberg[1], Joanna Aizenberg[1], Cynthia M. Friend[1], Robert J. Madix[1]
[1]Harvard University; [2]University of Pennsylvania

The opportunity for Au-based alloy materials to catalyze selective oxidation reactions using molecular O_2 as the oxidant, as compared to toxic alternatives, has generated significant research in this catalyst material. Dilute alloy catalysts offer opportunities to enhance selectivity and activity for such reactions. Highly dilute Pd-in-Au nanoparticle alloys partially embedded in porous silica (‘‘raspberry colloid templated” (RCT)-SiO_2) prove to be active and selective catalysts for oxidative coupling of methanol. Palladium concentrations in the bimetallic nanoparticles as low as ~3.4 atomic % Pd-in-Au catalyze the production of methyl formate with a selectivity of ~95% at conversions of ~30%, whereas conversions are low (<10%) for ~1.7 atomic % Pd-in-Au nanoparticle and pure Au nanoparticle catalysts. There is no conversion of methanol in the absence of O_2 at 420 K over any of the catalysts tested. The production of methyl formate over the 3.4 atomic % Pd-in-Au nanoparticle catalyst is greatly suppressed by co-feeding CO. The extent that co-fed CO suppresses the production of methyl formate diminishes with decreasing Pd content in the nanoparticles and the activity of the catalysts recovers once the CO is removed from the reactant mixture. All observations are consistent with a mechanism derived from model studies, indicating the availability if Pd sites is key to promoting activity for oxidative methanol coupling over the predominantly Au-based nanoparticle catalyst.

1-A-10: Site Densities, Rates, and Mechanism of Stable Ni/UiO-66 Ethylene Oligomerization Catalysts

[EFRC – ICDC] Benjamin Yeh[1], Stephen P. Vicchio[2], Saumil Chheda[1], Jian Zheng[3], Julian Schmid[3], Laura Löbbert[4], Ricardo Bermejo-Deval[4], Oliver Y. Gutiérrez[3], Johannes A. Lercher[3,4], Connie C. Lu[1], Matthew Neurock[1], Rachel B. Getman[2], Laura Gagliardi[5], Aditya Bhan[1]
[1]Unviersity of Minnesota; [2]Clemson University; [3]Pacific Northwest National Laboratory; [4]Technische Universität München; [5]University of Chicago

Nickel-functionalized UiO-66 MOFs oligomerize ethylene in absence of co-catalysts or initiators after undergoing ethylene-pressure-dependent transients and maintain stable oligomerization rates for >15 days on-stream. Higher ethylene pressures shorten induction periods and engender more active sites for ethylene oligomerization; these sites exhibit invariant selectivity-conversion characteristics to justify that only one type of catalytic center is relevant for oligomerization. The number of active sites is estimated using in-situ NO titration to disambiguate the effect of increased reaction rates upon exposure to increasing ethylene pressures. After accounting for augmented site densities with increasing ethylene pressures, ethylene oligomerization is first order in ethylene pressure from 100-1800 kPa with an activation energy of 81 kJ mol-1 from 443–503 K on Ni/UiO-66. A representative Ni/UiO-66 cluster model that mimics high ethylene pressure process conditions is validated with ab initio thermodynamics analysis, and the Cossee-Arlman mechanism is posited through comparisons between experimental and computed activation enthalpies from density functional theory calculations on these cluster models of Ni/UiO-66. The insights gained from experiment and theory can help guide the synthesis of Ni/UiO-66 MOFs which provide functional and tunable platforms for ethylene oligomerization that offer catalytic stability and opportunities to enhance reactivity.

1-A-11: Valorization of Polymer Waste via Fluorination: The potential to synthesize Amphiphilic Copolymers via Photocatalyzed decarboxylative Fluorination of Super-Absorbent Polymers or oxidized plastic waste

[EFRC – CPI] Michael R. Talley, Craig Machado, Panagiotis Dimitrakellis, Dion Vlachos, Thomas H. Epps, III, Mary P. Watson
University of Delaware

Polymer-to-polymer upcycling is an attractive complement to plastic recycling. It saves energy from depolymerizing and reforming a polymer, while adding functionality. Valorizing polar poly(acrylic acid) (PAA), a major component in disposable diaper waste, with fluorine would add hydrophobicity and self-cleaning properties, creating unique adhesive and fluorophobic polymers, which could see similar applications to other fluorocarbon polymers. Unfortunately, traditional copolymerization of polar acrylates and fluorinated olefins has had limited success. An alternative approach is the post-polymerization fluorination (PPF) of PAA. However, classic approaches to PPF require harsh chemicals, such as hydrofluoric acid and sulfur tetrafluoride. Recent efforts have utilized components such as silver nitrate to synthesize poly(acrylic acid-*r*-vinyl fluoride) (PAA-*r*-PVF). However, silver is reactive with other functional groups, complicating its application to mixed plastic waste streams.

We report a photoredox-catalyzed decarboxylative fluorination of a model PAA polymer, resulting in PAA-*r*-PVF. The extent of PVF incorporation (*e.g.,* fluorination) ranges from 33–99 mol% and is tuned based on light exposure. Furthermore, high molecular weight PAA (450 kDa) and industrial Super-Absorbent Polymers (SAPs) also undergo high levels of conversion with only 20 ppm catalyst loading. In addition to valorization of SAPs from disposable diaper waste, a long-term goal is to combine decarboxylative fluorination with plasma oxidation of plastic polymer waste (PPW) to produce various upcycled polymers for high-performance applications. We expect these unique materials to have a wide range of uses due to the easy tunability of fluoride content, making this an attractive and valuable method for repurposing plastic waste.

1-A-12: CATALYSIS BY DESIGN: UPCYCLING WASTE POLYETHYLENE VIA A PROCESSIVE MECHANISM

[EFRC – iCOUP] Akalanka Tennakoon[1], Xun Wu[1], Alexander L. Paterson[1], Ryan Yappert[2], Smita Patnaik[1], Yuchen Pei[1], Anne M. LaPointe[3], Salai C. Ammal[4], Ryan A. Hackler[5], Andreas Heyden[4], Igor I. Slowing[1], Geoffrey W. Coates[3], Massimiliano Delferro[5], Baron Peters[2], Wenyu Huang[1], Aaron D. Sadow[1], Frédéric A. Perras[1]

[1]Ames Laboratory; [2]University of Illinois at Urbana Champaign; [3]Cornell University; [4]University of South Carolina; [5]Argonne National Laboratory

The environmental, economic, and health-related consequences of single-use plastics are apparent. Current approaches to chemically recycle or upcycle polyolefin plastics are limited by poor selectivity, producing broad distributions of small molecule fragments. Natural enzymes are able to selectively depolymerize macromolecules through atomically-precise processive mechanisms, which involve the grasping of the macromolecule in a catalytic cleft. Here, we present a synthetic mesoporous shell/active site/core ($mSiO_2/Pt/SiO_2$) silica catalyst architecture that incorporates catalytic platinum sites at the base of the mesopores. This catalyst is designed to mimic the constrained catalytic site found in processive enzymes. A primary advantage of deconstructive conversions following a processive mechanism is that the product distribution is independent of both polymer chain length and reaction conversion time, which is ideal for potential industrial applications. Solid-state nuclear magnetic resonance experiments show that the polyethylene chains move readily within the pores of the mesoporous silica but are prevented from escaping the pores due to polymer-surface interactions. These results provide a direct analogy with the behavior of processive enzymes.

Our $mSiO_2/Pt/SiO_2$ catalyst can convert pre- and post-consumer polyethylene (M_n: 1,700 – 100,000 Da) into a narrow distribution of diesel-range to lubricant-range alkanes via hydrogenolysis. The median carbon chain length of the product distribution is tunable by changing the diameter of pores, longer using architectures with wider pores and shorter from narrower pores, demonstrating catalyst-controlled hydrocarbon distributions. Post-reaction analysis reveals that the catalyst is long-lived, resistant to sintering, and has high recyclability, which are important prerequisites for practical catalytic applications.

1-A-13: TOWARDS DISCOVERY OF ENZYMES THAT BREAKDOWN OR VALORIZE DIVERSE PLASTIC POLYMER WASTES

[EFRC – CPI] Gwendolyn Gregory[1], Hannah Valentino[2], Roman Dickey[1], Josh Michener[2], Aditya Kunjapur[1], Eleftherios Papoutsakis[1]

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The Center for Plastics Innovation (CPI) seeks to develop hybrid catalytic and biocatalytic approaches for the depolymerization and valorization of plastic polymer waste (PPW). This poster presents a few examples with a focus on the discovery of enzymes from environmental microbes that are capable of degrading pre-treated or raw PPW to form monomers for new materials.

Identification of enzymes that can hydrolyze or functionalize long-chain esters, fatty acids, or alkane substrates are of particular interest, as these are intermediate degradation products of polyethylene (PE) and polypropylene (PP) plastics, which are recycled at much lower frequencies. Environmental soil samples collected from a local recycling center were cultured, and consortia that formed biofilms on plastic sheets were collected. Several environmental consortia grow on hexadecane and mixtures of long-chain alkanes produced via catalytic conversion from another CPI project as sole carbon sources. Growth and alkane degradation will be determined. Sequencing and bioinformatics will identify the species profile of each consortia and key enzymes. Platform strains will then be engineered to utilize PPW-derived alkane feedstocks.

Our other projects showcase the opportunity to harness biocatalysts for selective transformation of depolymerized plastic waste streams. Here, we illustrate our envisioned process for imparting diamine functionality to aromatic or aliphatic monomers that are derived from polyethylene terephthalate (PET) or PE/PP, respectively. Initial characterization of these enzymes has identified a need to improve activity on envisioned substrates (in the case of alcohol dehydrogenase for alkane diols) or to confirm activity (in the case of transaminase for aryl aldehydes).

1-A-14: BUILDING TOWARDS THE FUTURE OF ELECTRONIC STRUCTURE CALCULATIONS AND WORKFLOWS FOR CATALYTIC SYSTEMS

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How scientists are using electronic structure codes is changing. Instead of running a single DFT calculation with an open-source code like NWChem on a simple molecule or surface, it is becoming very common to carry out many hundreds to thousands of calculations as part of a holistic modeling effort in which different approximations and layers of models feed into each other. As part of this project, we have been improving and developing NWChem/NWChemEx software suites. In addition to performing geometry optimizations, phonon-spectra, and NEB calculations at surfaces, workflows have been designed and implemented to make AIMD free-energy simulations (WHAM, PMF, metadynamics, and TAMD) easier to carry out. To assist in the development of workflows the NWChemEx software can be called as a standalone library that can be called from another program using a simple JSON string as input. Highly parallel workflows are also being developed for newer and more expensive free-energy methods based on discrepancy, and MD methods have been implemented directly into Arrows with JavaScript to make initial reaction paths at surfaces. We have also been expanding the capabilities and adding more simulation methods to NWChemEx, including various dispersion corrected DFT functions, metaGGAs, optimizers for metals and fractional occupation, Fermi surface plotting, calculation of polarizabilities, interface to the ASE python library, and plane-wave periodic many body methods. Finally, PNNL and Argonne have been working closely to develop new GPU versions of the plane-wave codes that will be able to run future DOE exascale systems at Argonne and other laboratories.

1-A-15: INTEGRATED MULTISCALE MODELING APPROACHES FOR POLYMER UPCYCLING

[EFRC – iCOUP] Max Meirow[1], Ryan Yappert[2], Salai Ammal[3], Kyung-Eun You[3], Armin Shayesteh Zadeh[2], Ziqiu Chen[2], Andreas Heyden[3], Erik Luitjen[1], Baron Peters[2]
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We highlight several interconnected modeling efforts aimed at testing mechanistic hypotheses, predicting catalyst activity, interpreting kinetic measurements, and extracting kinetic parameters. Bottom-up calculations starting from electronic structure theory and molecular simulations are combined with new tools for integration of microkinetic models and population balance models. We highlight several examples of synergy between theory efforts and joint efforts involving theory and experiment.

1-A-16: ADSORBATE PARTITION FUNCTIONS VIA PHASE SPACE INTEGRATION: QUANTIFYING THE EFFECT OF TRANSLATIONAL ANHARMONICITY ON THERMODYNAMIC PROPERTIES

[CCS – ECC] Katrín Blöndal[1], Khachik Sargsyan[2], David H. Bross[3], Branko Ruscic[3], C. Franklin Goldsmith[1]
[1]Brown University; [2]Sandia National Laboratories; [3]Argonne National Laboratory

A new method for computing anharmonic thermophysical properties for adsorbates on metal surfaces is presented. Classical Monte Carlo phase space integration is performed to calculate the partition function for the motion of a hydrogen atom on Cu(111). A minima-preserving neural network potential energy surface is used within the integration routine. Two different sampling schema for generating the training data are presented, and two different density functionals are used. The results are benchmarked against direct state counting results by using discrete variable representation. The phase space integration results are in excellent quantitative agreement with the benchmark results. Additionally, both the discrete variable representation and the phase space integration results confirm that the motion of H on Cu(111) is highly anharmonic. The results were applied to calculate the free energy of dissociative adsorption of H2 and the resulting Langmuir isotherms at 400, 800, and 1200 K in a partial pressure range of 0–1 bar. It shows that the anharmonic effects lead to significantly higher predicted surface site fractions of hydrogen.

B. ENERGY STORAGE (ROOM: *1B*)

1-B-1: STRUCTURED OIL-WATER ACTIVE PHASES AS BREAKTHROUGH ELECTROLYTES FOR ENERGY STORAGE

[EFRC – BEES] Adam Imel[1], Luke Heroux[1],Brian Barth[1],Nelly Cantillo[1], Camilo Zuleta[1], Jing Peng[1], Redwan Hassan[1], McKensie Nelms[1], Jack Heller[2], Nick Furth[2], Andrew Nyland[2], Doug Hayes[1], Tessa Calhoun[1], Mark Dadmun[1,3], Thomas A. Zawodzinski[1,3]
[1]University of Tennessee-Knoxville; [2]SMaRT-Oak Ridge Innovation Institute; [3]Oak Ridge National Laboratory

Current electrolytes generally have an inverse relationship between conductivity and energy density, with aqueous systems having high conductivity and low energy density because of the solubility of the molecules in water, i.e., high salt concentrations but low redox-active concentration, while organic systems are the opposite. Decoupling the conductivity and energy density could lead to breakthrough electrolytes for energy storage with high conductivity and high energy density. Our approach uses microemulsions, a thermodynamically stable mixture of oil and water stabilized by a surfactant. In microemulsions, the water and oil are separated on the nanoscale, with the surfactant bridging the two phases while macroscopically producing a clear homogenous solution. A stable solution with separated oil and water domains provides a pathway to decouple the conductivity (aqueous phase) and energy density (oil phase). Our collaborative approach to studying these electrolyte systems uses many electrochemical, scattering, spectroscopic, and machine learning methods. We will describe the path to preparing and using these electrolytes in electrochemical systems, from determining phase properties to electrochemical and bulk structural characterization, probing the microenvironments and near-electrode structure in the microemulsion, understanding transport and, finally, our first tests in flow battery configurations. Based on these (primarily) fundamental studies, we have identified additional topics for scientific investigation, begun to develop predictive machine learning models to aid in identifying the most favorable components and compositions and brought into focus aspects that require study or optimization for use in practical systems.

1-B-2: PROBING INTERFACIAL REACTIONS AND TRANSPORT KINETICS OF AQUEOUS BATTERIES WITH WATER-IN-SALT (WIS) ELECTROLYTE

[EFRC – m2M/t] Lei Wang[1,2], Yu-chen Karen Chen-Wiegart[2, 1], Shan Yan[1,2], Calvin D. Quilty[2], Jason Kuang[2], Mikaela R. Dunkin[2], Steven N. Ehrlich[1], Lu Ma[1], Kenneth J. Takeuchi[1,2], Esther S. Takeuchi[1,2], Amy C. Marschilok[1,2] Cheng-Hung Lin[2], Steven T. King[2], Jianming Bai[1], Lisa M. Housel[1,2], Alison H. McCarthy[2], Mallory N. Vila[2], Hengwei Zhu[2], Chonghang Zhao[2], Lijie Zou[2], Sanjit Ghose[1], Xianghui Xiao[1], Wah-Keat Lee[1], Mingyuan Ge[1]
[1]Brookhaven National Laboratory; [2]Stony Brook University

"Water-in-Salt" (WIS) electrolyte provides promise for both lithium-ion batteries (LIBs) and aqueous Zn-ion batteries (ZIBs). Limitations such as the narrow voltage window of water can be overcome as well as suppression of the dissolution of active materials. Our recent studies have probed the use of WIS in zinc based batteries as well as in lithium ion systems. In the aqueous zinc system, the use of WIS provided substantially improved capacity retention due to reduced cathode dissolution. Further, direct visualization of the interfacial reactions at the zinc surface was achieved for the first time in a Zn-MoO_3 system, using an operando optoelectrochemical measurement. In the lithium-ion system, transport kinetics using WIS electrolyte was considered for thin and thick (≥ 150 µm) porous electrodes cycled under different rates. Raman 3D mapping visualized the percolation of WIS electrolyte in the electrodes. Because the viscosity of WIS is notably higher, the reaction heterogeneity of the electrodes was quantified with X-ray absorption spectroscopic 3D nano-tomography visualizing the kinetic limitations of the WIS electrolyte. The chemical and morphological evolution from spectroscopic tomography were further coupled with structural evolution, characterized by in situ synchrotron X-ray diffraction. These works advance the mechanistic understanding of electrode–WIS electrolyte interactions and provide strategies to realize the benefits of WIS in three-dimensional electrode architectures.

1-B-3: ACTIVE COLLOIDAL OSCILLATORS AND VORTICES AT PLANAR ELECTRODES

[EFRC – CBES] Zhengyan Zhang[1], Hang Yuan[2], Yong Dou[1], Monica Olvera de la Cruz[2], Kyle J. M. Bishop[1]
[1]Columbia University,[2]Northwestern University

Dielectric particles immersed in weakly conducting fluids rotate spontaneously when subject to a strong DC electric field. Such a spontaneous rotation, called as Quincke rotation, near a planar electrode leads to particle translation that enables physical models of active matter. Here, we show that isolated Quincke particles can also exhibit oscillatory dynamics, whereby particles move back and forth about a fixed location. We explain how oscillations arise for micron-scale particles commensurate with the thickness of a field-induced boundary layer in the nonpolar electrolyte. For a cluster of oscillators, metastable collective states such as oscillating vortices show up as well, where particles constituting the vortex rotate alternatively clockwise and counterclockwise around the center of the vortex. We attribute this phenomenon to the short-ranged electrostatic and hydrodynamic couplings between individual oscillators. These findings enable the design and understanding of colloidal oscillators.

1-B-4: MECHANISMS GOVERNING CHARGE TRANSFER OF REDOX-ACTIVE SPECIES IN DEEP EUTECTIC SOLVENTS

[EFRC – BEES] Nora A. Shaheen[1], William Dean[1], Yong Zhang[2], Drace Penley[1], Miomir B. Vukmirovic[3], Burcu E. Gurkan[1], Edward J. Maginn[2], and Rohan Akolkar[1]
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Deep eutectic solvents (DESs) are a new class of electrolytes that have gained interest as electrolytes for grid-scale energy storage applications such as flow batteries. Here, we report on processes that govern the charge-transfer kinetics involving redox-active organic (4-hydroxy-TEMPO, HT) and inorganic ($CuCl/CuCl_2$) species in ethaline DES. Using polarization measurements on a platinum rotating disk electrode and microelectrode, we show that the apparent anodic charge transfer coefficient α for a one-electron oxidation of HT approaches 1. This is a significant deviation from the expected value of $\alpha \approx 0.5$ for a symmetric one – electron transfer reaction involving a soluble – soluble transition. To explain this unusual value of α, a two-step adsorption – desorption mechanism is proposed, wherein HT undergoes fast charge transfer and adsorption at the electrode surface, followed by slow desorption of the adsorbed species. Evidence collected using surface enhanced Raman spectroscopy, combined with density functional theory simulations and electrochemical measurements suggests the presence of the adsorbed oxidation product. Comparison to other chloride-containing aqueous and organic electrolytes is discussed. Findings from molecular dynamics simulations suggest that the secondary solvation shell around redox species in DESs has an influence on the concentration availability of redox-active moieties at the electrode surface, thus impacting the redox kinetics.

1-B-5: FUNDAMENTAL MECHANISTIC UNDERSTANDING OF ELECTROCATALYTIC SULFUR REDUCTION REACTION

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The sulfur reduction reaction (SRR), a complex 16-electron process, is central for high capacity in Li-S batteries. Despite considerable interest, the fundamental mechanism and the SRR molecular pathways remain elusive. By combining electrocatalysis, cyclovoltammetry (CV), and *operando* Raman studies, we reveal two main stages from S_8 to Li_2S, with Li_2S_4 as the separating intermediate. Density functional theory (DTF) calculations propose a detailed molecular pathway for the first stage, with the simulated CV and key species (S_8, Li_2S_8, Li_2S_6, and Li_2S_4) matching experimental results. Kinetic studies show that the first stage is relatively easy with low activation energy, whereas the subsequent conversion of the polysulfides into insoluble Li_2S_2/Li_2S has a much higher activation energy, contributing to the accumulation of soluble polysulfides that exacerbate polysulfide shuttling. Nitrogen and sulfur dual-doped holey graphene considerably improve the SRR kinetics, lowering the activation energy for the second stage. DFT calculations indicate that doping tunes the p-band centre of the active carbons to optimize adsorption strength and electroactivity. To further explore the atomic-level origins of the catalytic performance, we use two-dimensional ^{13}C-^{15}N NMR spectra to resolve four distinct types of N-heteroatom environments: pyrrolic, graphitic, edge/isolated pyridinic, and pyrazinic/pyridinic moieties, and establish that pyridinic moieties are more important for electrocatalysis. In parallel with this electrocatalytic work, we are taking a multiscale approach to the challenge of polysulfide shuttling is sulfur cathodes. Other research areas include the development of sulfur-coordinating conducting polymer binders and the use of multi-dentate boron clusters to anchor reduced sulfur species.

1-B-6: ELECTROCHEMISTRY AND STABILITY OF MXENES IN AQUEOUS AND WATER-IN-SALT ELECTROLYTES

[EFRC – FIRST] Kyle Matthews[1], Armin Vahid Mohammadi[1], Tyler Mathis[1], Xuehang Wang[1], Yangyunli Sun[2], De-en Jiang[2], Wan-Yu Tsai[3], Nina Balke[3], Yury Gogotsi[1]
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MXenes, specifically $Ti_3C_2T_x$ and V_2CT_x, have shown promise for energy storage applications. However, a narrow voltage window and degradation of these MXenes in their delaminated form, particularly in water containing environments, has been a limiting factor for their use in a wide range of electrochemical applications. In this poster, we first discuss new approaches to synthesis, stoichiometry, and surface chemistry control that result in $Ti_3C_2T_x$ and V_2CT_x MXenes with greatly improved chemical and electrochemical stability and having a shelf life of several months without degradation. Second, we discuss electrochemical properties of these MXenes in water-in-salt electrolytes as well as concentrated aqueous acidic and basic electrolytes. Water-in-salt electrolytes are a safer alternative to organic electrolytes, which can provide a wide potential window. Our studies showed that, $Ti_3C_2T_x$ MXene has an electrochemical anomaly in these highly concentrated electrolytes (19.8M LiCl, 19.2M LiBr, 15M LiTFSI), exhibiting distinct and separated anodic and cathodic peaks and an expanded voltage window of 1.6 V. In addition, investigation of V_2CT_x and $V_4C_3T_x$ MXenes in concentrated basic and acidic electrolytes (i.e., 6M KOH and 3M H_2SO_4), showed distinct differences between electrochemical response and redox potentials for these two MXenes, hinting at the role of transition metal layer structure on the electrochemical properties of these materials.

1-B-7: THE ROLE OF CATION-DRIVEN SOLVENT MOTION IN LITHIUM BATTERY ELECTROLYTES

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The rational design of new battery systems rests on a fundamental understanding of the factors that underpin the transport of the working ion (frequently a cation). While conductivity reflects the motion of both the cation and the anion, the transference number t_+^0 reflects the fraction of current carried by the cation relative to a reference velocity that is usually taken to be that of the solvent. At any instant, the cations will be present in different solvation environments; some cations may be entirely solvated by solvent molecules while others may have an anion in the first solvation shell. In this study, we combine electrophoretic NMR (e-NMR) measurements of ion and solvent velocities under applied electric fields with computer simulations to interrogate the different environments in a model liquid electrolyte: a mixture of bis(trifluoromethanesulfonyl)imide (LiTFSI) and tetraglyme. Measured values of t_+^0 agree quantitatively with simulation-based predictions. The simulations reveal two dominant solvation motifs: (1) where the cation is solvated by 2 solvent molecules, and (2) where it is solvated by 1 solvent molecule and an anion. While the eNMR results reflect the average velocity of all solvent molecules, combining these results with insights from simulation enables estimation of the field-induced velocity of *only* those solvent molecules that are in the solvation shells of the migrating cations. At a particular electrolyte concentration, 1.8 m, $t_+^0 = 0$ because the average field-induced velocities of the cation and solvent are identical; most of the solvent molecules are in solvation motif (1) at this concentration.

1-B-8: ALKALI-RICH METAL SULFIDES AS MODEL SYSTEMS TO UNDERSTAND ANION REDOX IN HIGH-CAPACITY BATTERY CATHODES

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Li-ion battery cathodes store charge via intercalation mechanisms. On charge, Li^+ is removed from a transition metal oxide while the redox active transition metal is oxidized. Cathode materials contain one equivalent of Li per transition metal yielding a one electron oxidation on the transition metal upon Li^+ removal. Unlocking the redox activity of the anions would yield higher capacities by allowing multielectron redox with respect to the transition metal content. Anion redox processes are poorly understood and can incur significant structural changes that shift the electrochemistry and cause poor reversibility. We study alkali-rich transition metal sulfides to develop the structure-property relationships associated with anion redox. Using the known Li_2FeS_2 phase, we show that oxidation of >1.8 mol e^- from the structure results in Fe^{2+} oxidation and S^{2-} oxidation to $(S_2)^{2-}$. The oxidation processes occur at discrete potentials with Fe^{2+} oxidation occurring below S^{2-} oxidation. The anion redox potential can be tuned by substituting Se on the S sublattice. The more covalent Fe-Se bond causes both Fe and Se to participate in charge compensation at overlapping potentials. We have also substituted Na for Li to prepare $LiNaFeS_2$. Cycling $LiNaFeS_2$ causes significant lattice contraction and expansion which cracks the particles as observed with transmission X-ray microscopy. Particle cracking can be alleviated by cyromilling, which both reduces the crystallite size and introduces defects. The cryomilled $LiNaFeS_2$ can accommodate the strain imposed during oxidation allowing it to oxidize as a solid-solution, while the as-prepared material undergoes a phase change at early states of charge.

1-B-9: INSIGHTS INTO THE FUNDAMENTAL MECHANISM OF AQUEOUS ZN/MNO2 BATTERIES

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Possible alternatives to Li-ion batteries for scalable energy storage are Zn/MnO_2 batteries. However, understanding of the $Zn/\alpha\text{-}MnO_2$ charge storage mechanism has remained elusive, where Zn^{2+} and/or H^+ insertion or conversion to the MnOOH have been suggested. This poster presents the first *operando* visualization and quantification of Mn dissolution and deposition during cycling of a $Zn/\alpha\text{-}MnO_2$ battery via synchrotron-based x-ray fluorescence (XRF) mapping, providing direct evidence that Mn^{2+} dissolution-deposition is the primary charge storage mechanism for non-alkaline, aqueous $Zn/\alpha\text{-}MnO_2$ batteries. The dissolution-deposition mechanism is corroborated using x-ray diffraction (XRD), x-ray absorption spectroscopy (XAS), and transmission electron microscopy (TEM) and related methods. The local high-resolution TEM studies establish the dissolution-deposition mechanism is applicable toward multiple non-alkaline aqueous electrolyte systems including zinc sulfate, acetate and triflate based electrolytes. Thus, the dissolution-deposition mechanism is shown to be more universally applicable toward the

Zn/MnO_2 system, representing a paradigm shift in understanding toward the ultimate realization of scalable stationary energy storage.

1-B-10: INVESTIGATION OF THE STRUCTURAL, TRANSPORT AND ELECTROCHEMICAL BEHAVIORS OF NANOSCALE HYBRID ELECTROLYTES ENABLING SUSTAINABLE ENERGY STORAGE

[EFRC – BEES] Tony G. Feric[1,2], Sara T. Hamilton[1,2], Md Ashraful Haque[3], Sahana D. Bhattacharyya[4], Emmanuel U. Mapesa[3], Javad Jeddi[3], Nelly M. Cantillo[3], Adam E. Imel[3], Mark D. Dadmun[3,5], Steven G. Greenbaum[4], Joshua Sangoro[3], Thomas A. Zawodzinski Jr.[3,5], Ah-Hyung Alissa Park[1,2]

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Nanoparticle Organic Hybrid Materials (NOHMs) are polymer-tethered nanoparticles and they possess favorable properties including negligible vapor pressure, thermal-oxidative stability, chemical tunability and high conductivity. NOHMs have been proposed to improve the energy and power densities of redox flow batteries (RFBs) by increasing redox species solubility and electrolyte conductivity. However, NOHMs are challenged by high viscosity, so they must be incorporated into electrolytes. In this work, the structure of ionic NOHM-based electrolytes has been elucidated through small angle neutron scattering combined with the measurement of transport properties. Polymers in the canopy of NOHMs were found to exist in different nanoscale environments, and their transport and relaxation behaviors were dependent on NOHMs concentration, ionic stimulus and solvent quality. Furthermore, spectroscopic evidence suggests that NOHMs form complexes of varying strength with redox active species typically used in RFBs (*i.e.,* Cu^{+2} and Zn^{+2}). For strongly-bound complexes, electrochemical oxidation and reduction were completely inhibited, though the reversibility was shown to be restored via a pH swing. For weakly-bound complexes, the reversibility of the reaction remained relatively unaffected, though smoother metal deposits were obtained, suggesting adsorption of NOHMs on the electrode surface. Significant differences were observed in the electrodeposition with the addition of untethered polymer versus NOHMs, indicating that the polymer organization in NOHMs may affect the local structure of the electrode-electrolyte interface. These results suggest that NOHMs-based electrolytes may improve the performance of RFBs, though a deeper understanding of their role at the electrode surface and effect on long term RFB performance is still required.

1-B-11: ROLE OF PRE-INTERCALATION ON THE ELECTROCHEMICAL PERFORMANCE OF $Ti_3C_2T_x$ MXENE IN AQUEOUS AND ROOM TEMPERATURE IONIC LIQUID ELECTROLYTES

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MXenes are electrically conductive two-dimensional transition metal carbides and nitrides that have shown a great potential as electrode material for supercapacitors. While intercalation plays an important role in the applications of MXenes since it is the mechanism for storing ions in it, less is known about the effect of pre-intercalation on the electrochemical performance of MXenes. We will discuss few examples where pre-intercalation introduced a significant change in

the electrochemical performance of MXenes. First example, Na^+, K^+, and Mg^{2+} pre-intercalated multilayer $Ti_3C_2T_x$ were explored as aqueous supercapacitor electrode with adjustable areal loadings (5.2 to 20.1 mg/cm^2). K-$Ti_3C_2T_x$ exhibited the highest capacitances at different scan rates, achieving a gravimetric capacitance of up to 300 F/g, comparable to delaminated MXene but with an ultra-high areal capacitance of up to 5.7 F/cm^2, which is manyfold higher than the 0.5 F/cm^2 which can be achieved for delaminated MXene. The other example is using pre-intercalation of alkylammonium (AA) cations with different chain lengths to study the effect of interlayer spacing in MXene on their performance as electrodes for supercapacitor in room-temperature ionic liquids (RTIL) electrolytes that offer larger potential windows, leading to higher energy density. We found that pre-intercalated MXene with an interlayer spacing of ≈2.2 nm can operate within a voltage window of > 3V in neat EMIMTFSI electrolyte and deliver a large specific capacitance of 257 F/g (1428 mF/cm^2 and 492 F/cm^3) -an order of magnitude higher than pristine MXene- leading to high-energy density achieving those of batteries without compromising their high-power density.

1-B-12: NOVEL MATERIALS, THEORETICAL METHODS, AND OPERANDO PROBES FOR ALKALINE-BASED ENERGY SYSTEMS

[EFRC – CABES] Aileen Luo[1], Xinyao Lu[1], Yao Yang[1], Pengtao Xu[1], Anuj Bhargava[1], Yuval Elbaz[2], Quynh Sam[1], Michelle A. Smeaton[1], Jonathan Lucas Rowell[1], Maytal Caspary Toroker[2], Xin Huang[1], Jesse Hsu[1], Ming Zhou[3], Héctor D. Abruña[1], Tomás Arias[1], Joel Brock[1], Jiye Fang[3], Lena F. Kourkoutis[1], Brett Fors[1], Richard Robinson[1], Jin Suntivich[1], Andrej Singer[1]
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We developed monodisperse, strain-engineered colloidal nanocrystals of ternary spinel oxides and probed their structures using high-resolution strain characterization methods, including direct lattice imaging and scanning nanobeam electron diffraction with exit-wave power cepstrum analysis. We demonstrate progress synthesizing ultra-small (9 nm), purely {101}-faceted $CoMn_2O_4$ spinel nano-octahedra that exhibit high mass activity, up to 60 A/g at 0.85 V, towards the ORR in alkaline media, superior to both the nano-spherical counterpart and commercial Pt/C catalysts.

We present a new, direct vinyl addition polymerization strategy for AAEMs that overcomes past difficulties in dealing with ionic species enabling incorporation of bulky, ultra-stable cations into mechanically favored vinyl addition backbones. We developed RRDE and EQCM protocols to assess membrane and ionomer stability in the presence of peroxide and peroxide intermediates.

We present a joint density-functional theory (JDFT) approach to study the alkaline ORR pathway on Co_3O_4 and find an unexpected pathway giving excellent agreement with experimental half-wave potentials. We present a new ab initio technique, computation of surface chemical strain tensors, that accelerates the prediction of strain impacts on catalyst performance.

We demonstrate the use of X-rays to characterize systems with atomic specificity under *operando* conditions. We describe anomalous scattering and resonant elastic scattering to measure the distribution of ions in solution near nanoparticle interfaces, as well as coherent X-rays to probe operando nanoscale heterogeneity to identify sites with improved electrochemical performance. We report the use of scanning electrochemical probes and nonlinear optical second-harmonic generation to probe the evolution of interfacial electric fields during electrocatalysis.

1-B-13: PREDICTIVE COMPUTATIONAL MODELING IN THE FIRST CENTER

[EFRC – FIRST] Peter Cummings[1], De-en Jiang[2], Jianzhong Wu[2], Stephan Irle[3], Paul Kent[3], Adri Van Duin[4]
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Computational modeling over many orders of magnitude of spatiotemporal scales, highly integrated with experiment, synthesis, and characterization, has always been fundamental to the success of the FIRST Center. We have termed this philosophy model-integrated synthesis, characterization, and experiment (MISCE). Our stated goal in the FIRST Center has always been to develop predictive modeling capabilities that would guide and inform experiment. In this poster, we highlight scientific achievements of the FIRST Center over the past two years in which phenomena/systems predicted/discovered computationally have been subsequently validated by experiment and/or the synthesis and characterization of new materials.

1-B-14: A CONCERTED PHYSICS-BASED MODEL–EXPERIMENTAL EFFORT TO DESCRIBE EVOLUTION OF LITHIUM-ION BATTERY CATHODES

[EFRC – m2M/t] Amy C. Marschilok[1,2], Alan C. West[3], Karthik S. Mayilvahanan[3], Alison H. McCarthy[1], Jason Kuang[1], Zeyu Hui[3], Krystian Ganko[3], Mikaela R. Dunkin[1], Steven T. King[1], Calvin D. Quilty[1], Lisa M. Housel[1,2], Yuan Yang[3], Xiao Zhang[4], Zhengyu Ju[4], Guihua Yu[4], Kenneth J. Takeuchi[1,2], Esther S. Takeuchi[1,2]
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Models to understand and predict degradation can play a key role in improving the utility of Li-ion batteries. For example, degradation of lithium trivanadate ($Li_xV_3O_8$) cathodes has been widely reported in the literature, but studies have offered little insight towards developing a detailed understanding of the evolution of the active material and have been inconclusive as to the root cause of degradation. While classical mechanistic models can describe the complex physics of degradation, more recently, data-driven machine learning models have been increasingly utilized for state estimation and lifetime prediction. A physics-based model – experimental feedback loop is described here, using $Li_xV_3O_8$ as a case study to describe phase evolution and material changes at the molecular to mesoscale level upon electrochemical (dis)charge, and resulting impact on transport properties and cycle life of the battery system.

1-B-15: REDOXMER DESIGN FOR HIGHLY CONCENTRATED REDOX ACTIVE ELECTROLYTES

[Hub – JCESR] Aman Preet Kaur[1], Anton S. Perera[1], Lily A. Robertson[2], Yilin Wang[3], T. Malsha Suduwella[1], Ilya A. Shkrob[2], Randy H. Ewoldt[3], Susan A. Odom[1]
[1]University of Kentucky; [2]Argonne National Laboratory; [3]University of Illinois, Urbana–Champaign

Nonaqueous redox flow batteries (NAqRFBs) with a wider operational voltage window and a broader choice of electrochemical couples, have shown great promise for grid-scale energy storage. NAqRFBs must operate with high active material concentrations to compete with aqueous counterparts while remaining economical. Systematic chemical modifications of the stable phenothiazine redoxmer has allowed us to improve its solubility in uncharged state. Addition of glycol chain at the N atom gave *N*-(2-(2-methoxyethoxy)-ethyl)phenothiazine (MEEPT), which is a liquid at room temperature and miscible with polar solvents. However, for use as a concentrated electrolyte, a redoxmer needs to be soluble at all concentrations in all states of charge. For the charged form (radical cation salt), we studied effect of anion identity on the solubility of the phenothiazine radical cation. MEEPT-X (X = BF_4, ClO_4, PF_6, $SbCl_6$, SbF_6, OTF, FSI, TFSI, PFSI, FTFSI) were synthesized via chemical oxidation to produce crystalline salts; their solubility was determined using NMR. A 5-fold enhancement in solubility was achieved by changing the anion in comparison with the commonly employed BF_4 salt. The trend in solubilities of MEEPT-X show dependence on differences in crystal packing and melting point analysis. In solution state, connection between molecular structure and macroscopic electrolyte properties (like viscosity and conductivity) was studied. To understand the fundamental factors affecting solubility of the charged forms, a QSPR model is proposed to demonstrate a correlation between solubility, solvent accessible surface area, and configurational entropy of anions. This study attempts to provide design principles for obtaining highly concentrated redox active electrolytes for NAqRFBs.

1-B-16: ENABLING A BREAKTHROUGH ELECTROLYTE THROUGH AN UNDERSTANDING REDOX ORGANIC DES

[EFRC – BEES] Nicholas Sinclair[1], Maria Escamilla[2], Raziyeh (Melina) Ghahremani[1], Sarah Mitchell[2], Derrick Poe[3], Ernesto Camilo Zuleta Suarez[4]
[1]Case Western Reserve University (lead institution); [2]Texas A&M University; [3]University of Notre Dame; [4]University of Tennessee at Knoxville

A breakthrough electrolyte must excel in three key aspects: energy density, efficiency, and lifetime. The first two aspects can be combined as the impact on discharge energy density. Using only energy density as a guiding metric for defining breakthrough electrolytes leads us to consider high solubility and large potential redox pairs in an electrolyte. When using the discharge energy density as a metric specifically, we must take into account electrochemical losses related to kinetic and transport properties as well as stability of both the electrolyte and redox active molecule (lifetime). Understanding all these thermo, kinetic, and transport properties in concert is crucial to the development of a breakthrough electrolyte for energy storage. This poster highlights key findings of our interdisciplinary team related systems based on redox organics in a hydrogen bonding electrolyte. We have investigated several material systems to understand how component functionalization and electron densities affect solubility and stability leading to a completely redox active DES. We are investigating how interaction of the redox molecule with the hydrogen bond network affects the kinetic and transport properties. We utilize electrochemical, synthesis, computational chemistry, and spectroscopy techniques across four universities to study these systems. We have shown that alcohol groups, while providing high conductivity, limit the electrochemical window and can polymerize at extreme potentials. We have discovered that electron density of redox molecules plays an important role in the chemical and electrochemical properties in DES. We are using this understanding to guide the synthesis of new molecules with enhanced properties.

1-B-17: UNDERSTANDING CHARGE TRANSPORT IN REDOX-ACTIVE MATERIALS AT THE SINGLE MOLECULE LEVEL

Jialing Li, Sanja Pudar, Hao Yu, Songsong Li, Jeffrey S. Moore, Joaquín Rodríguez-López, Nicholas E. Jackson, Charles M. Schroeder
University of Illinois at Urbana-Champaign

The development of new energy storage systems for next generation batteries and smart electronics has attracted substantial scientific attention. However, progress has been hindered by a lack of understanding of molecular-scale charge transport in redox-active materials. This work aims to develop a fundamental understanding of charge transport processes at electrode interfaces at the single molecule level. To achieve this goal, we use a combination of single-molecule and bulk-scale electrochemical characterization combined with computational

modeling. In particular, we built a custom electrochemical scanning tunneling microscope-break junction (ECSTM-BJ) instrument that allows for the direct characterization of molecular charge transport in viologens as a function of the redox state. Our results show that the intramolecular charge transport of viologens critically depends on the electrochemical environment, with an unexpected dependence on the counteranion species. Interestingly, we observe a large and reversible 10-fold enhancement in molecular conductance upon electrochemical reduction of the viologen redox pair ($V^{2+}/^{+}$) to the radical cationic state in electrolytic solution. Density functional theory (DFT) simulations show that molecular charge transport depends on the dihedral angles between adjacent pyridinium rings in viologen molecules, which is determined by the chemical identity of counterions and the redox state. In addition, our results indicate weakened electrostatic interactions between viologen molecules and the charged electrode surface in the reduced state. Overall, this work provides new information regarding charge transport mechanisms in redox-active molecules near electrode interfaces, which will aid in the design of new energy storage systems with programmable molecular properties.

1-B-18: DUAL ELECTRONIC AND IONIC CONDUCTING POLYMERS FOR BATTERY ELECTRODES

[EFRC – SCALAR] Pratyusha Das[1], Charlene Z. Salamat[2], Rodrigo Elizalde-Segovia[1], Billal Zayat[1], Gordon Pace[3], Bruce S. Dunn[2], Rachel A. Segalman[3], Sarah H. Tolbert[2], Sri R. Narayan[1], Barry C. Thompson[1]
[1]University of Southern California; [2]University of California, Los Angeles; [3]University of California, Santa Barbara

Polymers exhibiting both electron and ion conductivity serve as excellent candidates for electrode binders in a variety of battery architectures due to an extension of functionality beyond simple mechanical adhesion. Our efforts have focused on the development of cathode binders for lithium-ion batteries (LIBs) and binders for the sulfur electrode in lithium-sulfur batteries. With LIBs, we have focused on electron-rich 3,4-propylenedioxythiophene-based polymers (PProDOTs), which are known to be stable to repetitive oxidative doping/de-doping cycles. Our efforts have shown that alkyl-functionalized PProDOTs exhibit a significant increase in electronic conductivity upon doping along with a more modest increase in ionic conductivity while showing improved long-term stability and rate-capability with NCA cathodes relative to a PVDF binder. Further modification of the PProDOTs to incorporate oligoether side chains has led to an enhancement in ionic conductivity that also correlates well with the degree of swelling in the polymers. Current efforts are focused on increasing polymer elasticity through the use of conjugation break spacers and a focus on incorporating ionic-liquid side chains as a means to further enhance ionic conductivity. Our efforts on binders for sulfur electrodes have focused on n-dopable conjugated polymers that are redox active in the potential range of the sulfur electrode and can be reductively doped for high electronic conductivity. Here we have focused on well-known polymers such as N2200 as well as novel polythiophenes with ester functionality designed to enhance adhesion with sulfur. Experiments have shown a dramatic reduction in shuttle current in lithium-sulfur batteries with the employed polymers.

1-B-19: DATA-DRIVEN AUTOMATED CHEMICAL REACTION NETWORK ANALYSIS UNVEILS SEI FORMATION MECHANISMS

[Hub – JCESR] Evan Walter Clark Spotte-Smith, Xiaowei Xie, Samuel M. Blau, Kristin A. Persson
Lawrence Berkeley National Laboratory

Interfacial reaction cascades are extremely difficult to characterize, and the prediction of the chemical evolution, structure, and properties of the resulting surface film is one of the grand challenges of materials chemistry. The solid–electrolyte interphase (SEI), critical to metal-ion

battery function, exemplifies such a surface film. In lithium-ion batteries (LIB), despite decades of work, considerable controversy remains regarding the major components of the SEI as well as their formation mechanisms. In Mg-ion batteries (MIB), promising candidates for next-generation energy storage, even less is known, motivating the use of automated and data-driven techniques to explore electrolyte reactivity and SEI formation. Here, we demonstrate the first electrochemical reaction networks to probe SEI formation mechanisms. Leveraging high-throughput density functional theory and machine learning techniques, we construct a network containing hundreds or thousands of species and the millions of associated possible reactions. We then use automated pathfinding tools to explore reaction landscapes. We demonstrate the power of this approach through a study of LIB SEI formation, automatically obtaining previously proposed formation mechanisms as well as novel pathways for the competitive formation of key SEI products lithium ethylene dicarbonate (LEDC) and lithium ethylene monocarbonate (LEMC). We also show the promise of this technique to explain SEI formation in MIB through a study of gas evolution in a diglyme-based electrolyte.

1-B-20: UNDERSTANDING AND CONTROLLING REVERSIBILITY OF METAL DEPOSITION/STRIPPING PROCESSES

[EFRC – m2M/t] Regina Garcia Mendez[1], David C. Bock[2], Jingxu Zheng[1], Jiefu Yin[1], Duhan Zhang[1], Gaojin Li[1], Tian Tang[1], Qing Zhao[1], Xiaotun Liu[1], Alexander Warren[1], Yue Deng[1], Shuo Jin[1], Killian R. Tallman[3], Garrett Wheeler[2], Christopher D. Rahn[4], Amy C. Marschilok[2,3], Esther S. Takeuchi[2,3], Kenneth J. Takeuchi[2,3], Lynden A. Archer[1]

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The propensity of metal anodes such as Zn or Al to form non-planar, dendritic morphologies at liquid-solid interfaces is a fundamental barrier to achievement of full reversibility for next-generation rechargeable batteries. Our recent work has focused on both elucidating the interfacial phenomena as well as improving coulombic efficiency of metal plating/stripping processes through rational substrate design and modification. Rotating disk electrode experiments were used to demonstrate for the first time that the classical model of ion depletion-induced growth of dendrites is valid in dilute electrolytes but is irrelevant in concentrated (> 1M) electrolytes typically used in rechargeable batteries. Using Zn as an example, ion depletion at the mass transport limit could be overcome by spontaneous reorientation of Zn crystallites, from orientations parallel to the electrode surface to homeotropic orientations that maximize contact with ions outside the zone of depletion where morphology was found to directly determine the efficiency of the plating/stripping processes. Further, it was demonstrated how metal-substrate bonding can be used to regulate reversibility of electrodeposition. This new approach used metal-substrate chemical bonding to improve the electron transport pathways between the metal and substrate via solid-solid contact, facilitating uniform nucleation and growth of electrodeposits to achieve exceptional reversibility (99.6 – 99.8%) of Al metal anodes. These recent investigations have provided significant fundamental insights into the electrodeposition of metals while demonstrating effective strategies for improving the reversibility of systems suitable for large-scale energy storage.

1-B-21: USE OF CUTTING-EDGE IMAGING METHODS TO UNDERSTAND HOW CONTROL OF INTERFACES AND ARCHITECTURE CAN IMPROVE STABILITY IN MAIN GROUP ALLOY ANODES

[EFRC – SCALAR] Joseph Mazzetti[1], Qizhang Yan[2], David N. Agyeman-Budu[3], Andrew Dawson[1], Shu-Ting Ko[2], Doran Pennington[1], Grace Whang[4], Bruce Dunn[1], Johanna Nelson Weker[3], Jian Luo[2], Sarah H. Tolbert[1]
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Here we explore how control of nanoscale structure and interfacial engineering can improve cycling stability in high-energy-density alloy anodes. A combination of cryogenic scanning transmission electron microscopy (cryo-STEM) and *operando* transmission X-ray microscopy (TXM) are used to characterize material structure, both ex-situ and during electrochemical cycling. We specifically focus on heavier main-group alloys composed of SbSn or pure Sb because of their metallic conductivity. To improve cycling stability, we created nanoporous (NP) materials using selective dealloying or a combination of salt templating and dealloying. In the NP-SbSn system, TXM imaging indicates that the pores are well preserved upon (de)lithiation, a result that stands in sharp contrast to pure NP-Sn, which show significant pore fracture upon cycling. Diffraction indicates that the Sn component of NP-SbSn becomes amorphous upon cycling, and the amorphous fraction may increase ductility, stabilizing the pore system. In agreement with this idea, NP-Sb cycled with Li, which goes through a series of crystalline phases, shows significant particle fracture, even in nanoporous form. In contrast, NP-Sb cycled with Na, which shows amorphous intermediates, is highly resistant to cracking, despite larger overall volume expansion. Similar stability was also achieved in fully dense SbSn composites containing 2.8 at% Bi produced by ball milling. High resolution cryo-STEM imaging showed nanoscale SbSn crystallites separated by a Bi-rich interfacial phase. TXM imaging showed suppression of crack formation in the Bi-containing materials, suggesting that the liquid-like interfacial phase serves to relieve stress in these high-volume expansion anodes, akin to room-temperature superplasticity in Sn-Bi.

D. MATERIALS/CHEMISTRY BY DESIGN AND SYNTHESIS (ROOM: *1D*)

1-D-1: XYLAN STRUCTURE AND DYNAMICS

[EFRC – CLSF] Pu Duan[1], Theodora Tryfona[2], Madhulika Gupta[3], Samuel J. Kaser[1], Jan J. Lyczakowski[2], Pyae Phyo[1], Takat B. Rawal[3], Jeremy C. Smith[3], Loukas Petridis[3], Mei Hong[1] and Paul Dupree[2]
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Variable amounts of the hemicellulose xylan interact with cellulose microfibrils, depending on the source of plant biomass and xylan structure. This xylan coating may influence cellulose microfibril self-association and interaction with other wall components. A deeper understanding of the nature of the xylan-cellulose interactions will enable development of better approaches to produce sustainable fuels and biomaterials. Acetate and sugar substitutions on xylan have been suggested to influence xylan-cellulose interactions. We used unrestrained molecular dynamics (MD) simulations to study the interactions of various differently substituted xylans with cellulose fibrils. Our results suggest that substitutions that are evenly spaced and positioned on O-2 of the xylan backbone stabilize the twofold screw conformations of xylan on the cellulose surface. We analyzed xylan structure, dynamics, and interaction with cellulose using magic-angle-spinning solid-state NMR spectroscopy of ^{13}C enriched *Brachypodium distachyon (a model grass species)*. Quantitative one-dimensional ^{13}C NMR spectra and two-dimensional ^{13}C–^{13}C correlation spectra indicate that the secondary cell wall-rich stems of this grass contain more xylan and more cellulose compared to the leaves. Moreover, the xylan chains are more acetylated in the stem. These highly acetylated xylan chains adopt a twofold conformation more prevalently and interact more extensively with cellulose. These MD and NMR results support the notion that acetylated xylan in grass secondary cell walls is bound to cellulose in the twofold screw conformation. Since xylan is covalently linked to lignin, this may in turn promote cellulose–lignin interactions that are essential for the formation of the recalcitrant secondary cell wall.

1-D-2: LIGHT AND PH RESPONSIVE PROTEIN SYSTEMS

[EFRC – CSSAS] Hao Shen[1], Susrut Akkineni[1, 2], Zhiyin Zhang[3], Nicole Avakyan[3], Shuai Zhang[1, 2], Ying Xia[1], Eric Lynch[1], Justin DeCarreau[1], Joseph Watson[4], James J. De Yoreo[1, 2], F. Akif Tezcan[3], David Baker[1]
[1]University of Washington; [2]Pacific Northwest National Laboratory; [3]University of California – San Diego; [4]MRC Laboratory of Molecular Biology

We have developed light-responsive and pH-responsive protein assembly systems via rational and computational design. In the light-responsive system, host-guest supramolecular interactions drive the self-assembly of post-translationally modified proteins with the photo-isomerizable guest moiety (azobenzene) endowing the system with light-responsive properties. We have observed co-assembly of host/guest molecule-functionalized proteins in bulk solution and on a mineral surface in different morphologies, and, unexpectedly, the assembly of guest-modified proteins alone on a mineral surface. All structures disassemble upon the exposure to UV light. In the pH dependent system, de novo designed pH-responsive proteins assemble into micrometer-scale fibers with different geometries. Cryo-electron microscopy structures of designs are close to the computational design models. The pH-responsive fibers can reversibly assemble at neutral pH and disassemble at acidic pH. The ability to generate dynamic, and controllable highly ordered structures that span micrometers from protein monomers opens up possibilities for the fabrication of new multiscale metamaterials. Together, these designs address the challenge of imparting dynamic intervention over assembly-disassembly of hierarchical materials.

1-D-3: CONTROL OVER NON-EQUILIBRIUM TOPOLOGIES OF THERMO-RESPONSIVE GELS WITH HIERARCHICALLY PATTERNED SUBSTRATES

[EFRC – CBES] Ya Liu[1], Cathy T. Zhang[2], Joanna Aizenberg[2], Anna Balazs[1]
[1]University of Pittsburgh,[2]Harvard University

Surfaces with tunable microscale textures are vital in a large variety of technological applications, including heat transfer, antifouling, and adhesion. To facilitate such broad-scale use, there is a need to create surfaces that undergo reconfigurable changes in topology. Combining modeling and experiments, we design a geometrically patterned, thermo-responsive poly N-isopropylacrylamide gel film that undergoes controllable hierarchical changes in topology with changes in temperature. At the bottom, the film is covalently bound to a solid, curved substrate; at the top, the film encompasses longitudinal rectangular ridges that are oriented perpendicular to the underlying cylindrical curves. Through simulations, we show the interplay between the upper ridges and lower curves in the gel drives non-uniform, directional solvent transport, which produces transient microscopic blisters in the film. By tuning the width of the ridges, we are able to control the emergence, distribution, and alignment of the microscopic blisters. Experiments confirm our predictions and further highlight how our computational model enables the rational design of topological transitions in these tunable films. The development of actuatable, hierarchically structured films provide new routes for achieving switchable functionality in actuators, drug release systems, and adhesives.

1-D-4: BIOLOGICAL AND PHYSICAL APPROACHES TO STUDYING FORMATION OF PLANT SECONDARY CELL WALLS

[EFRC – CLSF] Sarah A. Pfaff[1], Joshua T. Del Mundo[1], Fabien Deligey[2], Jingyi Yu[1], Enrique D. Gomez[1], Esther W. Gomez[1], Tuo Wang[2], Daniel J. Cosgrove[1]
[1]The Pennsylvania State University; [2]Louisiana State University

Thickened secondary cell walls (SCWs) serve to mechanically reinforce plant tissues and are the main source of energy-rich polysaccharides harvested for conversion to biofuel. We are tracking the deposition of SCWs in developing Arabidopsis inflorescence stems with a variety of methods to connect the physical attributes of the cell wall to the mechanical strength of stems. Using inflorescence height as an indicator of developmental age, we analyzed the basal 1-cm segment of stems of increasing age, spanning the full range of SCW development. Histochemical staining revealed the accumulation of lignin in SCW-forming cell types during specific developmental stages. Tensile tests documented an increase in stiffness as SCW development progressed. Small-angle and wide-angle X-ray scattering measurements indicated that crystalline cellulose content increased linearly until stems had grown to half of their full height and then plateaued. Crystal lattice spacing, coherence length, and microfibril alignment changed most significantly directly before the leveling-off of cellulose accumulation. ^{13}C natural abundance solid-state nuclear magnetic resonance (SS-NMR) showed a consistent, low ratio of lignin in early development that tripled halfway through development and was maintained throughout the rest of maturity. These results pave the way for future SS-NMR work using ^{13}C-enrichment and unlabeled dynamic nuclear polarization to determine changes in the molecular interactions, hydration, and dynamics of key polymers as the SCW forms and matures. The ultimate goal of this multi-dimensional study is to discover the molecular bases for the emergence of the physical and chemical properties of SCWs.

1-D-5: HIERARCHICAL MATERIALS AND BIOMINERALIZATION

[EFRC – CSSAS] Madison Monahan[1], Jinrong Ma[1], Fatima Davila[1], Harley Pyles[1], Biao Jin [2], Lili Liu [2], François Baneyx[1], David Baker[1], Chun-Long Chen [1,2], James De Yoreo [1,2], Brandi Cossairt[1]
[1]University of Washington; [2]Pacific Northwest National Laboratory

The high information content of proteins drives their hierarchical assembly and complex function. Peptoids offer an organic scaffold very similar to proteins, but with a wider solubility range and easily tunable side chains and functional groups. By taking advantage of the unique structure-directing and organizational features of these systems we will create a new paradigm to direct the assembly and nucleation of inorganic materials or other hybrid matter to access new dimensions of function and fundamental science. In this work, peptoid monomers and peptoid assemblies are being investigated to direct the organization of inorganic nanoparticles and proteins. Protein design is used as a tool to interrogate the interfacial rules required to bind and/or nucleate metal oxide and CaCO3 crystals.

1-D-6: STRUCTURAL AND BIOPHYSICAL PRINCIPLES OF CELLULOSE MICROFIBRIL ASSEMBLY

[EFRC – CLSF] Hui Yang[1], Jim Kubicki[2], Albert Kwansa[3], Justin Williams[3], Yaroslava Yingling[3], Purushotham Palliniti[4], Jochen Zimmer[4]
[1]Pennsylvania State University; [2]University of Texas at El Paso; [3]North Carolina State University; [4]University of Virginia

Cellulose, a linear polymer of glucose molecules, is a fundamental cell wall component in vascular plants and the most abundant biopolymer on Earth. Because plants synthesize glucose from atmospheric carbon dioxide by photosynthesis, cellulose also represents a tremendous carbon dioxide sink. Cellulose is produced by a membrane-embedded nano-machine (called cellulose synthase or CesA) that polymerizes glucose into long chains and transports the polymers to the cell surface during biosynthesis. Here, the cellulose chains associate into cable-like microfibrils that are wrapped around the cell to form the load-bearing wall component. Cellulose microfibrils likely arise from supramolecular CesA complexes that spatially and temporally orchestrate the secretion of multiple cellulose polymers. To gain insights into cellulose biosynthesis and microfibril formation, we integrated structural biology techniques with classical molecular dynamics simulations, density functional theory calculations, and de novo modeling approaches. Cryo electron microscopy of a homotrimeric poplar CesA complex revealed the self-association of three catalytically active enzymes into a triangular complex producing three cellulose polymers. Modeling the emerging cellulose chains in an aqueous environment reveals spontaneous intermolecular interactions, suggesting the formation of protofibrils. Further, lower-resolution depictions of membrane-embedded CesA supramolecular complexes guide the *in silico* assembly of six CesA trimers into a pseudo sixfold symmetric rosette likely responsible for microfibril formation *in vivo*. These studies suggest that six cellulose protofibrils coalesce to form an 18-chain microfibril. Our work provides the first molecular and mechanistic insights into the formation of this ubiquitous biomaterial essential for countless biological and manmade processes.

1-D-7: KINETICALLY CONTROLLED LINKER BINDING IN RARE EARTH-DOBDC MOFS, AND ITS PREDICTED EFFECTS ON ACID GAS ADSORPTION

[EFRC – UNCAGE-ME] Susan E. Henkelis[1], Dayton J. Vogel[1], Peter C. Metz[2], David X. Rademacher[1], Nichole R. Valdez[1], Mark A. Rodriguez[1], Jessica M. Rimsza[1], Katherine Page[2,3], Tina M. Nenoff[1]
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Metal-organic frameworks (MOFs) have been shown to have applications in a range of areas including catalysis, gas selectivity and storage and sensors. Here, the full RE-DOBDC (RE = rare earth; DOBDC = 2,5-dihdroxyterephthalic acid) series of MOFs from yttrium to lutetium (Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu) has been synthesized and analyzed by a range of materials techniques including both single crystal and powder X-ray diffraction (XRD), and scanning electron microscopy (SEM). The lanthanide 3+ cations are known to contract across the series, and as such the pore size of the MOF decreases across the series as seen by XRD. This allows for the creation of a MOF with an ideal pore size by tuning the metal center.

Eu-DOBDC was seen to have a combination of monodentate and bidentate binding when synthesized under typical reaction conditions, resulting in a contortion of the structure. However, extended crystallization times determined that this binding is kinetically controlled, and that the monodentate binding option was eliminated by extended reaction times at higher temperatures. Computational modelling efforts were used to show distinct differences on acid gas (NO_2, SO_2) binding energies for RE-DOBDC MOFs when comparing the monodentate/bidentate combined linker (MD/BD@DOBDC) with the bidentate-only linker (BD@DOBDC) crystal structures. This study showed that the BD@DOBDC MOFs have projected lower binding energies and increased steric hindrance that inhibits NO_2 and SO_2 metal binding as compared to MD/BD@DOBDC MOFs.

1-D-8: STRUCTURE AND FUNCTION OF THE GATING LOOP IN PLANT CELLULOSE SYNTHASE

[EFRC – CLSF] Jason N. Burris[1], Mohamadamin Makarem[2], Erin Slabaugh[1], Arielle Chaves[3], Ethan T. Pierce[1], Jongcheol Lee[2], Sarah N. Kiemle[2], Albert L. Kwansa[1], Abhishek Singh[1], Sydney Duncombe[2], Charles T. Anderson[2], Jochen Zimmer[4], Yaroslava G. Yingling[1], Alison W. Roberts[3], Seong H. Kim[2], and Candace H. Haigler[1]
[1]North Carolina State University; [2]Pennsylvania State University; [3]University of Rhode Island; [4]University of Virginia

The properties of renewable, lignocellulosic biomaterials may ultimately be improved by modifying the synthesis of cellulose microfibrils within plant cell walls. First, we must understand structure/function relationships in plant cellulose synthase enzymes (CesAs). Useful modifications might increase the rate or stress resistance of cellulose synthesis or improve its properties. Our experiments on CesAs focused on a gating loop, which can modulate access of the UDP-glucose substrate to the catalytic site by intra-protein interactions and regulatory mechanisms that are still unknown in plants. We used modeling approaches to clarify the potential positioning and interactions of the gating loop in CesA monomers and trimers because this flexible protein region was not fully resolved in cryo-structures. We changed single amino acids or small domains in this region of three CesA isomers, including an isomer that forms secondary walls (=most of the world's biomass. Analysis of phenotypes arising from the engineered genes revealed a range of consequences of engineered CesAs, from no effect through low, medium, and high inhibition of cellulose synthesis. Vibrational sum frequency generation spectroscopy revealed cell- and organ-specific effects of altered cellulose synthesis. The results support the hypothesis that regulation of substrate access may modulate cellulose synthesis in different CesA isomers. We plan to extend these results with improved methods of imaging active cellulose synthases by super-resolution microscopy to test whether phenotypes are linked to changed rates or patterns of cellulose synthesis.

1-D-9: SHAPE-DRIVEN, DNA-MEDIATED ENGINEERING OF COLLOIDAL SUPERLATTICES

[EFRC – CBES] Wenjie Zhou[1], Yuanwei Li[1], Haixin Lin[1], Yein Lim[2], Sangmin Lee[2], Sharon C. Glotzer[2], Chad A. Mirkin[1]

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Colloidal assembly of nanoscale objects enables the synthesis of a wide range of hierarchical structures that can be obtained simply by changing the size, shape, and surface chemistry of the nanomaterials. Over the past decade, advances in colloidal nanoparticle (NP) synthesis have provided access to a library of well-defined nanoscale building blocks. The organization of isotropic NPs, i.e., uniformly functionalized nanoscale spheres or pseudo-spheres, has been extensively studied and design rules have been empirically set or theoretically explained. In contrast, very few design rules exist for anisotropic NPs. In this poster, we present methodologies for the assembly of designer 3D NP superlattices using DNA-functionalized polyhedral NPs and a series of geometry-inspired strategies. To realize these exotic structures, we have developed a series of polyethylene glycol-DNA ligands that enabled the assembly of polyhedral NPs into ordered and dense-packed superlattices, a challenging prospect due to the rigidity of pure DNA. Taking advantage of the highly customizable nature of oligonucleotides and geometry-inspired designs, polyhedral NPs of different sizes and shapes were densely assembled/co-assembled. This resulted in the introduction of eleven new structures to the DNA-engineered colloidal crystal family, including the first colloidal quasicrystal engineered with DNA. Moreover, we have shown the ability to inversely design and experimentally produce ordered superlattices based on polyhedral complementarity. Importantly, these colloidal particle synthesis platforms will enable the systematic exploration of structure-functional relationships, as well as on-demand design and fabrication of highly ordered nanoscale architectures of interest to the metamaterial communities.

1-D-10: POLYG2G: A NOVEL MACHINE LEARNING ALGORITHM APPLIED TO THE GENERATIVE DESIGN OF POLYMERS

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Georgia Institute of Technology

In this work, we describe an artificial intelligence (AI)-based approach for the design of novel polymers meeting complex property objectives. We call our approach polyG2G. The key concept underlying polyG2G is graph-to-graph translation. Graph-to-graph translation solves the inverse problem. First, the subtle chemical differences between high- and low-performing polymers are learned. Then, the learned differences are applied to known polymers, yielding large libraries of novel, high-performing, hypothetical polymers. Our approach, with respect to a host of presently adopted design methods, exhibits a favorable trade-off between generation of chemically valid designs and available chemical search space. As a proof-of-concept, we first use polyG2G to find thousands of potentially high-value dielectric polymers from an otherwise intractable search space. Density functional theory simulations of band gap and electron injection barrier confirm that a large fraction of the dielectric polymers designed by polyG2G are indeed of high value. Finally, we use polyG2G to search for CO_2/CH_4 gas separation membranes lying beyond the Robeson Upper Bound and reveal some promising designs.

1-D-11: ADVANCED SAMPLING WITH SSAGES: NEW DEVELOPMENTS AND APPLICATIONS

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Advanced sampling calculations within the SSAGES (Software Suite for Advanced General Ensemble Simulations) code expand the palette of tools available in classical and *ab initio* molecular dynamics simulations. Broadly, these methods work by defining collective variables on important combinations of atomic coordinates and using static or on-the-fly biasing forces to drive exploration of these variables and obtain free energies by flattening the landscape associated with these collective variables. The MICCoM center and SSAGES team have been at the forefront of developing new techniques for advanced sampling, particularly by integrating machine learning techniques to obtain free energy landscapes from a minimal amount of sampling. We highlight here new approaches to advanced sampling---combined force-frequency, sinusoidal representation network sampling, non-equilibrium trajectory sampling, driving dynamical coordinates with parallel biasing, and free energy surface tailoring---explored within the MICCoM center and their application to important materials problems. Regarding applications, we first illustrate the key features which may be accessed in the free energy landscape of metallic clusters using biased sampling applied to first-principles simulations using the Qbox code, and how calculations at larger scales can explain the aggregation of nanoparticulate materials. Then, we show how a detailed exploration of entropic contributions typically inaccessible in first-principles simulations is essential to chemical processes happening near metal interfaces. Finally, we demonstrate the molecular pathways and free energies associated with the formation of spin defects in silicon carbide used to create qubits for quantum technologies.

1-D-12: DYNAMIC CONTROL OF SILICA NANOPARTICLE ASSEMBLY WITH BIFUNCTIONAL AND SOLID-BINDING PROTEINS

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Bio-inspired systems, which make use of sequence defined macromolecules (e.g. proteins, peptides, peptoids) to control the assembly of inorganic nano-scale building blocks, are capable of forming hierarchically ordered hybrid material structures with unique properties. However, predicting how changes to sequence and chemistry translate to assembly outcomes remains challenging, majorly due to a lack of fundamental understanding of the temporal and spatial interplay between participants when it is mediated by fundamental physicochemical interactions over a wide range of scales. Additionally, another challenge in the predictable formation of ordered nanostructures is to understand how dynamic interventions connect to structural outcomes. To address these challenges, we use a system in which silica nanoparticles (SiNP) are reversibly and repeatedly assembled using a homobifunctional solid-binding protein and single unit pH changes under near neutral conditions as a model to integrate the experiments and simulations and develop a theoretical framework where interactions at the molecular and macroscopic scales are rigorously coupled based on colloidal theory and atomistic molecular dynamics (MD) simulations. We integrate these interactions into a predictive coarse-grained (CG) model that captures the pH-dependent reversibility of the system and accurately matches small-angle x-ray scattering experiments at collective scales. The framework provides a fundamental

basis to connect microscopic details with the macroscopic behavior of complex bio-inspired material systems, and a path forward to dynamically control their behavior through an understanding of both equilibrium and non-equilibrium characteristics.

1-D-13: BETTER SELF-INTERACTION CORRECTIONS TO MODERN DENSITY FUNCTIONALS

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Despite their success in describing the properties of materials, popular density functional approximations like the PBE generalized gradient approximation (GGA) and the SCAN meta-GGA still suffer from self-interaction errors, particularly when atoms are far from their equilibrium positions. The Perdew-Zunger (PZ) self-interaction correction (SIC) makes any approximation exact for a one-electron density and gives no correction if applied to the exact functional. It greatly improves the description of stretched bonds, but it spoils the slowly-varying limits of the uncorrected approximate functionals, where those functionals are right by construction. Interior scaling can be applied to the PZ-SIC energy density by using iso-orbital indicators to distinguish many-electron regions of the density where SIC should be scaled down from one-electron regions where it should not. However, a spurious correction to the exact functional would result unless the self-Hartree and exact self-exchange-correlation (xc) terms of the PZ-SIC energy density are expressed in the same gauge. Therefore, since only LSDA has the xc and Hartree energy densities in the same gauge, interior scaling can be applied to LSDA only. The transformation of the energy density that achieves the Hartree gauge for the exact xc functional can be applied to PBE and SCAN. The resulting scaled-down self-interaction correction (sdSIC) is more accurate for these functionals than PZ-SIC and local scaling methods for many molecular properties, including equilibrium bond lengths and the dissociation energies of weakly bonded complexes. We conclude that the largest errors of PZ-SIC can be removed by restoring the correct slowly-varying limits.

1-D-14: MACHINE LEARNING OF DYNAMIC SYSTEMS

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The self-assembly of nanomaterials is driven by the kinetic-thermodynamic interplay of intersurface interactions. By identifying critical time points, interventions such as a change in pH, temperature, or ionic strength may be applied to dynamically redirect the product of assembly. Executing dynamic control over the outcome of a self-assembly process requires several key capabilities, among these are the need for: (1) automated recognition of structural data; and (2) processing parameters that can be tailored dynamically to change outcomes. To this end, we are developing machine learning tools that can be applied to both electron microscopy and optical spectroscopy data. We are validating these tools and using them to better understand the effects of processing variables like ionic screening of electrostatic interactions.

1-D-15: FLOW-ENABLED TIME-RESOLVED SCATTERING & SPECTROSCOPY REVEL KEY INTERMEDIATES IN LIGAND SUBSTITUTION & METAL HYDROLYSIS REACTIONS

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Short-lived reaction intermediates play a critical role in mediating material synthesis. Such short-lived species often elude characterization because of the mismatch between their lifetimes and the time scale of measurements capable of describing them. Thus, we have limited ability to probe, understand, and control the mechanism for material synthesis. We demonstrated a new approach to *in situ* X-ray pair distribution function (PDF) measurements of dynamic nanomaterials structure that yields an unprecedented combination of reaction time resolution and sensitivity. Reaction time is resolved spatially as a function of position along a flow path. By applying this approach to the well-studied aqueous reaction leading to FeS, mackinawite, we identify a novel metastable intermediate, FeS_{layer}, that forms in the first second of the reaction and which can be described as individual FeS nanosheets. Recognizing these nanosheets as synthons in the reaction opens up the possibility to deliberately redirect this assembly of the nanosheet toward different phases, including novel heterostructures. We are now adapting this reactor to enable Raman and UV-Vis spectroscopies and to study Ti-hydrolysis and the reaction pathways leading to differentiation between TiO_2 polymorphs.

1-D-16: UNVEILING THE COMPLEX CONFIGURATIONAL LANDSCAPE OF THE INTRALAYER CAVITIES IN A CRYSTALLINE CARBON NITRIDE

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The photoelectrochemical and photocatalytic properties of carbon nitrides are of interest to the Center for Hybrid Approaches in Solar Energy Conversion to Liquid Fuels (CHASE), yet have been limited by their typically amorphous and/or highly-disordered framework structures. An optimized one-step flux synthesis (470 °C, 36 h, LiCl/KCl flux) was used to prepare the layered carbon-nitride poly(triazine imide) and its deuterated version in high purity. Its structure was characterized by a combination of neutron/X-ray diffraction and transmission electron microscopy. The range of possible atomic configurations of cations within its intralayer cavities were enumerated for the first time, and combined with total energy calculations, reveals a more complex energetic landscape than previously considered. Experimental data were fitted against all possible structural models, exhibiting the most consistency with a new orthorhombic model (Sp. Grp. *Ama2*) that also has the lowest total energy. A new Cu(I)-containing structure was also prepared, which also most closely matched with a partially-disordered structure in $Cmc2_1$. Thus, a complex configurational landscape is revealed to consist of a number of crystalline structures that are new synthetic targets, in particular for the coordination of transition metal catalysts in hybrid photoelectrodes for the solar production of liquid fuels in CHASE.

1-D-17: NEXT GENERATION TOOLS TO INTERROGATE, PREDICT & CONTROL SYNTHESIS

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GENESIS has expanded our ability to interrogate, predict, and control the pathways that govern synthesis, and lead to new materials through development of next generation data science and experimental tools.

- A platform, "MOSY", based on action graphs captures sequences of synthesis steps in a recipe. These are being integrated into structured databases together with recipes extracted from the existing literature using natural language processing. In parallel, we have developed a tool, "Syncheck", that allows researchers to verify the machine-readability of their synthesis protocols such that more accurate recipes will be extracted from new literature.
- New algorithms and infrastructure have been implemented to enable quasi-real time data analysis and interpretation, including at the fast data-rates encountered during *in situ* synthesis experiments at synchrotron beamlines. Key advances include data analysis pipelines for streaming data, and statistical/machine learning analyses to facilitate rapid data interpretation. Data pipelines are being integrated with MPcontribs/Materials Project so that data from *in situ* synthesis experiments can be stored in machine-readable format in a stable and curated database.
- New in-situ reactors have been designed to enhance the time- and/or temperature-resolution with which we can probe synthesis reactions. Our *in situ* measurements and on-the-fly analysis capabilities have been combined to actively control the state of a reaction. We achieved a target material state by using a recursive algorithm to control the material reaction based on real-time feedback on the system chemistry from *in situ* synchrotron data. This approach represents a new paradigm in autonomation for materials discovery and synthesis optimization.

1-D-18: DESIGN AND CONTROL OF ENERGY MATERIALS FOR ENHANCED STABILITY IN ALKALINE MEDIA

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The development of design rules for materials that show high hydroxide conductivity and are durable under operating conditions is critical to realizing practical alkaline-based energy systems. Here, we focus on alkaline-stable polymer membranes and ionomers using an integrated approach of synthesis, characterization, and theory. By evaluating alkaline stability of a series of organic cations, the key functional groups in alkaline anion exchange membranes, we not only quantified their degradation rates, but also identified their degradation pathways which lead to the advancement of cations with improved alkaline stabilities. Ab initio studies of degradation processes of membranes that incorporate these cations helped accelerate the development of base-stable membranes with improved lifetimes.

The performance of polymer membranes including durability and ion conductivity critically depends on their internal microscopic organization. Transmission electron microscopy studies have played a key role in the characterization of the microphase separated domains in these materials and demonstrate their effects on their conductivities and mechanical properties. Understanding the role of crystalline domains in these systems on ion conductivity, water uptake and durability has, however, been hampered by the lack of appropriate tools for mapping the spatial organization of crystalline domains. We will discuss recent advances in cryogenic 4D-scanning transmission electron microscopy (4D-STEM) which allow us to directly image the effects of cation incorporation on membrane crystallinity in polynorbornene polymer membranes and to correlate membrane architecture with key performance metrics. Looking forward, these studies will provide the framework to probe and understand degradation mechanisms and transport properties of alkaline energy systems.

1-D-19: CONNECTING DEFECT MICROSTRUCTURE TO PHYSICAL PROPERTIES OF CERAMICS

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Investigating the influence of microstructure changes on physical properties is an integral part of understanding the behavior of materials in energy systems. Extreme environmental conditions induce defect formation and continuous property evolution during operation. Here, thorium dioxide (ThO2) is used as a model system for fluorite oxides to understand microstructure evolution under bombardment by energetic particles and the impact of these changes on thermal transport. Single crystal ThO2 was irradiated with 2 MeV protons as a function of temperature and dose. Thermal conductivity was measured using the modulated thermoreflectance method, and microstructure was characterized using transmission electron microscopy, as well as optical and Raman spectroscopy. These experimental results are analyzed using first principles-based models for defect evolution and thermal transport.

Microstructure evolution is described using rate equations where defect formation and migration barrier energies, and clustering rates are the key physical parameters. Each is inferred from either first principles calculations or experimental observations. Thermal conductivity is modeled within the framework of the Boltzmann transport formalism. Phonons and their anharmonic interactions are determined from first principles and validated using inelastic neutron scattering measurements. The scattering cross-sections of phonons with defects are obtained using methods ranging from perturbation in the acoustic limit to Green's function approaches. These analyses suggest different defects play a limiting role on transport properties across a range of temperatures as conductivity is sensitive to the complex interplay between phonon-wavelength-dependent scattering and temperature-dependent microstructure evolution. Understanding each of these contributions is key to generating predictive models of material performance.

1-D-20: UNIQUE EXPERIMENTAL AND COMPUTATIONAL CAPABILITIES DEVELOPED IN THE CHOISE COLLABORATION

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We report on several unique experimental and computational capabilities that have been successfully established during the CHOISE collaboration period.

On the *experimental* side we have developed two-photon photoluminescence and photoconductivity spectroscopy of hybrid organic-inorganic perovskite systems (HOIS) in the spectral range of 0.4-2.3 μm for studying the electronic bands and in particular a possible Rashba splitting in these materials known for their strong spin-orbit coupling (SOC). This was also studied by the excitation dependence of the circular photogalvanic effect (CPGE) and microscopy. We have also developed and studied the Rashba splitting by the technique of doping induced absorption, where a typical optical transition occurs between the two Rashba split braches. A time-resolved (~0.2 ps resolution) scanning microscopy technique and steady state photoinduced Kerr rotation, reflectivity, and photoluminescence (PL) was developed and used for mapping defects in HOIS.

On the *computational* side we have demonstrated a dramatically extended capability to predict the electronic structure of complex HOIS, including defects, with simulation cells up to 1,500 atoms, employing SOC hybrid density functional theory (DFT) in a high precision, all electron approach. For excitons in HOIS we established multi-band K·P theory and the multi-band effective mass theory, parameterized by ab-initio hybrid DFT calculations. This approach allows description of magneto-excitons, excitonic chiro-optical effects and PL emission, as well as dynamic phenomena such as quantum beating. We have also used first-principles calculation of self-trapped exciton that induces broadband PL emission in these compounds and calculated the Rashba effect associated with various surface terminations of HOIS.

1-D-21: SELECTIVITY IN MATERIALS SYNTHESIS VIA LOCAL CHEMICAL POTENTIALS GRAPHED IN HYPERDIMENSIONAL PHASE SPACE

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In sharp contrast to molecular synthesis, materials synthesis is generally presumed to lack selectivity. The few known methods of designing selectivity in solid-state reactions have limited scope, such as topotactic reactions or strain stabilization. GENESIS researchers have discovered a general approach for searching large chemical spaces to identify selective reactions. Specifically, this novel approach explains the ability of a nominally "innocent" Na_2CO_3 precursor to enable the metathesis synthesis of single-phase $Y_2Mn_2O_7$ – an outcome that was previously only accomplished at extreme pressures and which cannot be achieved with closely related precursors of Li_2CO_3 and K_2CO_3 under identical conditions. By calculating the required change in chemical potential across all possible reactant-product interfaces in an expanded chemical space including Y, Mn, O, alkali metals, and halogens, using thermodynamic parameters obtained from density functional theory calculations, we identify that only the Na-based intermediates minimize the distance in the hyperdimensional chemical potential space to produce reactions that minimize the thermodynamic competition from intermediates. Experimental evidence validating this mechanism for pathway-dependent selectivity is provided by intermediates identified from in situ synchrotron-based crystallographic analysis. This approach of calculating chemical potential distances in hyperdimensional compositional spaces, when implemented within the inorganic reaction network methodology developed by GENESIS, provides a general procedure for designing selective solid-state syntheses.

1-D-22: MACHINE-LEARNING FOR ATOMIC AND MOLECULAR MULTIPOLE MOMENTS

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The steep computational scaling of ab initio electronic structure methods often prohibits the study of large systems or else requires the use of approximate methods. Techniques from the field of machine learning (ML) allow one to potentially avoid these limitations. ML models trained on finite datasets of expensive quantum chemistry data can provide accurate predictions of properties at massively reduced computational costs. We develop a pair of complementary ML techniques. The first ML technique, referred to as the Cartesian Message Passing Neural Network (CMPNN) is a graph neural network architecture that can be trained to predict atom-centered multipoles from geometric features. The CMPNN-predicted multipoles accurately capture long-range electrostatics, a necessary component of intermolecular interactions. The CMPNN is broadly transferable across intermolecular interactions and a promising tool for ab initio force field development. Secondly, the development of the density tensor representation (DTR) allows for the prediction of complex electromagnetic response properties from an actual wavefunction encoding. The DTR has several desirable properties, such as being compact, theoretically motivated, and systematically improvable. Additionally, kernel models trained with the DTR predict molecular dipoles with sub-milliDebye accuracy using little training data. Together, these techniques demonstrate both the value of collecting high quality ab initio quantum chemistry data and the potential impact of inexpensive, accurate ML models.

1-D-23: CHARACTERIZATION OF EARLY-STAGE LATTICE DEFECTS IN CERAMIC ENERGY MATERIALS

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Ceramic materials are subject to temperature and radiation extremes in a variety of energy-related applications where atomic-level collision cascades lead to the generation of point defects and small defect clusters that drastically alter material performance. Characterizing early-stage defects is challenging since statistically-significant defect populations cannot be imaged using ultrahigh resolution microscopy, a technique that is widely applied to irradiated nuclear fuels. This has necessitated the application of indirect techniques to quantify the presence of small-scale defects. Here, we employ a multi-modal approach for studying early-stage defects induced by ion irradiation in urania and thoria. In a first example, a combination of thermal conductivity and lattice expansion measurements is used to characterize point defects generated by low-dose proton and helium ion irradiation in urania. As a next example, photoluminescence and optical absorption spectra measured in proton-irradiated thoria are attributed to creation of defect states in the bandgap from electrons trapped at oxygen vacancy sites and used to estimate the oxygen vacancy concentration. Raman spectroscopy is also used to understand the symmetry and charge state of small defect clusters in proton-irradiated thoria. Finally, the elastic properties of the defect-bearing region of low-dose proton-irradiated thoria are measured using laser ultrasonics and compared to corresponding predictions using density function theory to understand the nature of point defects that influence elastic stiffness. Our combined experimental approach to characterize small-scale defects in ceramic energy materials, informed by theoretical calculations, can provide vital data needed for the validation and development of sophisticated computational materials science models.

1-D-24: PHASE STABILITY AND ION TRANSPORT IN OXIDE TUNNEL STRUCTURES: HOLLANDITES

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Titanate-based hollandite ceramics are promising nuclear waste forms for Cs immobilization and serve as the basis for an EFRC based working group on phase stability and ion transport in oxide tunnel structures. This work will summarize results on the prediction, synthesis and characterization of new tunnel structures including Al and Cr doped hollandites across a broad range of Cs content. Enthalpies of formation determined by high-temperature melt solution calorimetry indicated enhanced thermodynamic stability with increased Cs content. Complementary studies on a related series of $Ba_{1.33-x}Cs_xFe_{2.66-x}Ti_{5.34+x}O_{16}$ hollandite (x = 0, 0.1, 0.667, and 1.33) samples has been studied under the electron beam and ion beam irradiation in the transmission electron microscopes in order to better understand radiation damage. High energy X-ray scattering has been used to examine potential clustering of cations in the hollandite phase which may impact phase stability and radiation tolerance. Finally, the group is examining potential synthesis of actinide containinig hollandite strutures along with Cs/Ba as hierarchical waste forms.

1-D-25: MECHANISMS OF COMPETITIVE ADSORPTION AND REACTIVITY OF ACID GASES IN RE-DOBDC MOFS

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Acid gases (NO_2, SO_2) are commonly found in complex chemical streams and metal-organic frameworks (MOFs) have been extensively evaluated for their separation and removal. Additionally, during adsorption reactive gas formation can occur in the MOF pores and is a known mechanism of framework destruction. Understanding reaction mechanisms between nanoconfined gases and the MOF framework is key design of next generation adsorbents. Herein, an extensive set of ab initio molecular dynamics (AIMD) simulations are used for the first time to predict competitive adsorption of binary and tertiary mixed acid gases (NO_2, SO_2, H_2O) and in-pore reaction mechanisms for a series of rare earth (RE)-DOBDC (RE = rare earth; DOBDC = 2,5-dihdroxyterephthalic acid) MOFs. Spontaneous formation of nitrous acid (HONO) is identified as a result of deprotonation of the MOF organic linker, DOBDC for NOx mixtures. The mixed monodentate and bidentate DOBDC coordination to the metal clusters allows for proton transfer from the linker to the NO_2, impacting the MOF durability. This is a previously unreported mechanisms of HONO formation in MOFs based on framework reactivity. Additionally, competitive adsorption of SO_2 and NO_2 is evaluated based on competing binding mechanisms between the acid gas molecules and the MOF structure, including the formation of additional reactive species. The evaluation of nanoconfined tertiary acid gas mixtures in RE-DOBDC MOFs demonstrates a methodology that can be applied for prediction of future gas interactions in new nanoporous materials.

1-D-26: THERMAL TRANSPORT AND MICROSTRUCTURE EVOLUTION IN A-U AND δ-UZR$_2$

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A fundamental understanding of the structure, thermal and elastic properties of nuclear fuel play an important role in nuclear energy production. Recently, there has been a renewed interest in the U-Zr system due to its technological importance as a promising metallic nuclear fuel. However, despite large experimental and theoretical efforts, various mechanisms related to its microstructure stability and thermal transport are still not well understood. Here, we present detailed studies on microstructure evolution, thermal expansion, and elastic properties of δ-UZr$_2$ and α-U samples. Thermal expansion studies of α-U crystals show large magnetostriction below the Charge-Density-Wave transition at T_{CDW} = 43 K and highly anomalous Grüneisen parameter, pointing to significant anharmonic effects in this material. Anisotropic thermal conductivity of δ-UZr$_2$ is observed (at room temperature and elevated temperatures), and the anisotropy ratio varies with temperature. The APT and TEM measurements of δ-UZr$_2$ show that it undergoes a nanoscale phase separation into U-rich and Zr-rich regimes during irradiation or thermal annealing. This phase instability may be able to explain changes in thermal transport properties observed in this material. Experimental studies have been accompanied by theoretical calculations. Using Density Functional Theory (DFT) calculations, two ab-initio thermal conductivity models and an empirical interatomic potential that describe thermal transport by both electrons and phonons were developed. These tools extended our multi-scale modeling capability of thermal properties by using DFT and Molecular Dynamics (MD), including the conductivity of α-U containing point defects. We will discuss the implications of these new results.

1-D-27: ILLUMINATING OPTICAL FLOATING ZONE SINGLE CRYSTAL GROWTH WITH SYNCHROTRON X-RAY SCATTERING

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Although the optical floating zone (OFZ) method has had a transformative impact on the availability of large single crystals of emerging materials for DOE priority research directions, OFZ crystal growth remains more of an art than a science due to the lack of information about the growth environment. To gain quantitative insights into OFZ crystal growth processes, GENESIS developed novel infrastructure that enabled the first synchrotron experiments designed to probe OFZ growth mechanisms. The first step was the design of a mini-FZ furnace small enough to fit in a synchrotron beamline yet powerful enough to heat sample rods to melting. This furnace was used to measure temperature gradients in heated rods with excellent spatial and temporal resolution, with the temperature at each point calculated from powder diffraction patterns via known thermal expansion behavior. Using physical models parameterized through advanced machine learning (ML) methods, the observed temperature profiles under many experimental

conditions were accurately reproduced in a versatile manner that allowed the extraction of unknown sample properties during the fitting process. Additionally, it was demonstrated that the shape of the buried solid-liquid interface can be resolved for a sample rod heated above its melting point. Finally, we have developed rapid experimental methods and computational algorithms that use synchrotron diffraction maps to precisely follow grain growth and crystal perfection in sample boules. These methods are being used to elucidate the relationship between crystal growth parameters and crystal quality, including unexpected improvements in TiO_2 crystal quality at faster growth rates.

1-D-28: FIRST PRINCIPLES PHONON LIFETIMES VALIDATED VIA INELASTIC NEUTRON SCATTERING

[EFRC - TETI] Enda Xiao[1], Hao Ma[2], Matthew S. Bryan[2], Lyuwen Fu[1], J. Matthew Mann[3], Michael E. Manley[2], and Chris A. Marianetti[1]
[1]Columbia University; [2]Oak Ridge National Laboratory; [3]Air Force Research Laboratory

Thermal conductivity is an important property for extracting useful heat from nuclear materials. A major contributor to thermal conductivity is the heat carried by phonons. Phonon linewidths – which are inverse lifetimes – are critical ingredients in many theories of thermal conductivity, yet the ab-initio linewidths are rarely compared with linewidths from inelastic neutron scattering (INS); and existing comparisons in the literature show glaring discrepancies. We demonstrate that the reciprocal space voxel (q-voxel), which is the smallest finite region in reciprocal space that must be sampled within INS to achieve sufficient neutron counts, must be explicitly accounted for within first principles calculations to have a meaningful comparison with INS. We illustrate the importance of the q-voxel using two ionic insulators having the fluorite structure: ThO_2 and CaF_2. We show that when first-principles linewidths are computed within the same q-voxel as INS, the linewidths are in good agreement. The thermal conductivity computed from the Boltzmann transport equation, using our DFT based q-point phonons and linewidths, is also in good agreement with experiment, consistent with other band insulators in the literature. Given the current neutron flux achieved from modern sources, one cannot easily extract q-point linewidths of the scattering function, but the fidelity of theory can be evaluated by comparing to the same q-voxel within INS, which is a far more stringent test of theory than only comparing with thermal conductivity.

1-D-29: EXPLORING STRONG AND WEAK SCALING FOR MSN INPUTS WITH DEEP LEARNING

[CCS – HETCAT] V. Sundriyal[1], Masha Sosonkina[1], Jorge Galvez-Vallejo[2]
[1]Old Dominion University; [2]Iowa State University

MSN inputs of fragment size of 10, 11, 16, 27 and 32 were tested on 15 nodes of Turing cluster at ODU for examining change in execution time with number of fragments, number of nodes, processor frequency and input parameters. Keras sequential class was utilized to create a 4-layer neural network with ReLu activation function. The total dataset size was about 100 data points. With training and testing set kept the same, a prediction accuracy of 99.65% was observed for the strong scaling case. Moreover, with K-fold validation for a value of K=5, the average RMSE observed was 2.4%. In the case of weak scaling, for a value of K=5 under K-fold validation, average RMSE of 3.5% was observed.

E. NUCLEAR SCIENCE (ROOM: *1AE*)

1-E-1: TOWARD A MODEL OF IRRADIATION AND CORROSION

[EFRC – FUTURE] Aaron Kohnert[1], Amitava Banerjee[1], Shivani Srivastava[2]
[1]Los Alamos National Laboratory; [2]University of California, Berkeley

In oxidizing environments, metals corrode by the formation of oxide scales on the surface. These thin oxide films may either grow uncontrollably or reach a stable thickness depending on how fast matter can be transported through the film, thereby governing corrosion resistance. Irradiation introduces point defects, which can mediate accelerated mass transport and change the kinetics and nature of corrosion. Here, accelerated molecular dynamics and density functional theory are both applied to discover the fundamental properties of point defects in Hematite, Magnetite, and Chromia – key oxides which govern the passivation of steel. Formation energy which controls thermal defect content, migration energy which controls defect mobility, and diffusional anisotropy are all revealed through this approach. These fundamental properties then inform spatially resolved cluster dynamics, which is used to understand changes in defect content, defect charge state, mass transport, and oxidation kinetics between thermal and radiation environments. This work reveals a profound impact of irradiation on the growth kinetics of oxide scales, highlighting the need to understand the coupled effects of these environments more completely.

1-E-2: ENHANCED CORROSION OF NUCLEAR WASTE FORMS DRIVEN BY LOCALIZED CORROSION OF STAINLESS STEEL

[EFRC – WastePD] Xiaolei Guo[1], Chandi Mohanty[1], Stephane Gin[2], Penghui Lei[3], Tiankai Yao[3], Kun Yang[3], Huseyin Kaya[4], Hongshen Liu[4], Daniel K. Schreiber[5], Dien Ngo[4], Gopal Viswanathan[1], Tianshu Li[1], Zelong Zhang[6], Seong H. Kim[4], John D. Vienna[5], Joseph V. Ryan[5], Jianwei Wang[6], Jincheng Du[7], Jie Lian[3], Gerald S. Frankel[1]
[1]The Ohio State University; [2]Commissariat à l'énergie atomique et aux énergies alternatives (CEA); [3]Rensselaer Polytechnic Institute; [4]Pennsylvania State University; [5]Pacific Northwest National Laboratory; [6]Luisiana State University; [7]University of North Texas

The corrosion of surrogate nuclear waste glass and ceramics has been found to be accelerated in a simulated repository environment when in close contact with stainless steel undergoing localized corrosion. This localized form of metal corrosion creates an aggressive environment at the anodic sites, where a solution concentrated in metal cations and acidity is generated. The increased acidity enhances the corrosion of nearby glass or ceramics within one month as evidenced by comprehensive characterization of the exposed surfaces. The cathodic reaction occurring on the portion of the stainless steel surface exposed to the bulk solution also promotes glass degradation due to the enhanced alkalinity and the accompanied precipitation of zeolite minerals. Here we report the effects of long-term exposure of glass and stainless steel in close proximity for up to one year. Large pits (>100 µm) formed on the stainless steel near the boundary of the contacting area. Additionally, unique and highly localized corrosion patterns were observed on the glass surface that was in direct contact with the large pits in the stainless steel. Although corrosion products accumulated near the boundary of the contact area, the degree of corrosion of both the glass and stainless steel after one year of exposure was higher compared to that of one month, suggesting that this self-accelerated corrosion at the interface of metal and glass or ceramics could be a long-lasting issue that should be properly addressed.

1-E-3: REVEALING MORPHOLOGICAL AND CHEMICAL EVOLUTION OF METAL-MOLTEN SALT INTERFACES BY MULTIMODAL, MULTISCALE IMAGING

[EFRC – MSEE] Xiaoyang Liu[1], Kaustubh Bawane[2], Arthur Ronne[1], Bobby Layne[3], Yang Liu[1], Panayotis Manganaris[2], Yachun Wang[2], Jagadeesh Sure[3], Lin-Chieh Yu[1], Simerjeet K. Gill[3], Kotaro Sasaki[3], Ruchi Gakhar[2], Michael Woods[2], Mingyuan Ge[3], Cheng-Hung Lin[1], Xiaoyin Zheng[1], Phillip Halstenberg[4,5], Dmitry S. Maltsev[5], Alexander S. Ivanov[4], Stephen Antonelli[3], Sheng Dai[4,5], Wah-Keat Lee[3], Xianghui Xiao[3], Anatoly I. Frenkel[1,3], Shannon M. Mahurin[4], Simon M. Pimblott[2], James F. Wishart[3], Lingfeng He[2], Yu-chen Karen Chen-Wiegart[1,3]

[1]Stony Brook University; [2]Idaho National Laboratory; [3]Brookhaven National Laboratory; [4]Oak Ridge National Laboratory; [5]The University of Tennessee, Knoxville

Gaining a fundamental mechanistic understanding of the molten salt-metallic materials interaction, especially at the interfaces, is important for molten salt corrosion processes, which are major challenges for molten salt reactors and concentrated solar power plants. We utilized a combination of synchrotron X-ray imaging and advanced transmission electron microscopy (TEM) techniques to reveal the morphological, chemical, and structural evolution of Ni and Ni-20Cr binary alloy in molten chloride salts. Real-time *in situ* synchrotron X-ray nano-tomography directly visualized dealloying and coarsening events in three dimensions (3D). The quantification of 3D morphological parameters determined the rate-determining steps for both processes. Chemical environments characterized by X-ray absorption spectroscopic imaging and modeling show limited surface oxidation of the metals. The progression of corrosion at the metal-salt interfaces was imaged at higher spatial resolution with quasi *in situ* TEM analysis, revealing the development of cracks during corrosion. Electron energy loss spectroscopy (EELS) was proven to be effective in identifying the oxidation states of alloying elements Ni and Cr in corrosion products. An oxidation state mapping technique using principal component analysis and multiple linear least squares fitting in a Python package was developed. Both X-ray and electron microscopy techniques were capable to capture key corrosion events and mechanisms on various time and length scales. The results demonstrate that multimodal, multiscale imaging has the potential to bring greater insight and deeper understanding beyond conventional analysis, particularly for examining and quantifying molten salt corrosion kinetics.

1-E-4: TRANSURANIUM MOFS - SYNTHESIS, DESIGN, AND APPLICATIONS

[EFRC – CAST] Joseph M. Sperling, Thomas E. Albrecht-Schoenzart
Florida State University

A large family of metal-organic frameworks have been prepared using transuranium elements as the metal nodes. The synthesis, structure, and spectroscopy of these materials are described in this poster along with an analysis of the chemical bonding. Several unusual properties such as stabilization of low oxidation states and ease of recycling of these materials will be presented.

1-E-5: MULTIMODAL ANALYSIS OF POINT DEFECTS IN CR2O3

[EFRC – FUTURE] Rasheed Auguste[1], Ho Lun Chan[2], Elena Romanovskaia[2]
[1]University of California, Berkeley; [2]University of Virginia

Oxidation can occur at different temperatures altering point defect types and concentrations, which play an important role in corrosion. Chromium, specifically, has been widely studied and implemented because the passivating chromium oxide film formed during oxidation can be highly corrosion resistant. Point defects play an important role in understanding the effectiveness and the limits of Cr_2O_3 corrosion protection, so significant theoretical, experimental, and modelling efforts have been done to understand the nature of point defects and their diffusion mechanisms. While each of these approaches provides its own insights on the nature of point defects' charge state, mobility, and formation energies, there have been no efforts to unite the results and insights of these techniques. In this project, the objective was to obtain a comprehensive understanding of overall oxide layer point defect density during oxide formation. This work combines oxide microstructure and chemical composition analysis from Raman spectroscopy and transmission electron microscopy (TEM) with point defect analysis from positron annihilation spectroscopy (PAS) and electrochemical impedance spectroscopy (EIS), thereby addressing the knowledge gaps between each technique. Even though each technique relies on different fundamental physical phenomena for defect observation, they all confirmed the same trend of decreasing defect density in thicker oxide layers. In addition, PAS and EIS were able to quantify the decreases in defect density.

1-E-6: SHORT ANSWERS TO LONGSTANDING QUESTIONS ABOUT THE STRUCTURE, DYNAMICS AND THERMODYNAMICS OF MOLTEN SALTS

[EFRC – MSEE] Shobha Sharma[1], Matthew S. Emerson[1], Waruni V. Karunaratne[1], Fei Wu[1], Santanu Roy[2], Haimeng Wang[3], Ryan DeFever[3], Yong Zhang[3], Martin Brehm[4], Phillip Halstenberg[2,7], [5]Leighanne C. Gallington, Simerjeet K. Gill[6], Milinda Abeykoon[6], Gihan Kwon[6], Mehmet Topsakal[6], Bobby Layne[6], Kotaro Sasaki[6], Dmitry S. Maltsev[7], Shannon M. Mahurin[2], Sheng Dai[2,7], Benjamin M. Ocko[2], Alexander S. Ivanov[2], Vyacheslav S. Bryantsev[2], Edward Maginn[3], Claudio J. Margulis[1]

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Molten salts have been studied for a century, and yet there is still a struggle when attempting to unequivocally answer basic questions about the coordination of the ions and the speciation of minority components that may appear as a result of corrosion, let alone answering the more difficult questions related to their structure and dynamics at and away from interfaces in the presence of electric fields, or the prediction of certain thermodynamic and transport properties. Even less is known about kinetic rates for processes, and the prediction of these starting from atomistic models has always been a challenge. MSEE has made tremendous progress towards answering all of these important questions using cutting-edge scattering techniques, experimental and computational methods development, groundbreaking quantum chemistry for the prediction of Raman spectroscopy, alchemical computational methods, and even the engineering of new devices to make extremely difficult measurements possible for us and the larger community. This poster will present selected discoveries about X-ray and neutron scattering of molten salts, X-ray reflectivity, the prediction of Raman spectra and its interpretation, results from several different models for the ions including the fixed charge, polarizable, Drude-based and machine learning versions for the study of structure, rate theory, and thermodynamic properties such as the liquidus for mixtures. Our goal is to shift from longstanding questions to accurate and long-standing answers that will inform the molten salt community and withstand the test of time.

1-E-7: STABILITY, STRUCTURE, AND DYNAMICS OF SYNTHETIC BRINES REPRESENTATIVE OF HIGH-LEVEL NUCLEAR TANK WASTES

[EFRC – IDREAM] Emily T. Nienhuis[1], Yihui, Wei[2], Hsiu-Wen Wang[3], Maxime Pouvreau[2], Trent R. Graham[1], Aurora E. Clark[2,1], Zheming Wang,[1,2] Carolyn I. Pearce[1,2]
[1]Pacific Northwest National Laboratory; [2]Washington State University; [3]Oak Ridge National Laboratory

In highly caustic solutions, like those in legacy radioactive waste stored at the Hanford site, there is insufficient water to form complete solvation shells around each ionic species. This leads to peculiar behavior in salt and metal ion solubilities for which we still have no mechanistic basis to predict. Advances require probing and understanding the dynamical processes leading to formation of ion pairs and compact polyhedral networks. In our studies of concentrated NaOH-$NaNO_2$ solutions, the presence of hydroxide promotes ion pairing compared to those containing only $NaNO_2$. At the solubility limit, molecular dynamics (MD) simulations and subensemble analyses reveal a complex distribution of polyhedral ion-water networks that is responsible for mid-range pair correlations in neutron and X-ray scattering profiles. Future work will investigate cation effects on these polyhedral distributions and network connectivity. In solutions of NaOH-$NaAl(OH)_4$, homogenous solutions can be obtained above the solubility limit, which exhibit different propensities and timescales for precipitation. Pairwise distribution function analysis of these solutions reveal that they are highly complex, showing subtle variations of solution behavior that necessitate multimodal characterization by vibrational spectroscopy. Ab initio MD simulations of aluminate species in solution, and their respective infrared FTIR and Raman spectroscopic signatures, are supporting interpretation of our scattering data. The combined experiments and computational simulations reveal how dynamical ion correlations lead to organizational structures in solutions that affect solubility limits. Ultimately, our work could enable a framework for understanding and predicting saturation states in highly alkaline solutions based on types of underlying ion networks present.

1-E-8: THE NATURE OF BONDING IN AMERICIUM DITHIOPHOSPHATES

[EFRC – CAST] Cristian Celis-Barros, Ryan D. M. Greer, Thomas E. Albrecht-Schoenzart
Florida State University

Dithiophosphonates such as Cyanex 301® are promising extractants for separating americium(III) from used nuclear fuel. In an effort to understand the origin of selectivity in this class of ligands, a variant has been prepared that lack P-C bonds. The coordination chemistry and spectroscopy of Am(III) dithiophosphate complexes as well as a theoretical analysis of the bonding is presented in this poster.

1-E-9: SPECTROSCOPIC AND DYNAMICAL ANALYSIS OF WATER RADIOLYSIS ON THE PHYSICO-CHEMICAL TIMESCALE

[EFRC – IDREAM] Lixin Lu[1], Andrew Wildman[1], Linda Young[2], Thomas M. Orlando[3], Aurora E. Clark[4,5], Jay A. LaVerne[6], Gregory A. Kimmel[5], Xiaosong Li[1,5]
[1]University of Washington; [2]Argonne National Laboratory; [3]Georgia Institute of Technology; [4]Washington State University; [5]Pacific Northwest National Laboratory; [6]University of Notre Dame

Understanding the initial reactive species that form in aqueous systems after exposure to ionizing radiation is an important aspect of predicting the long-term behavior of aluminum (Al)-containing radioactive waste currently stored in million-gallon tanks at the Hanford and Savannah River sites. Ab initio Ehrenfest dynamics have provided a more complete description of ultrafast processes that occur upon photoionization of pure water, including hole localization and proton transfer,

within the first 25 femtoseconds. In more complex environments, inner-shell vacancy decay represents a first step in radiolysis. Intermolecular Coulombic decay of water has been observed upon creation of a core-hole at low energies in the OH groups of micro-solvated boehmite (AlOOH) nanoplatelets. Ab initio computational analysis has shown that the electron transfer mediated decay process is a favorable decay path upon creation of an Al core-hole at higher energies. The dynamics occurring at this ultrafast time scale affect chemical reactions over longer time scales, such as the formation of hydrogen and other byproducts, relevant to the behavior of AlOOH and gibbsite ($Al(OH)_3$) at the solid-liquid interface. Ongoing studies focus on: (i) radiolysis-induced dynamics in complex, highly alkaline solutions; (ii) the link between bulk and interfacial processes; and (iii) nucleation of Al-containing phases. These studies are being conducted using advanced X-ray pump/X-ray probe techniques at the Linac Coherent Light Source, with the experimental design guided by theoretical prediction of X-ray spectra and the response to radiolysis, providing insight into radiolysis mechanisms.

1-E-10: MOLTEN SALT RADIATION-INDUCED REDOX CHEMISTRY - FROM IONS TO NANOPARTICLES!

[EFRC – MSEE] Gregory P. Horne[1], Sheng Dai[2], Elaine T. Dias[3], Anatoly Frenkel[3,4], Ruchi Gakhar[1], Simerjeet Gill[3], Phillip Halstenberg[2], Jiahao Huang[4], Kazuhiro Iwamatsu[3], Jay A. LaVerne[5], Yang Liu[4], Shannon Mahurin[2], Julia Mausz[6], Simon M. Pimblott[1], Alejandro Ramos-Ballesteros[5], James F. Wishart[3], Michael E. Woods[1]

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Because of the increasing interest in molten salt media for nuclear fuel cycle applications – power reactors and pyroprocessing of nuclear fuel – it is critical to close knowledge gaps concerning radiation-induced phenomena. Irradiation of molten salts has the capacity to generate highly reactive radical, ionic, and molecular species that can influence the physical and chemical properties of the medium. For example, the radiolytic reduction of dissolved metal ions by solvated electrons can lead to significant changes in redox potential, which in turn dictates the distribution and speciation of metal ions. Understanding these non-equilibrium processes at temperature is complicated, but the fundamental mechanistic insights thus attained lead to the prediction and eventual control of such radiation-induced processes. To this end, MSEE has developed deterministic reaction kinetic computational methods and high-temperature time-resolved (pulsed electron) and steady-state (gamma and *X*-ray) experimental techniques to interrogate radiation-induced phenomena over multiple time and distance regimes. Here we present examples of each of these scientific advancements to demonstrate the transition of radiation energy through time, from ions to nanoparticles: *(i)* initial salt radiolysis products 'frozen' in the solid state, as identified by electron paramagnetic resonance (EPR) and diffuse reflectance; *(ii)* reaction kinetics of the primary molten salt radiolysis products with the solvent and metal cation solutes, as measured by transient absorption pulse radiolysis and evaluated by deterministic reaction kinetic modeling; and *(iii)* the formation of metal nanoparticles by steady-state synchrotron *X*-ray irradiation of multivalent metal cation molten salt solutions.

1-E-11: THE INTERACTION OF RADIATION-INDUCED DEFECTS WITH INTERFACES BETWEEN IRON AND IRON OXIDES

[EFRC – FUTURE] Farida Selim[1], Djamel Kaoumi[2]
[1]Bowling Green State University; [2]North Carolina State University

The core mission of FUTURE – Fundamental Understanding of Transport Under Reactor Extremes – is to understand the synergies between irradiation and corrosion on the evolution of materials. In oxide forming systems, this necessitates examining how radiation-induced damage interacts with the interfaces between oxides and metals and how the interface drives defect evolution. To elucidate how interfaces might impact damage evolution, and thus corrosion mechanisms, we use multiple experimental approaches to interrogate these interfaces. First, using positron annihilation spectroscopy, we examine the impact of low dose irradiations on defect formation at interfaces between metallic iron and iron oxides. We find some interesting behavior where, even when the damage is confined to the oxide alone, damage evolution is induced in the metal, highlighting the complex interplay between damage in these materials. These measurements probe the very smallest defects in the material – isolated vacancies and small vacancy clusters. To complement these positron experiments, we use transmission electron microscopy to watch damage evolve at similar interfaces as they are being irradiated to much higher doses. The microscope reveals the evolution of larger scale defects, such as dislocation loops, under these conditions. However, surprisingly, the metal accumulates much more damage than the oxide. Further, the oxide exhibits significant defect denuded zones at grain boundaries. Together, these sets of experiments reveal the complex interaction of radiation-induced defects at interfaces and the potential impact of those defects on corrosive behavior.

1-E-12: CONFORMATIONAL DYNAMICS OF F-BLOCK CROWN ETHER COMPLEXES

[EFRC – CAST] Hesam Arabzadeh, Thomas E. Albrecht-Schoenzart
Florida State University

Crown ether complexes have been tailored for use in industrial-scale separations of lanthanides from one another as a part of rare earth mining and refining. In particular, dicyclohexyl-18-crown-6 is known to be among the best complexants for the separation of rare earths from one another based solely on cation size. However, the synthesis of this ligand leads to the formation of five different diastereomers of which two are the major products. The nature of complexation and selectivity is different between these two diastereomers. To under the origin of selectivity, molecular dynamics simulations have been performed with both diastereomers as well as with numerous different *f*-elements in both trivalent and divalent oxidation states. The results of these studies will be presented.

1-E-13: RADIATION ENHANCED DIFFUSION IN FE2O3 AND CR2O3

[EFRC – FUTURE] Kayla Yano[1], Aaron Kohnert[2]
[1]Pacific Northwest National Laboratory; [2]Los Alamos National Laboratory

Corrosive degradation of structural alloys in reactors is mitigated by thin protective oxide layers that separate the metal from a corrosive media. Irradiation can dramatically affect this protectiveness by generating a non-equilibrium point defect population that fundamentally alters atomistic transport through the irradiated oxide. However, the direct impact of irradiation on ion transport is as yet broadly unexplored. In this work molecular beam epitaxy embeds isotopic tracers (18O and 57Fe) in thin films to monitor and quantify atomic transport in model irradiated oxide systems (Fe_2O_3 and Cr_2O_3) with atom probe tomography. Scanning transmission electron microscopy is used to characterize higher order irradiation induced defects (dislocations, dislocation loops, voids) in the thin films. These results show orders of magnitude increases in anion diffusivity in both proton irradiated hematite and argon irradiated chromia and hematite. Increases in Fe cation diffusion are also captured. Preliminary results on transport across oxide heterolayers and transport upon phase transformation will be discussed. Combining these experimental observations with a chemical-rate theory model provides insights on fundamental transport mechanisms and rates. These understandings are essential when working to reduce degradation of structural alloys in extreme environments.

1-E-14: A HOLISTIC APPROACH FOR UNRAVELING THE COMPLEXITIES OF METAL ION SPECIATION IN MOLTEN SALTS

[EFRC – MSEE] Santanu Roy[1], Yang Liu[2,3], Mehmet Topsakal[3], Elaine Dias[3], Ruchi Gakhar[4], William C. Phillips[4], Michael E. Woods[4], James F. Wishart[3], Denis Leshchev[3], Phillip Halstenberg[1,5], Sheng Dai[1,5], Luis Betancourt De Leon[3], Simerjeet K. Gill[3], Anatoly I. Frenkel[2,3], Matthew S. Emerson[6], Shobha Sharma[6], Waruni V. Karunaratne[6], Fei Wu[6], Dmitry S. Maltsev[5], Milinda Abeykoon[3], Yuanpeng Zhang[1], Shannon M. Mahurin[1], Claudio J. Margulis[6], Alexander S. Ivanov[1], and Vyacheslav S. Bryantsev[1]
[1]Oak Ridge National Laboratory; [2]Stony Brook University; [3]Brookhaven National Laboratory; [4]Idaho National Laboratory; [5]The University of Tennessee, Knoxville; [6]The University of Iowa

The phenomena of speciation of minority components (e.g., dilute metal ions) in molten salts (MS) are nontrivial to understand due to their complex solvation behavior reflected in key observables such as coordination structures, solubility, and transport properties. While conventional techniques such as neutron/X-ray scattering or Raman spectroscopy complemented by molecular dynamics (MD) simulations can provide remarkably accurate insights into the short-to-intermediate range structural ordering in MS, what happens locally around a metal ion dissolved in MS is obscure due to mixing of the solute-solvent scattering patterns or vibrational spectroscopic features. Optical spectroscopy addresses this problem to some extent, but the assignment of the absorption peaks to specific coordination structures is sometimes ambiguous. To circumvent such ambiguity, we have introduced a holistic approach by advancing three major techniques: *(1)* X-ray scattering adapted to measure differential pair distribution functions (d-PDF) that can isolate local solvent structure around the solute, *(2)* extended X-ray absorption fine structure (EXAFS) tuned to account for multiple, co-existing coordination structures with correct populations, and *(3)* rate theory revealing kinetics of ion exchange/clustering that directly correlates with time-dependent coordination structures. In conjunction with *ab initio* MD, these methods have revealed unprecedented results; examples include persistent, octahedrally coordinated, dimeric Cr(III)-Cr(III) clustering dynamics in an MS mixture, despite the low concentration of Cr(III), and multiplicity and metastability of coordination structures of Ni(II) linked to temperature- and solvent composition-dependent anion exchange kinetics. This holistic

approach provides a way to fundamentally advance understanding and control of metal ion speciation in molten salts.

1-E-15: MIXED N,S-DONOR LIGANDS FOR SELECTIVE COMPLEXATION OF AMERICIUM

[EFRC – CAST] Zach K. Huffman, Thomas E. Albrecht-Schoenzart
Florida State University

With the goal of selectively complexing americium(III) and curium(III) over lanthanides, examples of pyridinethiol complexes of lanthanides and americium have been prepared and fully characterized. The crystal chemistry, spectroscopy, and quantum mechanical analysis of bonding of this large family of complexes is presented. In particular, the origin of the switch from the formation of mononuclear to dinuclear complexes is explained.

F. QUANTUM SCIENCE AND MICROELECTRONICS (ROOM: *1F*)

1-F-1: A NON-PERTURBATIVE STUDY OF BULK PHOTOVOLTAIC EFFECT ENHANCED BY AN OPTICALLY INDUCED PHASE TRANSITION

[CMS – NPNEQ] Sangeeta Rajpurohit[1], C. Das Pemmaraju[2], Tadashi Ogitsu[3], Liang Z. Tan[1]
[1]Lawrence Berkeley National Laboratory; [2]SLAC National Accelerator Laboratory; [3]Lawrence Livermore National Laboratory

Solid systems with strong correlations and interactions under light illumination have the potential for exhibiting interesting bulk photovoltaic behavior in the non-perturbative regime, which has remained largely unexplored in the past theoretical studies. We investigate the bulk photovoltaic response of a perovskite manganite with strongly coupled electron-spin-lattice dynamics, using real-time simulations performed with a tight-binding model. The transient changes in the band structure and the photoinduced phase transitions, emerging from spin and phonon dynamics, result in a nonlinear current versus intensity behavior beyond the perturbative limit. The current rises sharply across a photoinduced magnetic phase transition, which later saturates at higher light intensities due to excited phonon and spin modes. The predicted peak photoresponsivity is orders of magnitude higher than other known ferroelectric oxides such as $BiFeO_3$. We disentangle phonon-and spin-assisted components to the ballistic photocurrent, showing that they are comparable in magnitude. Our results illustrate a promising alternative way for controlling and optimizing the bulk photovoltaic response through the photoinduced phase transitions in strongly correlated systems.

1-F-2: EXCITONIC QUANTUM PHASES AND PROCESSES

[EFRC – Pro-QM] Ana Asenjo-Garcia[1], D.N. Basov[1], Cory Dean[1], James Hone[1], James Shuck[1], Michal Lipson[1], Andrew Millis[1], Abhay Pasupathy[1,3], Xavier Roy[1], Xiaoyang Zhu[1], Daniel Gamelin[2], Jiun-haw Chu[2], Di Xiao[2], Xiaodong Xu[2]
[1]Columbia University (lead institution); [2]University of Washington; [3]Brookhaven National Laboratory

An exciton is a bosonic quasi-particle consisting of an electron and a hole bound by the Coulomb potential. The excitonic transition dominates the optical responses in low dimensional semiconductors and can also form in the electronic ground state. The Pro-QM team has made breakthroughs in realizing and controlling a number of quantum phases and processes by

excitons. This poster highlights major advances in: 1) the formation of strain induced quantum emitters in transition metal dichalcogenide (TMDC) monolayers and the realization of 0D or strain-induced 1D moiré exciton lattices in TMDC heterobilayers. These findings open the door to controllable quantum light or quantum simulators; 2) the discovery of spin-orbit coupled (SOC) exciton-polariton condensates in optical microcavities consisting of anisotropic cesium lead bromide perovskite crystals. This finding provides a starting point for the experimental exploration of a range of phenomena in SOC quantum fluids in a solid state and high-temperature model system; 3) the realization of programmable hyperbolic polaritons in a van der Waals TMDC crystal, attributed to quantum transitions of excitons within the Rydberg series. This discovery offers an encouraging modus operandi for directional control of light propagation on the nanometer scale; 4) the theoretical exploration of field-controlled excitonic insulators that can be used to realize a range of quantum processes such as Thouless charge pumps, enormously enhanced coherent photovoltaic effects, and ferroelectric or quantum anomalous Hall states. These theoretical results are guiding the search of new exciton insulators.

1-F-3: CORRELATED HOFSTADTER SPECTRUM AND FLAVOR PHASE DIAGRAM IN MAGIC ANGLE GRAPHENE

[EFRC – QSQM] Jiachen Yu[2], Benjamin A. Foutty[2], Zhaoyu Han[2], Mark E. Barber[2], Yoni Schattner[2], Kenji Watanabe[4], Takashi Taniguchi[4], Philip Phillips[1], Zhi-Xun Shen[2], Steven A. Kivelson[2], Benjamin E. Feldman[2]
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In magic angle twisted bilayer graphene (MATBG), the moiré superlattice potential gives rise to narrow electronic bands which support a multitude of many-body quantum phases. Further richness arises in the presence of a perpendicular magnetic field, where the interplay between moiré and magnetic length scales leads to fractal Hofstadter subbands. In this strongly correlated Hofstadter platform, multiple experiments have identified gapped topological and correlated states, but little is known about the phase transitions between them in the intervening compressible regimes. Here, using a scanning single-electron transistor microscope to measure local electronic compressibility, we simultaneously unveil novel sequences of broken symmetry Chern insulators (CIs), which are instances of topological crystalline insulator order, and resolve sharp phase transitions between competing states with different topological quantum numbers and spin/valley flavor occupations. Our measurements provide a complete experimental mapping of the energy spectrum and thermodynamic phase diagram of interacting Hofstadter subbands in MATBG. In addition, we observe full lifting of the degeneracy of the zeroth Landau levels together with level crossings, indicating moiré valley splitting. We propose a unified flavor polarization mechanism to understand the intricate interplay of topology, interactions, and symmetry breaking as a function of density and applied magnetic field in this system.

Reference: J. Yu, B. A. Foutty, Z. Han, M. E. Barber, Y. Schattner, K. Watanabe, T. Taniguchi, P. Phillips, Z.-X. Shen, S. A. Kivelson, B. E. Feldman, Correlated Hofstadter Spectrum and Flavor Phase Diagram in Magic Angle Graphene, arXiv:2108.00009

1-F-4: AN ACCURATE TIGHT BINDING MODEL FOR TWISTED BILAYER GRAPHENE

[CMS – QMC-HAMM] Shivesh Pathak[1], Tawfiqur Rakib[1], Run Hou[2], Andriy Nevidomskyy[2], Elif Ertekin[1], Harley T. Johnson[1], Lucas K. Wagner[1]
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An exciting new task in condensed matter physics is understanding the microscopic mechanisms behind flat band superconductivity in twisted bilayer graphene (TBLG). A major hurdle to understanding superconductivity in TBLG are the roles of lattice relaxation and electronic structure on isolated band flattening near magic twist angles. State of the art tight binding calculations indicate that lattice relaxation is required to achieve isolated flat bands with fragile topology in TBLG, however the phenomenological origin of commonly used tight binding models obfuscates whether the lattice relaxation or model inaccuracy leads to this conclusion.

In this work, we develop an accurate local environment tight binding model (LETB) and fit it using training data from first principles density functional theory calculations. By computing the band structures using the LETB, we observe the emergence of flat bands near the magic twist angle accompanied by Wannier obstruction, associated with a fragile topology, without needing lattice relaxation. Geometry relaxation is shown only to quantitatively enhance band flattening and band gaps. Our work demonstrates that an accurate electronic structure model for TBLG can generate topological flat bands without geometric relaxation, in contrast to conclusions made using phenomenological models for TBLG.

The accurate tight binding model for twisted bilayer graphene and data used in this work are available via qmc-hamm.github.io.

1-F-5: VISUALIZING ELECTRON LOCALIZATION AND MINIBANDS IN WS2/WSE2 MOIRÉ SUPERLATTICES

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The ability to engineer flat electronic bands by controlling interlayer effects in moiré superlattices of two-dimensional materials has opened the door for material physicists to make inroads to understanding and one day controlling correlated electron phenomena in an unprecedentedly broad class of materials. Despite a wide-ranging transport and optical signatures of correlated phases and restructuring of the electronic character in 2D superlattices, a holistic understanding of changes to the broader band structure, which can provide insight into the evolution from weakly-coupled to strongly-coupled layers as the superlattice control parameters are tuned, is only just emerging. We combined nano-ARPES and optical reflectance contrast spectroscopy to observe how the electronic structure evolves from weakly interacting to strongly localized as the superlattice constant is increased in the heterobilayer WS_2/WSe_2 family. The combination of novel electronic structure measurements with reflectance contrast spectroscopy permits us to directly associate the band structure modifications for long wavelength, aligned superlattices with a broader range of phenomena already observed in moirés. We find with increasing lattice constant that the electronic structure evolves into a highly localized regime with increasingly flat bands at both the K and Γ points. By comparison to the valence band spectroscopy of aligned homobilayer

MX_2 and existing photoemission results on superlattice TMDs, we suggest a significant role for interlayer hybridization in electron localization at Γ. Our results advance our current understanding of electron localization in setting the preconditions for correlations and explore opportunities for ARPES in providing insight into more complex superlattice systems.

1-F-6: DETECTING AND MANIPULATING SYMMETRY, TOPOLOGY AND CORRELATIONS IN VDW LAYERED MATERIALS

[EFRC – CATS] Anyuan Gao[1], Zhiren Zheng[2], Kenji Yasuda[2], Qiong Ma[2,3], Su-Yang Xu[1], Pablo Jarillo-Herrero[2]
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Within CATS, we leverage strengths from multiple groups to investigate topological and correlated states in highly-tunable vdW crystals with cutting-edge heterostructure assembly techniques, advanced device fabrication, precision electron transport and optoelectronic techniques. The collaborative efforts have led to a few exciting findings. First, we observed the layer Hall effect in even-layered $MnBi_2Te_4$ thin flake. The even-layered AFM $MnBi_2Te_4$ hosts nontrivial topology and layer-locked Berry curvature, the detection of which is challenging due to the layer symmetry and zero net magnetization. In a dual-gated device, we can break the layer symmetry by applying out-of-plane *E*-field, leading to a strong electrical Hall response from uncompensated layered Berry curvature. Such a new Hall effect provides strong evidence for a topological Axion insulator state, paving the way for realizing a quantized magnetoelectric effect. Second, we demonstrated a designer approach to realize 2D ferroelectrics from assembling non-ferroelectric parent compounds. Particularly, we showed parallel-stacked BN exhibits electrically switchable polarization from the interlayer stacking order. We also introduced layer-specific moiré potential through encapsulating bilayer graphene with BNs at different angles and observed unconventional ferroelectricity emerging from layer-asymmetric interaction strength. This novel ferroelectric ordering can further couple with other emergent phenomena such as topology and magnetism in moiré lattices. Third, we discovered a spontaneous gyrotropic order in a correlated layered semimetal $TiSe_2$. Using nonlinear infrared photocurrent as a symmetry-sensitive probe of low-energy electrons, we found the system spontaneously develops an electronic geometric chirality at low temperature, which can be further manipulated through optical chiral induction during the cooldown.

1-F-7: MOIRE SCALE EFFECTIVE INTERACTION IN TWISTED BILAYER GRAPHENE

[CMS – QMC-HAMM] Run Hou[2], Andriy Nevidomskyy[2], L. K. Wagner[1]
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The rich phase diagram of magic-angle twisted bilayer graphene (TBLG) has been studied by various models. The strong interaction plays an important role in the low energy physics around the flat bands. While some estimations have been made to build one-body Hamiltonians, the form and magnitude of effective interaction in the Moire scale remain unclear.
In this work, we will present a repeatable workflow to obtain effective interaction in magic-angle flat bands. The input one-body Hamiltonian can be taken from Moon and Koshino tight-binding (MKTB) model [1], or local environment tight-binding (LETB) model. Using atomic level Hartree-Fock (HF) calculation, applying an atomic scale estimate of Coulomb interaction, the flat band HF orbitals are obtained. To avoid fragile topology, instead of using the maximally localized Wannier function (MLWF) method, we directly take the HF orbitals as the optimal Moire scale wave functions to compute the momentum space effective interaction on these active flat bands. Finally, we can extrapolate the interaction function to show the form and magnitude of effective interaction. This model sets the stage to study the many-body effects and phase diagram of the

TBLG system using many-body methods like Auxiliary-Field Quantum Monte Carlo (AFQMC) in the future.
[1] Moon, Pilkyung, and Mikito Koshino. "Energy spectrum and quantum Hall effect in twisted bilayer graphene." Physical Review B 85.19 (2012): 195458.

1-F-8: QUANTUM MONTE CARLO STUDIES OF MONOLAYER SYSTEMS – GESE AND CRI$_3$

[CMS – CPSFM] Guoxiang Hu[1], Daniel Staros[2], Juha Tiihonen[3], Ravindra Nanguneri[2], Kevin Gasperich[4], Hyeondeok Shin[4], Jaron T. Krogel[3], M. Chandler Bennett[3], Paul R.C. Kent[3], Anouar Benali[4], Olle Heinonen[4], P. Ganesh[3], Brenda Rubenstein[2]
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In recent years, 2D materials have garnered a wealth of interest because of their unique low-dimensional physics, including their generally stronger and longer-range electron-electron correlation, many forms of exotic magnetism, and the relative ease with which their properties can be tuned via doping, crinkling, strain, and stacking. Group-IV monochalcogenides have received a great deal of attention because their unique thermoelectric and electronic properties. In particular, GeSe is a 2D layered p-type semiconductor with interesting optical properties. The first magnetic 2D material to be discovered, monolayer (ML) CrI$_3$, is particularly fascinating due to its ground state ferromagnetism, which can be employed to design spintronic materials and induce magnetism in ordinarily nonmagnetic materials through proximity effects. Yet, because mono- and few-layer materials are notoriously difficult to probe experimentally, much remains unresolved about the structural, electronic, and magnetic properties of monolayers. Here we use quantum Monte Carlo (QMC) methods to study the chemical, electronic and magnetic (CrI3) structures of GeSe and CrI$_3$. We show that density functional theory-based methods in general cannot obtain consistent results for structure, bandgap, and magnetic moments. Using an efficient surrogate method, we optimize the chemical structures using QMC and show that the energy minimum is rather shallow, which necessitates highly accurate methods. We obtain electronic bands gaps and magnetic moments in excellent agreement with experiments, where such comparisons can be made directly. Our work demonstrates the pivotal role that quantum Monte Carlo calculations can assume in the study 2D materials.

1-F-9: UNDERSTANDING AND ENGINEERING FERROELECTRICITY IN WURTZITE THIN FILMS

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3-dimensional ferroelectric microelectronics promise substantial reductions in the energy cost of computation. However, scaling has stalled with perovskite-type ferroelectric thin films, due to a combination of high processing temperature and strong thickness-dependence to the functional properties. To overcome this challenge, our interdisciplinary research team developed ferroelectric wurtzite $Al_{1-x}Sc_xN$, $Al_{1-x}B_xN$, and $Zn_{1-x}Mg_xO$ thin films through a partnership between experiment and theory. In all cases, magnetron co-sputtering produces dielectric layers with smooth surfaces, abrupt interfaces, and homogeneous structure. Robust remanent polarizations (~100 µC/cm^2) are observed at room temperature; coercive field values range between 2 and 6

MV/cm, and are strongly temperature-dependent for the nitride formulations. $d_{33,f}$ values of 2.7 pm/V and 4.0 pm/V for $(Al_{0.9}B_{0.1})N$ and $Zn_{0.7}Mg_{0.3}$ O, respectively were determined by interferometer-integrated scanning probe microscopy. Optical characterization of $Zn_{1-x}Mg_xO$ reveals a broad low-loss transparency window between 0.35 µm and 14 µm with second harmonic generation coefficients of 25 pm/V in the visible spectrum – for reference, this value is about twice that of $LiNbO_3$. A distinguishing feature of this new ferroelectric crystal family is the ability to process films – in all formulations – at substrate temperatures at or below 100 °C. For $Zn_{1-x}Mg_xO$ Density functional theory (DFT) computations predict lattice structure, polarization, and bandgap trends as a function of magnesium concentration, all agree generally with experiment. DFT calculations also predict a low-energy switching pathway involving lateral motion of inversion domain boundaries. Companion calculations were made for ferroelectric $Al_{1-x}B_xN$ showing similar agreement to experimental observations.

1-F-10: THERMAL PROPERTIES OF ULTRA MATERIAL INTERFACES

[EFRC – ULTRA] Richard Wilson[1], Alexander Balandin[1], Martin Kuball[2], Srabanti Chowdhury[3], Debdeep Jena[4], H. Grace Xing[4], David J. Smith[5], Marco Saraniti[5], Yuji Zhao[5], Timothy Grotjohn[6]
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Thermal performance of ultra-wide bandgap devices can be severely impeded by interfaces. Before high-power ultra-devices reach their potential, key gaps in the understanding of transport at ultra-interfaces need to be filled. These gaps include: (i) understanding how bulk vs. interfacial properties govern heat flow at ultra-material interfaces, (ii) developing metrologies that can distinguish how bulk properties, sub-continuum transport, and interfacial resistance combine to govern thermal performance, and (iii) identifying ultra-material combinations and synthesis processes that lead to thermally conductive interfaces. In this poster, we report the status of our efforts to address these issues. To better understand the materials science of interfacial transport, we are studying a series of ultra-material samples, e.g. nitride-metals on c-BN, AlN, GaN. These samples have systematic variations in both interfacial structure and bulk vibrational properties. We use Brillouin light spectroscopy, Raman, and TEM to characterize vibrational and structural properties. We use time-domain thermoreflectance to study interfacial heat transfer. We are also exploring how improvements in temporal- and spatial-resolution in our heat-transfer experiments improves our ability to separate bulk, sub-continuum, and interfacial effects. Monte-Carlo flux-based or particle-based simulations allow us to theoretically study these issues. Finally, another key ULTRA EFRC goal is to discover methods for integrating high thermal conductivity heat spreading layers, e.g., AlN or diamond, into ultra-device heterostructures. Integrating heat-spreaders enhances performance if resistive interfaces are avoided. We use a combination of transient thermoreflectance, Raman thermometry, and finite element simulations to identify how interfaces effect heat transfer in ultra-material heterostructures, e.g. GaN/AlN/SiC and diamond/SiN/AlGaN/GaN.

1-F-11: QUANTUM TRANSPORT AND PROXIMITY EFFECTS IN Cd_3As_2 THIN FILMS AND DERIVATIVE HETEROSTRUCTURES

[EFRC-IQM] Run Xiao[1], Sayak Ghosh[2], Arpita Mitra[1], Wilson Yanez[1], Jiwoong Kim[3], Santu Baidya[3], Juan Chamorro[4], Junyi Zhang[4], Rishi Bhandia[4], David Barbalas[4], Yongxi Ou[1], Supriya Ghosh[5], Jacob Held[5], Andre Mkhoyan[5], Natalia Drichko[4], Peter Armitage[4], David Vanderbilt[3], Yi Li[4], Tyrel Mcqueen[4], Brad Ramshaw[2], Morteza Kayyalha[1], Nitin Samarth[1]
[1]Pennsylvania State University; [2]Cornell University; [3]Rutgers University; [4]Johns Hopkins University; [5]University of Minnesota

Monopole superconductivity is a topological state of matter predicted to exist in a Weyl superconductor with broken time-reversal symmetry. We describe our progress toward the development of a quantum materials platform for realizing a monopole superconductor via the molecular beam epitaxy of heterostructures that interface the archetypal Dirac semimetal Cd_3As_2 with ferromagnetism and superconductivity. In this poster, we focus on a thorough understanding of the fundamental properties of high mobility Cd_3As_2 thin films in the quasi-2D limit (thickness < 20 nm). These films are characterized using atomic force and electron microscopies, x-ray diffraction, angle resolved photoemission spectroscopy, Raman spectroscopy, and THz spectroscopy. Quantum transport measurements in top-gated Hall bar devices are carried out at low temperature and in high magnetic field ($B < 20$ T). We observe strong Shubnikov de Haas oscillations over a wide temperature range (10 mK $< T < 50$ K) and the integer quantum Hall effect at dilution fridge temperatures. We measure quantum oscillations as a function of temperature, magnetic field (magnitude and direction), and gate-tuned chemical potential. By comparing these measurements with density-functional electronic structure calculations for finite slabs, we disentangle bulk and surface quantum-oscillation contributions. We also study the integer quantum Hall effect via multiterminal measurements to search for possible signatures of Weyl orbits involving surface Fermi arcs. Finally, we demonstrate proximity-induced superconductivity in Nb-Cd_3As_2-Nb Josephson junction devices and find tentative evidence for proximity-induced ferromagnetism in Cd_3As_2/(Ga,Mn)Sb heterostructures.

1-F-12: NEW INTERFACES FOR PROGRAMMABLE QUANTUM MATERIALS

[EFRC – Pro-QM] Abhay Pasupathy[1,3], Ana Asenjo-Garcia[1], D.N. Basov[1], Cory Dean[1], James Hone[1], James Shuck[1], Michal Lipson[1], Andrew Millis[1], Abhay Pasupathy[1,3], Xavier Roy[1], Xiaoyang Zhu[1], Jiun-haw Chu[2], Di Xiao[2], Xiaodong Xu[2], Matt Yankowitz[2], Valentina Bisogni[3]
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The control of interfaces in van der Waals materials can be utilized to drive new programmable properties in quantum materials. In this poster, Pro-QM co-PIS will highlight two sets of advances pioneered by the EFRC team. The first is in the area of magnetic van der Waals materials. Here, the EFRC team has pioneered the synthesis and study of two magnetic systems, VI_3 and CrSBr. VI_3 is an out of plane ferromagnet with a number of possible stacking orders including monoclinic, rhombohedral and chiral. Characterization of this material has been performed down to the monolayer limit, with ferromagnetism actually being enhanced in the monolayer limit. CrSBr is a layered in-plane ferromagnet in the monolayer limit. Magnetism in this material is strongly coupled to the electronic structure. Multilayer samples can be tuned from antiferromagnets at zero field to ferromagnets at a modest field of a few thousand gauss, opening up new possibilities to engineer lateral magnetic domains. The second set of advances is to exploit new methods to engineer the atomic and electronic properties at interfaces. Pro-QM team developed a facile technique to create “noodles” of van der Waals materials with continuously varying strain and moiré patterns at interfaces. The second is the use of work function engineering to induce large

charge transfer at van der Waals interfaces. We demonstrate this using the Kitaev compound $RuCl_3$ and monolayer graphene, where contact with the $RuCl_3$ withdraws a large charge from the graphene, creating a strong polar interface.

1-F-13: MOLECULE-BASED MAGNETS AND SPIN-CROSSOVER MOLECULES ON SURFACES AND IN HETEROJUNCTIONS

[EFRC – M^{2}QM] John Koptur-Palenchar[1], Miguel Gakiya-Teruya[2], Andrew Brooks[1], Yundi Quan[1], Yue Yu[1], Xuanyuan Jiang[1], Tao Jiang[1,3], Duy Le[3], Shuang-Long Liu[1], Jun Jiang[1],
Arthur Hebard[1], Michael Shatruk[2], Xiao-Xiao Zhang[1], Hai-Ping Cheng[1], Richard Hennig[1], Talat Rahman[3], Xiao-Guang Zhang[1]
[1]University of Florida; [2]Florida State University; [3]University of Central Florida

Sublimated pinhole-free crystalline films of spin-crossover (SCO) molecule $Fe(tBu_2qsal)_2$ and molecule-based magnet CoPc, with the film thickness of 20 nm and 5 nm, respectively, have been incorporated into heterojunction structures comprising metal base electrodes and "soft landing" eutectic GaIn (EGaIn) top electrodes. In addition, the SCO material has been reduced to ultrathin 2D flakes, offering the first example of a mechanically exfoliated 2D material based on molecules that are not covalently bonded to one another. Raman and optical absorption spectra of the exfoliated 2D SCO molecules agree with the DFT calculations of Raman modes and oscillator strength, respectively, showing the materials remain intact down to the monolayer limit. Temperature dependence of optical absorption shows a significant increase in SCO transition thermal hysteresis with decreasing the number of molecular layers. I-V and dI/dV-V measurements on the CoPc heterojunctions show the superconducting gap, confirmed by DFT and Eliashberg calculations for the metastable β-Ga phase with a T_c = 6 K. The proliferation of magnetic field sensitive conductance peaks at characteristic voltages promises a detailed understanding of how molecule-based magnets can be exploited for thin film quantum device applications.

1-F-14: TOPOLOGY, SYMMETRY AND SURFACE STATES IN THE DIRAC SEMIMETAL CD3AS2

[EFRC – CATS] Tyler Pardue[1], Manik Goyal[1], Susanne Stemmer[1], Pablo V. Arribi[2], Jianxin Zhu[3], Anton A. Burkov[4], Olle Heinonen[5]
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Cadmium arsenide, Cd_3As_2, is a Dirac semimetal. It has only two Dirac nodes very near the Fermi energy, and the topologically nontrivial bands are well separated from trivial bands. This makes Cd_3As_2 in principle ideal to explore and to use as a testbench to manipulate the topology of the electronic states. It is, however, a complex crystal to use for thin film growth. We have at UCSB developed techniques to grow very high-quality thin film Cd_3As_2 both in a (112) direction with both Dirac nodes projected on the (112) surface, as well as in (001) direction; by using different substrates we can homogeneously strain the film in plane, and we can also gate the film to move the Fermi energy relative to the Dirac nodes. Using these thin films together with theory and computational modeling, we are exploring how breaking inversion or C_4 symmetry can transform the topological phases of Cd_3As_2, and how the topological surface states and their transport properties are affected by strain and applied fields. In the thin film limit, the topological surface states survive to sub-10 nm thickness, and thin films exhibit a quantum Hall effect irrespective of applied strain, but biaxial strain breaks the C_4 symmetry in (112)-oriented films and gaps the Dirac nodes. Thin films also exhibit weak anti-localization that is attributed to the topological surface states. Our work highlights the extraordinary tunability of the topological states of thin film Cd_3As_2, which can serve as a platform for a multitude of new quantum phases.

1-F-15: EXPERIMENTALLY VALIDATED PHASE-FIELD SIMULATIONS OF VOLTAGE/LIGHT-DRIVEN INSULATOR-METAL TRANSITION AND PHASE OSCILLATION IN VO_2

[CMS – COMMS] Yin Shi[1], Shriram Ramanathan[2], Aditya Sood[3], Xiaofeng Xu[1], Haidan Wen[4], Shaobo Cheng[5], Yimei Zhu[5], Amy E. Duwel[6], Dennis M. Callahan[6], Aaron Lindenberg[3], Jinchao Xu[1], Venkatraman Gopalan[1], Roman Engel-Herbert[1], Long-Qing Chen[1]

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Vanadium dioxide (VO_2) possesses coupled structural and insulator-metal transitions near room temperature and thus is a promising candidate for novel electronic applications such as Mott field-effect transistors and artificial neurons. Here we combine mesoscopic phase-field modeling and cutting-edge experiments to explore various intriguing phase transition behaviors of VO_2. We theoretically predicted the development of a transient charge density wave under an ultrafast photoexcitation. We theoretically demonstrated and experimentally verified that in the capacitive insulator-metal phase oscillation, the oscillation frequency scales monotonically with the bias voltage and series resistance and terminates abruptly at lower and upper device-dependent limits. We revealed the essential role of the nonequilibrium carrier dynamics and a fundamental limit to the oscillation frequency in the phase oscillation. We further showed that an intrinsic phase oscillation exists, which has distinct characteristics from the capacitive phase oscillation. We also simulated the voltage-driven insulator-metal transition in a polycrystalline VO_2 thin film and revealed the formation of transient metallic monoclinic phase islands stabilized by heterogeneity. Finally, we predicted the domain structures of VO_2 thin films in different voltage-pulse cycles and showed that small fluctuations may lead to different stable domain structures. Our results have important implications for exploring both the fundamental physics and various potential applications of VO_2.

1-F-16: IMPACT OF TRANSPORT AND BREAKDOWN ON POWER ELECTRONICS FIGURES OF MERIT: A CO-DESIGN APPROACH

[EFRC – ULTRA] Robert Kaplar[1], Stephen Goodnick[2], Srabanti Chowdhury[3], Jack Flicker[1], Arunima Singh[2], H. Grace Xing[4]

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Ultra-wide bandgap (UWBG) materials hold the promise for dramatically improved power electronic systems for high voltage applications, a major goal of the ULTRA EFRC. Of critical importance is the understanding of the impact of UWBG material properties, particularly their high field electronic transport and breakdown characteristics, on circuit and system level performance, which is the focus of the ULTRA co-design effort. One of the main connections between material properties and system level performance are so-called Figures of Merit (FOMs), which incorporate performance metrics such as the breakdown voltage, on-resistance, and switching speed into a single metric encapsulating system performance for particular applications, where larger FOMs indicate superior performance. Such FOMs are often used in comparing different material technologies for different application spaces. Hence, a major effort of the ULTRA co-design effort is in assessing the impact of the measured and theoretical transport properties of UWBG materials of interest to the ULTRA EFRC on specific figures of merit such as the traditional unipolar Baliga FOM, which is the ratio of the breakdown voltage squared over the specific on-resistance of unipolar devices, relevant to power converters. In particular, we focus on how the detailed material dependencies on doping, temperature and other factors lead to a much more nuanced interpretation of particular FOMs than the simplistic comparisons that appear in the current literature.

1-F-17: PHASE-FIELD MODEL OF COUPLED ELECTRON AND LATTICE DYNAMICS IN CORRELATED MATERIAL SYSTEMS

[CMS – COMMS] Tiannan Yang, Yihuang Xiong, Yin Shi, Yi Wang, Ismaila Dabo, Venkatraman Gopalan, Long-Qing Chen
Penn State University

We established a phase-field model for coupled electron and lattice dynamics in correlated material systems under ultrafast excitation. The model integrates a phase-field description of phase transitions with key mesoscale mechanisms at picosecond-to-nanosecond timescales including electronic carrier excitation and relaxation, electron-phonon coupling, and non-equilibrium thermal processes, to produce spatiotemporal profiles of excitation and relaxation transients of the correlated system. We also develop a computational package to provide fundamental thermodynamic and kinetic parameters as inputs based on first-principles calculations of electronic and phononic systems, thus, allowing for a multiscale modeling combining atomistic and mesoscale models. As an example, we theoretically examine the light-excited electron and lattice dynamics of strongly correlated material $Ca_3Ru_2O_7$ involving a coupled electronic and magnetic phase transition. We demonstrate that the excited-state dynamics contains a three-component relaxation process of carrier concentration across picosecond-to-nanosecond timescales, which is supported by evidence from our prior experimental measurements. A strong temperature dependence of all relaxation components within a wide range across the phase transition temperature is revealed. This model provides in-depth theoretical insights of the dynamical properties of complex electronic systems and ultrafast phenomena that lies within them. It can be applied to various material systems for predicting the electronic and lattice dynamics and mesostructure evolution under different types of ultrafast external stimuli, including light pulses, electric fields, and currents, etc.

1-F-18: APPLICATION OF SYSTEMATICALLY IMPROVABLE ELECTRONIC STRUCTURE CALCULATIONS TO REAL MATERIALS

[CMS – CPSFM] Anouar Benali[1], Kevin Gasperich[1], Thomas Applencourt[1], Ye Luo[1], Fionn Malone[2], Miguel A Morales-Silva[3], M Chandler Bennett[4], Jaron T Krogel[4], Pierre-Francois Loos[5], Anthony Scemama[5], Michel Caffarel[5], Kenneth Jordan[6], Joshua Townsend[7], Raymond C Clay III[7], Thomas R Mattsson[7], Sergio D Pineda-Flores[2], Eric Neuscamman[8], Luning Zhao[8], Ronald E. Cohen[9], Luke Shulenburger[7], Paul RC Kent[4]
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We present work towards the application of electronic structure calculations on condensed matter where all approximations may be systematically controlled and reduced in order to produce calculations with verified accuracy. First, we detail the application of advanced wavefunction optimization techniques to the classic case of iron oxide. Then we show how multideterminant expansions allow for two techniques, auxiliary field Monte Carlo and diffusion Monte Carlo to reach absolute convergence of total energies for primitive cells of several materials. Finally, we extend this approach to larger systems and show that is possible to systematically control the fixed node approximation in the thermodynamic limit, for the case of diamond.

1-F-19: PHASE-FIELD MODEL OF FORMATION AND DYNAMICS OF TOPOLOGICAL POLAR STRUCTURES IN THE PRESENCE OF LIGHT-EXCITED CARRIERS

[CMS – COMMS] Tiannan Yang[1], Cheng Dai[1], Jacob A. Zorn[1], Huaiyu Wang[1], Tatiana Kuznetsova[1], Vladimir A. Stoica[1], Haidan Wen[2], John Freeland[2], Roman Engel-Herbert[1], Venkatraman Gopalan[1], Long-Qing Chen[1]
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Upon excitation by external stimuli like light or current pulses, electronic carrier concentrations in solids can be transiently raised by orders of magnitude from their ground state, thus, giving rise to properties and phenomena vastly different from those at equilibria. Here we develop a phase-field model for modeling the simultaneous evolution dynamics of electronic charge carriers and ferroelectric polar structures. We discover a two-stage relaxational carrier evolution and a polar structural evolution containing multiple oscillational and relaxational components across picosecond to nanosecond time scales. We are also developing a computational tool to directly compute the diffraction patterns of ferroelectric polar structures predicted from phase-field simulations, which allows direct comparisons of phase-field simulation predictions of topological polar structures with experimentally measured X-ray diffraction patterns. The computational model offers a theoretical framework for predicting and manipulating carrier-related ultrafast dynamics of topological polar structures and is expected to stimulate future ultrafast experiments on the formation and dynamics of topological polar structures.

1-F-20: HARNESSING SPIN AND CHIROPTICAL EFFECTS IN NOVEL HOIS HETEROSTRUCTURES

[EFRC – CHOISE] Young-Hoon Kim[1], Haipeng Lu[1], Ji Hao[1], Yaxin Zhai[1], Ruyi Song[2], Julian Vigil[3], Joseph J. Berry[1], Yanfa Yan[4], Z Valy Vardeny[5], Michael F. Toney[6], Jeffrey L. Blackburn[1], Volker Blum[2], Joseph M. Luther[1], Matthew C. Beard[1]
[1]National Renewable Energy Laboratory; [2]Duke University; [3]Stanford Linear Accelerator Center; [4]Univeristy of Toledo; [5]University of Utah; [6]University of Colorado, Boulder

The interconversion of spin, charge and light are being investigated in novel hybrid organic inorganic semiconductors (HOIS). Chiral-induced spin selectivity (CISS) occurs when the chirality of the transporting medium selects one of the two spin ½ states to transport through the media while blocking the other. Monolayers of chiral organic molecules demonstrate CISS but are limited in their efficiency and utility by the requirement of a monolayer to preserve the spin selectivity. We showed that chiral organic ligands incorporated into the 2D layered HIOS system produces a chiral-semiconductor that exhibits CISS with an efficiency of up to 90%. The CISS layer consists of oriented, self-assembled small chiral molecules within a layered organic-inorganic metal-halide hybrid semiconductor framework. We developed a spin-LED by developing a heterostructures between light emitting HOIS nanocrystals (NCs) and a CISS layer that emits circularly polarized light at room temperature without external magnets. We have also developed Chiral HOIS NCs, the chiral ligands attached to the NC surfaces induce a structural centro-asymmetric distortion of the surface lattice leading to chiral-optical properties. Heterostructures between carbon nanotubes and chiral-HOIS enables discernment of circularly polarized photons. We also discovered that neuromorphic functionality can be induced with heterostructures of carbon nanotubes and HOIS NCs that exhibit persistent photoconduction lasting thousands of seconds beyond absorption of a weak light pulse.

1-F-21: ADVANCES IN QUANTUM MATERIAL SPIN DEVICES FOR NEUROMORPHIC COMPUTING

[EFRC – Q-MEEN-C] Junwen Xu[1], Yizhang Chen[1], Nicolás M. Vargas[2], Pavel Salev[2], Pavel N. Lapa[2], Mohammed Salah El Hadri[2], Jonathan Gibbons[3], Yuxuan Xiao[2], Haowen Ren[1,2], Hanu Arava[4], Yuzi Liu[4], Zhaowei Liu[2], Iana Volvach[2], Danijela Marković[5], Alice Mizrahi[5], Juan Trastoy[5], Eric E. Fullerton[2], Julie Grollier[5], Axel Hoffmann[3], Vitaly Lomakin[2], Amanda Petford Long[4], Ivan Schuller[2], Mark D. Stiles[6] and Andrew D. Kent[1]
[1]New York University; [2]University of California San Diego; [3]University of Illinois Urbana-Champaign; [4]Argonne National Laboratory; [5]Université Paris-Saclay; [6]National Institute of Standards and Technology

Spin-based devices have recently been shown to enable neuromorphic functions, such as vowel and letter recognition. A key component to these demonstrations is the spin torque oscillator, an oscillator in which a spin current creates magnetization oscillations—that can emulate both neurons and synapses. Their key characteristic for neuromorphic computing includes their nanoscale size, nonlinear response to external perturbations, phase locking and synchronization. However, thus far, spin-based devices used for neuromorphic computing consist of ferromagnetic metal tunnel junctions. Quantum materials can enhance spin-based device functionality and their energy efficiency.

In this poster we show several Q-MEEN-C research advances toward these goals. We present new implementations of spin-torque oscillators and oscillator arrays, including a novel means of wirelessly coupling oscillators. We then discuss materials and structures that can improve the properties and energy efficiency of such spin-based devices. First, we show higher charge-to-spin conversion efficiency with interfacial states in Au/Si. Second, we demonstrate that FeRh—an antiferromagnet—can enable both large charge-to-spin conversion efficiency and control of the spin-current's polarization direction by the Neel antiferromagnetic order. Further, micromagnetic modeling shows that antiferromagnetic coupled layers permit more energy efficient and higher frequency spin torque oscillators. Finally, we demonstrate that a hybrid metal insulator transition metal oxide (V_2O_3)/ferromagnetic nanoconstriction type resonator—a quantum material spintronic resonator—exhibits hysteresis and memory of use as synapse. In this structure a dc current can set a synaptic weight (and then be removed, set to zero) to systematically vary the oscillator's frequency and output signal.

1-F-22: MULTISCALE QUANTUM TRANSDUCTION BETWEEN SPINS, MAGNONS, AND PHOTONS

[EFRC – CMQT] Stephen von Kugelgen[1], Huma Yusuf[2], Michael S. Mattei[3], Danna E. Freedman[1], Ezekiel Johnston-Halperin[2], Randall H. Goldsmith[3]
[1]Massachusetts Institute of Technology; [2]Ohio State University; [3]University of Wisconsin – Madison

The grand challenge of quantum transduction between different quantum degrees of freedom (DOF) requires an all-in approach. Within quantum information science, quantum systems relying on different DOF each have strengths that prime them for specific roles in the quantum ecosystem. Through our three Thrusts, CMQT is integrating atomistic control over the local interactions between molecular DOF like quantum spins, integrating these molecular DOF with tunable magnonic DOF that span larger length scales, and integrating these materials with mobile DOF like photons and excitons. Our foundation within each of these areas will enable cross-cutting science at their intersections. One such strategy, which aims to explore quantum transduction among the aforementioned DOFs, involves single-magnon detection using microwave photons generated by a superconducting LC resonator. Microwave circuits are currently the most active forms of quantum information processing. In this context, a resonator-magnon system can be viewed as a sensitive detector of magnon excitations, enabling it to be a "read-out circuit" for spin-magnon interactions of intercalated spin qubits in molecule-based magnets like V[TCNE]x. This will act as a channel that can be directly transduced to other quantum systems, such as strain-induced single photon emitters and chiral optical cavities, which will facilitate long-range quantum transduction between local and distributed systems in a single hierarchical quantum manifold. The combined efforts of our thrusts form an integrated framework of tunable local, distributed, and mobile DOFs, allowing multiscale quantum transduction within hierarchical quantum systems.

1-F-23: UNDERSTANDING SPATIOTEMPORAL INSTABILITIES FOR NEUROMORPHIC FUNCTIONALITIES IN QUANTUM MATERIALS

[EFRC – Q-MEEN-C] Rodolfo Rocco[1], Javier del Valle[2,3], Pavel Salev[2], Yoav Kalcheim[2,4], Coline Adda[2], Nicolas M. Vargas[2], Pavel N. Lapa[2], Min-Han Lee[2] , Paul Y. Wang[2], Lorenzo Fratino[1], Peter O. Sprau[2], Ivan Zaluzhnyy[2], Sarmistha Das[2], Qi Wang[5], Zhen Zhang[5], Yifei Sun[5], Mathew J. Cherukara[6], Martin V. Holt[6], Evgeny Nazaretski[7], Xiaojing Huang[7], Hanfei Yan[7], Mingyuan Ge[7], Yong Chu[7], Shriram Ramanathan[5], Alex Frano[2], Oleg G. Shpyrko[2], Ivan K. Schuller[2], Marcelo J. Rozenberg[1]

[1]Université Paris-Saclay; [2]University of California, San Diego; [3]University of Geneva; [4]Technion - Israel Institute of Technology; [5]Purdue University; *[6]Argonne National Laboratory; [7]Brookhaven National Laboratory*

Strongly correlated Mott insulators are quantum materials that promise the implementation of spiking neurons for future Neuromorphic Computers. As in biological brains, artificial neural networks that operate with spikes are energy efficient since they are in the off state unless activated. The physical phenomenon that enables this is the electric breakdown, which is the sudden collapse, and posterior spontaneous recovery, of the resistance under a strong electric field. The electric current surge during the resistive collapse may be exploited to implement spiking neurons. Understanding this out-of-equilibrium phenomenon is a difficult challenge. It involves the formation and reabsorption of conductive filaments, which is a complex spatiotemporal instability where phase separation coexists with strong electric and thermal gradients. We tackle the problem both experimentally and with numerical modelling. Some of our most significant recent are as follows. We established that the incubation time of filaments varies on several orders of magnitude. While is fast and predictable at large applied voltage, approaching the threshold it becomes slow and strongly stochastic. Remarkably, the stochasticity realizes the "exponential escape rate" used in models of biological neurons. We discovered a long-time relaxation in the reabsorption of filaments, which allows for "subthreshold firing", opening the way to implement synaptic short-term-potentiation. We discovered that conductive tree-like structures can be realized and tuned by electric pulses in H-doped insulating nickelates, opening the way to implement dense synaptic connectivity. We found the dual effect to conductive filaments, the formation of insulating barriers, opening the way to model synaptic short-term-depression.

1-F-24: METAL-INSULATOR TRANSITIONS IN CORRELATED OXIDES

[CMS – CPSFM] M. Chandler Bennett[1], Qiyang Lu[2] Changhee Sohn[1], Guoxiang Hu[2], Guangming Wang[3], Xiang Gao[1], Matthew F. Chisholm[1], Ilkka Kylanpaa[4], Paul R.C. Kent[1], Jaron T. Krogel[1], P. Ganesh[1], Ho Nyung Lee[1], Olle Heinonen[5]
[1]Oak Ridge National Laboratory; [2]City University of New York; [3]North Carolina State University; [4]Tampere University; [5]Argonne National Laboratory

Oxygen defects are essential building blocks for designing functional oxides with remarkable properties, ranging from electrical and ionic conductivity to magnetism and ferroelectricity. Oxygen defects, despite being spatially localized, can profoundly alter global properties such as the crystal symmetry and electronic structure, thereby enabling emergent phenomena. In particular, oxygen defects can drive metal-insulator transitions (MIT), often with concomitant changes to the magnetic properties of the ground state. We are here focusing on two different systems, VO_2/TiO_2 heterostructures and perovskites ABO_x, and elucidate the mechanisms that drive MITs in these systems. In the VO_2/TiO_2 heterostructures, we use a combination of experimental techniques, quantum Monte Carlo (QMC) and density functional theory (DFT) to show how thermodynamics drive oxygen vacancies from TiO_2 to VO_2, yielding a tunable MIT and providing a new approach to designing oxide heterostructures for novel ionotronics and neuromorphic-computing devices. The ABO_x perovskites can exhibit an MIT as the oxygen content is reduced to x=2.5, at which point they order and the material assumes a brownmillerite structure. Using a combination of QMC and DFT we show that the ABO_3 perovskites most prone to MIT are self-hole doped materials, reminiscent of a negative charge-transfer metal. Upon n-doping the metallic phase, an underlying charge-lattice coupling drives the metal to a charge and bond-disproportionated gapped insulating state, thereby achieving ligand hole passivation at certain sites only. The size of the band gap is linearly correlated with the degree of hole-passivation at these ligand sites.

1-F-25: STRANGE METAL PHYSICS IN COMPLEX OXIDES

[EFRC – QSQM] Philip Phillips, Peizhi Mai, Dale V. Harlingen, Nadya Mason, Peter Abbamonte
University of Illinois, Urbana-Champaign

The standard theory of metals predicts that while the resistivity should increase with temperature, it should ultimately saturate once the mean free path drops below the interatomic spacing. A wide class of materials violate this principle and are hence termed strange metals, most notably the cuprates, some heavy fermions, and more recently twisted bi-layer graphene where the twist is engineered to create a flat band in which the kinetic energy is quenched and the electron interactions dominate. Since electrons cannot scatter at length scales smaller than the interatomic spacing, the key question of strange metals is what are the charge carriers. We have designed and are carrying out several experiments to test precisely what is carrying the charge. These include strange metal/normal metal junctions, determining the magnetoresistance in strange metal sample in which the quantized magnetic flux is known, and momentum-resolved electron-energy loss (M-EELS) spectroscopy measurements that have revealed anomalous density fluctuations and new collective modes in correlated metals such as $Bi_2Sr_2CaCu_2O_{8+x}$ and Sr_2RuO_4. M-EELS has also provided information regarding phonon interactions which we have used to uncover the universal origin of the kink seen in the electron dispersion along the nodal direction in the cuprate superconductors.

Reference: E. W. Huang, K. Limtragool, C. Setty, A. A. Husain, M. Mitrano, P. Abbamonte, P. W. Phillips, Extracting correlation effects from momentum-resolved electron energy loss spectroscopy: Synergistic origin of the dispersion kink in $Bi_{2.1}Sr_{1.9}CaCu_2O_{8+x}$, Phys. Rev. B **103**, 035121 (2021).

1-F-26: QUANTUM PHASE-FIELD OPENSOURCE PACKAGE (Q-POP)

[CMS – COMMS] Jacob Zorn, Daniel Fortino, Xiaofeng Xu, Qingguo Hong, Limin Ma, Tiannan Yang, Hari Padmanabhan, Venkatraman Gopalan, Yi Wang, Ismaila Dabo, Jinchao Xu, Long-Qing Chen
Penn State University

One of the main objectives for the CMS Center COMMS is to develop an open-source phase-field package, Quantum Phase-field Opensource Package (Q-POP), that can be employed to predict the formation and dynamics of mesoscale structural patterns during electronic, structural, ferroelectric, magnetic, and superconducting phase transitions in quantum and functional materials. The main components of the software package include: (1) a set of preparation tools that allow one to compute thermodynamic and kinetic input parameters from density function theories in data formats that are compatible with phase-field simulation codes, construction of thermodynamic energy functions, and computation of equilibrium domain and phase diagrams to reduce the number of expensive phase-field simulations; (2) a group of adaptable, extendible, and efficient numerical solvers based on the multigrid finite-element method for both relaxational and dynamical phase-field equations and designed for peta-scale and exascale calculations; and (3) a group of mesoscale structure characterization and visualization routines for direct comparison with experimental measurements in both real and reciprocal spaces such as real-space electron microscopic images and Fourier-space diffraction patterns. This poster will present our progress in developing the necessary tools, models, and solvers for all three components including a user-friendly I/O interface, a domain and phase diagram computational tool, developments of relaxational phase-field models and codes for coupled electronic, structural, magnetic, and superconducting phase transitions, efficient and scalable multigrid methods for solving electrostatic, elastic and phase-field equations, as well as topological polar structure identification tools, codes for computing x-ray diffraction patterns of computed mesoscale structures, etc.

1-F-27: MULTISCALE QUANTUM TRANSDUCTION BETWEEN STATIONARY QUBITS AND PHOTONS

[EFRC – CMQT] Michael S. Mattei[1], Anushka Dasgupta[2], Pufan Liu[2], Riddhi Ananth[2], Tumpa Sadhukhan[2], Kobra Nasiri-Avanaki[2], Iqbal Utama[2], Vinod Sangwan[2], Hongfei Zeng[2], Wooje Chang[2], Shawn Irgen-Gioro[2], Albert Vong[2], Justin Provazza[2], Andrew Salij[2], Stephan van den Wildenberg[3], Brandon Mehlenbacher[1], Michael R. Wasielewski[2], Roel Tempelaar[2], Joel Yuen-Zhou[3], George C. Schatz[2], Xeudan Ma[4], Mark C. Hersam[2], Nathaniel P. Stern[2], Emily A. Weiss[2], Randall H. Goldsmith[1]
[1]University of Wisconsin – Madison; [2]Northwestern University (lead institution); [3]University of California – San Diego; [4]Argonne National Laboratory

Long-distance quantum information transfer between stationary degrees of freedom (DOFs) in a quantum network requires transduction of localized and distributed coherences to flying qubits (photons). We study quantum transduction between stationary qubits and photons through three synergistic strategies. First, we are investigating the use of chemical functionalization and mechanical strain in low-dimensional materials to induce single-photon and heralded-photon emission, with application in probing coherent processes in light harvesting and quantum communication. Second, we are exploiting strong light-matter coupling between chiral optical cavities and embedded low-dimensional materials to enhance the typically weak interaction between the optical angular momentum DOF and material spin and valley DOFs. Third, we are exploring the interactions of single-photon emitters and chiral material DOFs with topological photonic systems to realize robust long-range coherence transfer and spatially biased propagation of excitons and polaritons. Combined, these efforts achieve quantum transduction of localized DOFs to a variety of photonic DOFs for robust information transfer in complex hierarchical quantum systems across multiple length scales.

1-F-28: TOWARD DFT-EASE-OF-USE IN FLOSIC: COMPLEX FLOS, THE MULTIPLICATIVE HAMILTONIAN, AND HIGH-THROUGHPUT FOD SEARCH ALGORITHMS

[CCS – FLOSIC] Alex I Johnson[1], Kushantha Withanage[1], Mark R Pederson[1], Tunna Baruah[1], Juan Peralta[2], C.B. Shahi[1,2,3], Koblar A Jackson[2]
[1]The University of Texas at El Paso; [2]Central Michigan University; [3]Temple University

Widespread use of the Fermi-Löwdin-Orbital Self-Interaction Correction (FLOSIC), especially in applications to transition metals and rare earths, requires automated determination of an initial electronic geometry (e.g. Fermi-Orbital Descriptors) that can subsequently be iteratively optimized using gradient techniques [M.R. Pederson, JCP **142** 064112 (2015)] to find a FLOSIC solution. Three technical aspects are described in this poster: First to improve upon the Jacobi-rotation-based approximate solution of the FLOSIC Hamiltonian [Z-H Yang, M.R. Pederson and J.P. Perdew, PRA **95**, 062505 (2017)] we introduce a method that fully exploits the unitary invariance, inherent in the Fermi-Orbital construction, and thus leads to a single multiplicative Hamiltonian that is diagonalized with the same speed as DFT Hamiltonians. The success of this method at fixing simple charge-transfer problems is highlighted. Second, as one means for achieving nearly automated FLOSIC calculations and as a means for generalizing FLOSIC to include complex localized orbitals we introduce the concept of complex FODs. This naturally leads to softer less noded orbitals, modifies chemical binding energies, and makes it easier to find positive definite FO overlap matrices. Initial applications to simple molecules and the Cr dimer are presented. As the ultimate step towards DFT-simplicity we describe a high-throughput computational search method that can fully remove the need for any user-intervention at the set up stage. Examples of how this method can be used to find FODs for rare-earth atoms, trianions $Cr(C_2O_4)_3$ in solution and molecules of interest to quantum science [$Mn_{12}O_{12}(COOR)_{16}(H_2O)_4$] will be provided.

POSTER SESSION II: TUESDAY, OCTOBER 19, 2021; 3:30 – 5:30 PM

A. CATALYSIS AND POLYMER SCIENCE (ROOM: *2AG*)

2-A-1: THE INFLUENCE OF ARCHITECTURE ON TRANSPORT IN ALKALINE MEDIA

[EFRC – CABES] Cheyenne R. Peltier[1], Alex J. Macbeth[1], Wei You[1], Brian G. Ernst[1], Hsin-Yu Ko[1], Zhifei Yan[2], Jeremy Hitt[2], Akshay Venkatesh[2], Michael Colletta[1], Elliot Padgett[1], David A. Muller[1], Lena F. Kourkoutis[1], Thomas E. Mallouk[2], Robert A. DiStasio Jr.[1], Geoffrey W. Coates[1]
[1]Cornell University; [2]University of Pennsylvania

In alkaline-based energy technologies, the architecture of each component influences the transport of reactive species which, in turn, influences device performance. The interplay between and among electrode architecture, ion and gas transport, and catalysts has been studied in both the conventional membrane-electrode assembly (MEA) geometry, and when the catalyst is supported on a network of PTFE fibers. In the conventional MEA geometry, the soluble ionomer that carries/transports OH- ions blocks the O_2 transport to the cathode catalyst, suggesting that more O_2-permeable ionomers are needed in this architecture. In the fiber architecture, the optimum ionomer loading was far lower, especially for silver ORR catalysts, where operation without ionomer was optimal.

Polymer architecture also plays a role in hydroxide and water transport. In a series of imidazolium-functionalized polyethylene membranes, with differing (and controlled) backbone architectures, there were clear differences in water management and hydroxide transport, with a cross-linked random copolymer architecture providing the best performance. The observed difference in membrane performance was attributed, in part, to differences in the organization of hydrophilic and hydrophobic domains.

We will also describe our efforts to employ highly accurate hybrid density functional theory calculations, in conjunction with machine learning, to study how the confined membrane environment affects the diffusion of OH- across experimentally relevant length and time scales. Together, these studies elucidate how changes in the catalyst, support, ionomer, or membrane structure can impact transport in an alkaline environment and affect device performance.

2-A-2: THE TRANSPORT AND ADSORPTION ENGINEERING OF POLYMERS IN POROUS SOLIDS

[EFRC – CPI] Chuting Deng[1], Maria Ley Flores[1], Juan de Pablo[1], Tian Ren[2], Renjing Huang[2], Raymond Gorte[2] and Daeyeon Lee[2]
[1]University of Chicago; [2]University of Pennsylvania

The transport of reactants in pores and their adsorption on catalytic sites are processes of central importance in heterogeneous catalysis and in the application of porous solids for the chemical recycling of commodity polymers. We used molecular simulations and machine learning to understand the transport of mixtures of n-alkanes (reaction intermediates) in a polymer matrix and simulated the confinement effects of a cylindrical cavity on polyethylene melts and on hydrogen solubility and diffusion. Carried over pores of different dimensions, these results will help elucidate the behavior of reacting polymer melts under catalytic reaction conditions. To further study the interactions between the polymer and the surface of the catalyst pores, we demonstrate that the interactions between molten polystyrene and disordered packings of silica nanoparticles can be modulated by changing the surface composition of the nanoparticles using atomic layer deposition (ALD). Based on the time required to fully infiltrate ALD-modified nanoparticle packings via capillarity, the contact angles for polystyrene on different surfaces prepared via ALD are determined. The method can be extended to study the interactions between a wide range of polymers and surfaces in porous media: these results will have important implications for designing new catalytic materials for polymer upcycling reactions and for nanoparticle-polymer composite films and membranes with enhanced mechanical and transport properties.

2-A-3: THE DYNAMIC ACIDITY OF PHOSPHORUS MODIFIED ZEOSILS

[EFRC – CCEI] Han Chen[1], Jason Gulbinski[1], Tarnuma Tabassum[2], Sheetal Jain[2], Matheus DeMello[3], Choongsze Lee[4], Anatoly Frenkel[3,5], Anibal Boscoboinick[3], Paul J. Dauenhauer[4], Dionisios G. Vlachos[6], Stavros Caratzoulas[6], Michael J. Tsapatsis[7], Songi Han[2], Susannah Scott[2], Wei Fan[1], Omar A. Abdelrahman[1]
[1]University of Massachusetts, Amherst; [2]University of California, Santa Barbara; [3]Brookhaven National Laboratory; [4]University of Minnesota; [5]Stony Brook University; [6]University of Delaware; [7]Johns Hopkins University

All-silica phosphorus containing zeolites like P-SPP and P-BEA are highly selective catalysts for multiple chemistries crucial to the catalytic upgrading of biomass resources to value added chemicals. P-SPP is a highly selective catalyst in the Diels-Alder cycloaddition of ethylene and dimethylfuran to p-xylene, as well as the dehydra-decyclization of biomass derived cyclic ethers to butadiene and pentadienes. P-Zeosil catalysts have been limited however by their mild catalytic activity, requiring long residence times to achieve quantitative conversion. Through catalyst synthesis, in-situ characterization, and reaction kinetics, we elucidate the origin of P-zeosil catalytic activity and how to significantly enhance it. When synthesized, increasing phosphorus content does not lead to a proportional increase in catalytic activity. ^{31}P NMR reveals the presence of increasingly oligomerized phosphorus species on the silica surface with increasing phosphorus content, resulting in less-dispersed phosphorus active sites. The distribution of phosphorus active sites is found to be temperature and water sensitive, confirmed by electronic structure calculations. Leveraging this information, the effect of water on P-zeosils with varying phosphorus content was investigated using alcohol dehydration and alkylamine Hofmann elimination as acid-catalyzed probe chemistries. While water alone has a mild effect, we discover that the presence of an organic base alongside water results in a more than two orders of magnitude enhancement in catalytic activity. A combination of kinetic investigations, ^{31}P NMR, operando FT-IR, and high-powered x-ray characterization methods, reveal that the presence of an organic base catalyzes the redistribution of phosphorus species to monomeric forms.

2-A-4: ANALYSIS OF DIFFUSION AND REACTIVITY IN MESOPOROUS SILICA NANOPARTICLES

[CCS – HETCAT] Yulim Kim, Yong Han, Ellie Fought, Mark S. Gordon, James W. Evans, Theresa L. Windus
Iowa State University

Mesoporous silica nanoparticles (MSN) are effective and highly selective heterogeneous catalysts. They are synthesized in the Ames Laboratory by the Igor Slowing group. In collaboration with Professor Slowing, we are applying both *ab initio* electronic structure theory and non-equilibrium statistical mechanics to understand both the reactivity of key reactions within the pore (in the presence of solvent) and the diffusion of reactants and products through the pore whose diameter varies from 2-4 nm. In collaboration with the Slowing group, the Evans group has constructed a model of the MSN system which reproduces the key experimental findings. Fought and Windus has taken the basic structure determined by Han and Evans, added the necessary hydrogen atoms required for correct chemistry, and are in the process of performing molecular

dynamics (MD) simulations on the system. Kim, Han, Gordon and Evans have collaborated on using the highly accurate effective fragment potential (EFP) to predict diffusion co0efficients for key species in the pore. The first paper on this work has been published [J. Phys. Chem. A, 125, 3398 (2021). DOI: 10.1021/acs.jpca.1c01865] and a second is in preparation.

2-A-5: AUTOMATIC GENERATION AND ANALYSIS OF MICROKINETIC MODELS

[CCS – ECC] Chris Blais[1], Oscar H. Díaz-Ibarra[2], Emily Mazeau[1], Maciej Gierada[2], Eric D. Hermes[2], Cosmin Safta[2], Kyungjoo Kim[2], Habib N. Najm[2], Eric J. Bylaska[3], Judit Zádor[2], C. Franklin Goldsmith[3], Richard H. West[1]

[1]Northeastern University; [2]Sandia National Laboratories; [3]Brown University

We present a workflow for automatic mechanism generation and analysis for heterogenous catalysis using an ensemble of software tools developed under the ECC project. The Reaction Mechanism Generator (RMG), originating from MIT, was used to generate a mechanism for methanol synthesis on Cu(111) using H_2, CO, and CO_2. RMG systematically builds a detailed kinetic model using a rate-based algorithm, which proposes species and reactions using estimates or known values for kinetics and thermodynamics, then iteratively adds the species and reactions that have the highest flux to the “core” model. The computational singular perturbation (CSP) library (CSPlib) was used to analyze the resulting model; in particular to highlight sources of stiffness and to identify the most important reactions in the RMG model. These CSP analysis results were used to identify reactions that had the greatest impact on the solution, and thus required more accurate kinetic and thermodynamic estimates in RMG. CSPlib relies on the TChem package to compute species thermodynamic properties, production/consumption rates, and Jacobian matrices for canonical reactor models. Both packages rely on the Tines mathematical utilities package and on the Kokkos infrastructure for performance portability on heterogeneous architectures, expected in future exascale computing platforms. We found that, in some cases, barrierless reactions or fast reverse reactions resulting from inaccurate thermo were the leading causes of stiffness. Correcting barrier heights and re-estimating species thermodynamic parameters for the offending reactions and species made it possible to analyze the resulting kinetic model in other simulation software, such as Cantera and Chemkin.

2-A-6: TWO-TIER MACHINE-LEARNING ACCELERATION OF MOLECULAR DYNAMICS SIMULATIONS FOR HETEROGENEOUS CATALYSIS

[EFRC – IMASC] Jin Soo Lim[1], Lixin Sun[1], Jonathan Vandermause[1], Yu Xie[1], Simon Batzner[1], Albert Musaelian[1], Nicola Molinari[1], Jacob Florian[1], Kaining Duanmu[2], Matthijs A. van Spronsen[1,3], Christopher R. O’Connor[1], Tobias Egle[1], Robert J. Madix[1], Philippe Sautet[2], Cynthia M. Friend[1], Boris Kozinsky[1]

[1]Harvard University; [2]University of California, Los Angeles; [3]Lawrence Berkeley National Laboratory

Restructuring of interfaces plays a crucial role in materials science and heterogeneous catalysis. In particular, bimetallic surfaces often adopt very different composition and morphology compared to the bulk. Such restructuring processes often occur over much longer timescales compared to chemical reactions, preventing dynamical simulations using first principles-based methods such as *ab initio* molecular dynamics (MD). To overcome this limitation, we develop a two-tier strategy to accelerate MD simulations using machine learning methods.

In the first tier, computationally expensive first-principles calculations are replaced with machine-learning models of the potential energy landscape. Highly accurate and linearly scaled Bayesian force fields are developed to describe interatomic forces for dilute Pd/Ag alloy surfaces. In combination with microscopy and spectroscopy, large-scale and long-timescale MD simulations

have revealed a detailed atomistic picture of the restructuring of Pd deposited on Ag for the first time. In the second tier, a data-driven multitask learning framework is designed to discover important low-dimensional representations of reaction coordinates for surface restructuring in an unbiased fashion. The representation is used as collective variables for enhanced sampling, which enables accurate estimation of reaction free energies for complex systems. The two-tier machine learning framework can accelerate MD simulations by several orders of magnitude while maintaining *ab initio* level of accuracy. Our approach is applicable to other alloy systems of interest and enables the previously intractable mechanistic characterization of restructuring dynamics at atomic resolution, as well as the discovery of metastable structures that are vital to catalytic processes.

2-A-7: REFINING AUTOMATICALLY GENERATED MICROKINETIC MECHANISMS IN A WORKFLOW

[CCS – ECC] Richard H. West[1], Chris Blais[1], Eric D. Hermes[2], Maciej Gierada[2], David H. Bross[3], C. Franklin Goldsmith[4], Eric J. Bylaska[5], Judit Zádor[2]

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Determining and predicting the elementary steps that occur at a catalyst surface, where experimental and computational data are often limited, is difficult and time consuming; determining thermodynamic properties and rate expressions is even more challenging. In this work we couple several of our new or improved open-source tools to facilitate this process, as we work towards a highly automated workflow. The example goal is to (re)create a well-studied system: methanol synthesis from H_2, CO, and CO_2 on Cu(111). First, Reaction Mechanism Generator (RMG) constructs a detailed model comprising elementary steps using known data and informed estimates of thermodynamic and kinetic properties. Linear scaling relations are used for estimating binding energies on different metals. New species and reactions are determined by systematically applying reaction templates, arranged in reaction families, including several new ones for this work. Kinetic estimates are derived from rate rules for reactions that fit a similar template, gathered from the literature. Species are selected and pathways explored using a flux-based algorithm. Cantera and TChem were used to analyze the model and determine important parameters for refinement. Pynta is our new code to automatically explore elementary reactions of adsorbates on a metal surface and is suited to run on HPC resources using the Balsam workflow manager. Coupled with Sella, our recently developed highly efficient generalized saddle point optimizer, Pynta can locate transition states and determine reaction barriers. We also demonstrate NWChem and its interface Arrows to perform plane-wave density functional theory (DFT) calculations to better determine binding energies and barrier heights.

2-A-8: BIFUNCTIONAL INTERFACE IN A HETEROGENEOUS PAIR-SITE CATALYST

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Oxide supported metal catalysts are broadly used for industrial fuel and chemical manufacturing. It is often suggested from experimental evidence that active sites exist at metal-support interfaces and function though bifunctional mechanisms. The development of accurate theoretical models of bifunctional catalysis at interfacial active sites is challenging because of the broad distribution of coordination environments and required non-mean field descriptions, which precludes the

design of metal-support interfaces for new chemistries. We overcome these limitations by synthesizing a model catalytic interface consisting of atomically dispersed Rh-WO_x pair sites. The simplicity of the Rh-WO_x interface facilitates accurate theoretical modelling. Multiple characterization techniques including CO probe molecule infrared spectroscopy and aberration-corrected scanning transmission electron microscopy suggested that Rh could be preferentially located near a single WO_x species. The Rh-WO_x pair sites exhibit stable >95% selectivity at a propanal formation rate of > 0.1 g_l/cm^3/hr in gas-phase ethylene hydroformylation. Experimental and theoretical analyses in the context of ethylene hydroformylation demonstrate that the interface is activated and catalytically functions through bifunctional mechanisms. Furthermore, H_2/D_2 kinetic isotope effect measurements and first principles based microkinetic simulations indicate the cooperative H_2 activation across Rh-W to be a rate-controlling step and reveals a reaction mechanism distinct from other Rh catalyzed heterogeneous hydroformylation reactions. Our results highlight emergent reactivity in atomically dispersed pair site catalysts and their potential use in fundamental studies of metal-support interfaces.

2-A-9: INVESTIGATION OF TRANSITION METAL CATALYSTS IMMOBILIZED ON NU-1000

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Transition metal complexes deposited on highly porous metal–organic frameworks (MOFs) offer a unique opportunity to combine the benefits of homogeneous and heterogeneous catalysis. However, the active sites of these catalysts are often extremely difficult to characterize, and catalytic activity can drastically change as a function of experimental synthesis and/or preprocessing conditions. These factors present a great challenge for standard approaches to rational design of next generation heterogeneous catalysts, which generally require the active site to be well-defined. To overcome this issue, we invoke a multi-faceted strategy towards developing transition metal catalysts supported on a Zr-based MOF called NU-1000. Our approach capitalizes upon tools such as high-throughput experimentation, spectroscopic characterization, computational modeling, and a machine-learning framework to probe catalyst active sites with atomic scale precision. In this work, we use the above approach to target the development of catalysts for hydrocarbon functionalization. First, we target the selective dimerization of propyne to *cis*,*trans*-hexa-2,4-diene through deposition of 18 transition metals under different reaction conditions. We believe this has the potential to greatly accelerate the discovery of promising MOF-based catalysts and can be expanded to a wider range of industrially-relevant chemical reactions. Second, we investigate C–H activation of aromatic and aliphatic hydrocarbons *via* an organometallic iridium complex tethered to the sulfated, Zr-based node of NU-1000. Atomic-level insights into the catalyst and support structures are gained through a synergy of computational and spectroscopic methods, showcasing the stereoelectronic control of transition metal reactivity when MOFs are implemented as a catalyst support.

2-A-10: DYNAMICS OF BRØNSTED ACID SITES ON PTWO$_X$ INVERSE CATALYST

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Metal-metal oxide (M-MO) inverse catalysts are broadly applied to many biomass reactions. However, the nature and the dynamics of active sites (Brønsted acid sites, redox sites, and metal sites) under working conditions remain poorly understood due to multiple material functionalities, hindering the design of more efficient catalysts and catalytic processes. Combining DFT-based thermodynamic calculations, in situ characterization, and probe chemistry, we demonstrate that the density of Brønsted acid sites on the $PtWO_x/C$ inverse catalyst could be modulated by up to two orders of magnitude by altering the reaction parameters and by the chemistry itself. Leveraging our understanding of the catalyst dynamics, we demonstrate a periodic hydrogen pulsing strategy that increases the average reaction rate of acid-catalyzed dehydration by one order of magnitude.

2-A-11: BINDING OF HYDROGEN TO BINARY MATERIALS AND ELECTRODES

[EFRC – CME] James M. Mayer[1], Sharon Hammes-Schiffer[1], Samantha I. Johnson[2], Simone Raugei[2], Robert E. Warburton[1], Hyunho Noh[1], Peter Rice[2], Nico Dwarica[1], Murielle Delley[1,3]

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The controlled movement of hydrogen atoms—proton/electron pairs—is frequently crucial in electrocatalysis. The prodigious catalytic activity of platinum is often attributed to its roughly isoergic binding of hydrogen atoms to its surface. Prompted by the scarcity of Pt, many other materials have been developed as (electro)catalysts, including oxides, phosphides, and carbides. Yet little is known about the binding of H to the surfaces of these materials. The Center for Molecular Electrocatalysis has long focused on the thermochemistry of hydrogen binding to soluble molecules as a path to understanding and improving electrocatalysis. The new Interfaces Thrust within the CME is using our molecular approach to examine H binding at solid/solution interfaces. Electrochemical oxidation of nickel oxide electrodes in aqueous buffer demonstrated that the electrochemical potentials directly indicate the O–H bond dissociation free energies (BDFEs) of the redox-active surface states. The equivalence of $E°[Ni^{II}(OH)_2 \rightarrow Ni^{III}(O)OH + e^- + H^+]$ with the surface O–H BDFE was shown through equilibration of these states with solution reagents with known BDFEs. Our experiments indicate a significant range of surface O–H BDFEs, in contrast to molecular species that are characterized by a single bond strength. A large range of surface O–H BDFEs has been revealed by computational studies of TiO_2/water interfaces and for nanoscale cobalt phosphide (CoP) and iron carbide nanoparticles. Our experimental and computational results suggest that the variability of surface–H bond strengths may be an inherent property of interfaces of catalytically active materials.

2-A-12: THE REACTIVITY OF NO_x ON VANADIUM OXIDES: THE SELECTIVE CATALYTIC REDUCTION OF NO_x IN THE PRESENCE OF NH_3

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The selective catalytic reduction (SCR) of NO_x with NH_3: $4NH_3 + 4NO + O_2 \rightarrow 4N_2 + 6H_2O$ has been used to reduce NO_x emissions from power plants by 95-100% since its development in the 1970s. The SCR reaction is catalyzed by transition metal oxides and especially vanadium oxides supported on TiO_2 are important due to their high selectivity and resistance to deactivation by sulfur oxides (SO_2/SO_3). High level electronic structure calculations in combination with experimental efforts are used to resolve fundamental issues about the surface reaction intermediates and initial reaction mechanisms. *In situ* IR spectroscopy reveals that the reaction is initiated by Lewis acid-base addition of NH_3 to a vanadium oxide site forming the neutral surface 'NH_3' species and formation of a surface 'NH_4^+' species on the protonated vanadium oxide site. Addition of doublet NO in combination with proton transfers leads to formation of a surface NH_2NO intermediate. The surface NH_2NO desorbs and undergoes gas phase rearrangements to form the final environmentally benign products of $N_2 + H_2O$. The predicted pathways are consistent with the available experimental data and show that the complete SCR mechanism is quite complex and proceeds via multiple steps. For example, the presence of open shell NO leads to reduction of a vanadium oxide site and transfer of the spin to this site. The addition of NO_2 to model surface vanadium oxide sites also shows the possibility of spin transfer to the vanadium or to the oxygen atoms.

2-A-13: INTERFACIAL CHEMISTRY AS A STRATEGY TO CONTROL THE ELECTROCATALYTIC ACTIVITY OF TRANSITION METAL PHOSPHIDES AND DICHALCOGENIDES

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Modifying the interfaces of materials alters their electrocatalytic activity through inner-sphere active site control and by altering outer-sphere active site-substrate interactions. Here, we demonstrate how covalent functionalization and intercalation affect the hydrogen evolution reaction (HER). First, we functionalized Ni_2P nanocrystals with aryl-groups that span a range of Hammett parameters. The Hammett parameter of the surface functional group linearly correlates with the change in Ni and P core-electron binding energies and the nanocrystal's work function. While covalently functionalizing Ni_2P improves its HER activity and stability, a simple trend based on electrostatics was not evident. We used density functional theory calculation to understand this discrepancy and found that H adsorption energies on the covalently functionalized Ni_2P also do not follow the electrostatic trend and are predictive descriptors of the experimental results. In addition, we modified MoS_2 and WS_2 through metallocene intercalation. Interestingly, the apparent redox potential of the intercalated metallocene shifts to a more negative potential and depends on the concentration and hydrophilicity of the electrolyte cation. We attribute this phenomenon to the charge transfer process involving cation motion, which requires additional energy to transport the cation from the bulk electrolyte into the van der Waals gap of the host material. Our preliminary results also show that metallocene intercalation impacts the electronic structure of the host material and consequently the HER activity of the intercalated dichalcogenide.

2-A-14: OXOPHILICITY DRIVES OXYGEN TRANSFER AT A PALLADIUM-SILVER INTERFACE FOR INCREASED CO OXIDATION ACTIVITY

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Palladium-silver alloys are potential catalysts for selective oxidation reactions. They can form oxides in the presence of oxygen with relatively low thermodynamic stability, and transport of oxygen between coexisting phases can significantly influence the kinetics of catalytic reactions. We investigated the migration of oxygen across interfaces and the surface reactivity towards CO in Pd/AgO_x/Ag(111) systems using X-ray photoelectron spectroscopy, infrared reflection absorption spectroscopy, temperature-programmed reaction spectroscopy, and density functional theory. Our results show that oxygen efficiently migrates from a single-layer AgO_x phase grown on Ag(111) to Pd clusters located on the AgO_x overlayer at room temperature. Furthermore, oxygen preferentially binds to the edges of the Pd clusters, thereby producing a heterogeneous spatial distribution of oxygen. The oxygen coverage on Pd increased with decreasing size of the Pd clusters. CO binds on both O-rich edges and terraces of the Pd clusters in high coverages at 100 K. The oxidation of the adsorbed CO consumes nearly all the oxygen that transferred from AgO_x domains during subsequent heating. In contrast, a pure AgO_x overlayer exhibits limited reactivity toward CO at similar conditions. These results demonstrate that differences in oxophilicity drive facile oxygen transfer from Ag to the edges of Pd clusters and thereby give rise to an efficient pathway for CO oxidation on Pd-Ag surfaces.

2-A-15: MEDIATED ELECTROCHEMISTRY FOR ENERGY CONVERSION AND STORAGE

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The Molecular Mediators thrust within the Center for Molecular Electrocatalysis (CME) focuses on investigation of *electron-proton transfer mediators* (EPTMs) to enable "redox communication" between an electrode and an off-electrode catalyst. EPTMs support anodic and cathodic processes in mediated fuel cells (**MedFCs**; Anson & Stahl *Chem. Rev.* **2020***, 120,* 3749-3786) and have also been used as redox-active electrolytes for redox flow batteries and decoupled water splitting. Efforts within the CME have prioritized the design and study of water-soluble EPTMs compatible with strongly acidic or basic conditions. A family of tetrasubstituted high-potential quinones, $E°(Q/QH_2) > 600$ mV vs. NHE, have been developed that show orders-of-magnitude increased stability relative to existing high-potential sulfonated quinones. These EPTMs, together with complementary low-potential anthraquinone derivatives, have been implemented for cathodic and anodic processes, respectively, in MedFCs using membrane-electrode assemblies. These mediators are paired with off-electrode heterogeneous catalysts to achieve high current and power densities. Recent efforts have prioritized mechanistic characterization of catalytic oxidation of hydroquinone (QH_2) by O_2 using M-N-C materials composed entirely of earth-abundant elements. We are exploring whether novel mechanisms may arise, involving cooperative interactions between the mediators and heterogeneous catalysts, similar to previous results obtained from studies of mediators and molecular catalysts. Experiments studies are using conventional solution-phase kinetic methods to establish the catalytic rate law and mechanism of QH_2 oxidation. Complementary efforts are interrogating the possibility of catalysis arising from parallel and independent half reactions of H_2Q oxidation and O_2 reduction, a mechanistic paradigm uniquely available to catalysts on conductive materials.

2-A-16: FUNDAMENTAL SCIENCE DRIVERS FOR ELECTROCATALYSIS IN ALKALINE MEDIA

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We explore and tune the factors that govern electrocatalysis in alkaline media. Using a tight and integrated feedback loop combining synthesis, characterization, and theory, we examine the chemical and physical effects that strain and supports exert on electrocatalysts in alkaline media, and how they are reflected in catalyst structure, activity, stability, and selectivity. We show that the volcano plots/relationships developed for acid environments cannot be directly applied to alkaline media. Instead, strain effects tend to be better predictors and we have developed high-resolution and precision electron microscopy methods to map strain in catalyst nanoparticles.
For kinetics, proton-coupled electron transfer (PCET) is an important step in a wide range of electrocatalytic processes. Here we explore how PCET, involving the OH- ion and other molecules prevalent at pH 14, affect the conversion and transport (especially ionic and electronic) of energy. WE developed a new approach to measure the kinetics of fast electroadsorption reactions via high scan rate CV. The rate constant in acidic media was ~2 orders of magnitude higher than in alkaline media. While the H+ concentration had an influence on the H adsorption rate, the OH- concentration did not. We have developed a general theory to describe this PCET reaction as a series of nonadiabatic transitions between reactant and product diabatic electron–proton vibronic states. The calculated transfer coefficients and kinetic isotope effects are in qualitative agreement with experimental measurements, predicting a potential-dependent kinetic isotope effect.

2-A-17: M-N-C MODEL COMPOUNDS FOR OXYGEN REDUCTION ELECTROCATALYSIS

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Metal-Nitrogen-doped carbons (M-N-Cs) are a highly promising class of earth-abundant metal catalysts for the oxygen reduction reaction (ORR). However, rational design and optimization of M-N-C catalysts is hindered due to the nature of the high temperature pyrolysis used in their synthesis, leading to highly heterogeneous materials with many possible active sites. Spectroscopic studies suggest that ORR catalysis by these materials is mediated by single metal atom active sites with pyridinic $M-N_4$ ligation. While metal tetrapyrrole complexes have long been known to catalyze electrochemical ORR, there existed a paucity of tetrapyridinic macrocycles complexes akin to those proposed in M-N-C materials. In a recent CME study, we presented a tetrapyridinic Fe macrocycle, $(phen_2N_2)Fe$ and found that it is an improved spectroscopic model for Fe-N-Cs relative to Fe tetrapyrrolic complexes. Additionally, $(phen_2N_2)Fe$ was found to be a highly active and selective ORR catalyst. In ongoing work, the CME has developed a large family of Fe and Co complexes bearing pyridinic, pyrrolic, and carbene ligation motifs. We have found that these complexes are active both as homogeneous ORR catalysts in nonaqueous media and as heterogenized ORR catalysts in aqueous media. Through integrated experimental and computational efforts, our center is unraveling the mechanistic basis for high efficiency ORR catalysis across these new ligand platforms. By studying these well-defined model compounds, we seek to elucidate the role of the carbon-framework and ligating atoms in ORR catalysis by M-N-Cs. Through this bottom-up approach, the CME aims to build bridges between molecular and heterogeneous electrocatalysis.

C. ENERGY-WATER (ROOM: *2C*)

2-C-1: STRUCTURAL EVOLUTION OF WATER AND PROTONS CONFINED IN HZSM-5 ZEOLITES: INSIGHTS FROM IR SPECTROSCOPY AND MOLECULAR DYNAMICS SIMULATION

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Hydration of acidic zeolite catalysts introduces complex interactions between water molecules and zeolite acid sites under extreme confinement, which can have surprising effects on chemistry. For example, we find that the rate of methanol dehydration over HZSM-5 zeolite increases in the presence of small quantities of water, contrary to expectations since water is a reaction product. To study the role of water in zeolite acid chemistry, a molecular-level understanding of water structure under confinement is required. We use a combination of Fourier-transform and ultrafast 2D IR spectroscopy in the O-H stretch region to monitor the structural configuration of water molecules and protons confined in the pores of HZSM-5 zeolites as a function of hydration. Spectral signatures are assigned to structural configurations with the aid of *ab initio* molecular dynamics (AIMD) simulations and spectral calculations, which provide insight into proton solvation structure and proton transfer between the zeolite framework and water cluster. At high hydration, we utilized 2D IR correlations to measure the statistics of water's hydrogen bonding topology, finding good agreement with our AIMD simulations of the protonated water octamer under confinement. At low hydration, spectral decomposition suggests that the evolution of the IR spectrum with hydration level can be described with a few distinct spectral signatures, which we will connect to structural motifs using our combined 2D IR spectroscopy and AIMD simulation approach. In future studies, we will expand on our kinetic measurements of methanol dehydration reactions to correlate zeolite activity with water structure as a function of hydration.

2-C-2: STRONG ENHANCEMENT OF NANOCONFINED WATER MOBILITY BY A STRUCTURE BREAKING SALT

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Physico-chemical properties of water vary dramatically between bulk state, confined state, and solutions. These properties are important in processes associated with energy storage applications as well as in transport of ions in biological membranes. Therefore, studies of structure and dynamics of water in various environments remain one of the paramount topics in multiple research areas because of the unique water behaviors that are not transferable from one set of conditions to another. A decade ago, it was fascinating for us to observe that, upon addition of structure-breaking K ions (e.g., by dissolving some KCl), the diffusivity of bulk water goes not down, but up by a few percent. However, our present study reports that, in a tight hydrophilic confining environment, addition of K speeds up the diffusivity the water not merely by a few percent, as is the case in the bulk fluid, but by a factor of 2, which is a very large effect. The implications of this behavior must be important for both inorganic and organic nanoscopic phenomena, from energy and desalination applications to biological plasma membrane permeability. The full impact of the structure breakers on the mobility of tightly confined water remains to be explored.

2-C-3: MULTISCALE SIMULATION AND EXPERIMENTATION OF CONFINED FLUID PROPERTIES

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Mesoporous confinement impacts a diversity of disciplines from CO_2 sequestration, water migration/purification, oil and gas extraction, heterogeneous catalysis and mineralization, and chemical separation. Consequently, transferrable theories need to apply to a diverse set of fluid and substrate properties, in addition to predicting both the local molecular (10^{-9} m) and continuum scale (10^{0} m) behavior. Further, rapid experimentation aids in the validation of modelling predictions for the vast diversity of fluid-substrate combinations impacted by confinement processes. Leveraging the collaborative structure provided by the MUSE-EFRC, we demonstrate a multiscale simulation and experimental framework to translate from local molecular thermodynamic and transport properties to collective behavior in real and complex geometries. Atomistic molecular simulations of phase transitions, fluid structure, and transport properties provide detailed insight into the impact of changing state conditions and the impact of fluid/substrate properties. These results are supported experimentally by gravimetric adsorption, pulse field gradient NMR, and phase transition measurements provided by differential scanning calorimetry. Scaleup of atomistic processes using dissipative particle dynamics (DPD) enables computationally feasible modeling of interconnected and complex pore geometries. Automated parameterization of DPD simulations provides an adaptable and transferrable means to vary fluid properties to capture local molecular behavior. To link with even larger scales, highly optimized and GPU-accelerated DPD simulations provide upscaling to simulate flow patterns through realistic mesopore networks reconstructed from 3D CT image stacks. In summary, this collaborative and multidisciplinary approach provides for molecular insight through continuum-scale processes to tackle the diverse challenges of predicting confined fluid properties and transport characteristics.

2-C-4: NANOPARTICLE TRANSPORT IN CONFINED AQUEOUS ENVIRONMENTS

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Precise understanding of the mechanisms of solute transport through nanoporous structures enhances the design of next-generation separation devices, such as water purification membranes. Here, nanoporous silicon nitride (SiN_x) membranes with cylindrical pores are fabricated using techniques of nanofabrication, directed self-assembly of block copolymers, sequential infiltration synthesis (SIS), and atomic layer deposition (ALD). The transport of spherical cadmium sulfide/cadmium selenide (CdS/CdSe) nanoparticles stabilized with zwitterionic ligands through the SiN_x membranes is investigated using a custom cross-flow filtration device. The nanostructure and surface chemistry of the nanoparticles and pore walls are well controlled at an electroneutral condition to analyze the effect of steric hindrance. Additionally, the transport of nanoparticles in the form of diffusion within the confined environment is studied with respect to

particle shape and concentration. We adopt an immersed boundary–General geometry Ewald-like method (IB-GgEm) to simulate the dynamics of a mixture of particles of different shapes and relative concentrations with the consideration of both short- and long-range fluctuating hydrodynamic interactions. We find that increasing the fraction of cylinders induces particle segregation, where the spherical particles are pushed toward the wall, while the cylinders prefer to be near the center of the cavity. In addition, increasing the fraction of cylinders also affects the diffusive-to-anomalous transition and the severity of the anomaly. In summary, these findings are relevant for describing nanoparticle transport within confined aqueous environments, and they provide guidance to understand and effectively design a wide range of physical and biological processes.

2-C-5: UPSCALING ATOMISTIC SCALE SIMULATIONS AND MEASUREMENTS TO CORE SCALE INCLUDING MINKOWSKI FUNCTIONS AND RATIONALIZED VIA NMR MEASUREMENTS

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Due to differences in accessible length and time scales, it is generally difficult to compare simulations on the molecular scale with experiments. However, when the variable of interest is a functional, e.g. the free energy and excess adsorption, the Minkowski functionals and functions provide a method to upscale results from the molecular scale to the experimental scale. The Minkowski functionals are a concept from integral geometry and in three dimensions they are related to the volume, surface area, Gaussian curvature, and Euler characteristic of a structure. When the functional under consideration is additive, motion invariant, and conditionally continuous, they completely characterize the structural heterogeneities, interfaces, and disorder of a structure; the functional can be expressed as a linear combination of the Minkowski functionals and coefficients. To test this theory, imaging techniques, sorption experiments, and atomistic scale simulations are combined to match lab-scale experimental sorption isotherms in real disordered porous media with predictions from simulations. This is complemented by liquid-state NMR to detect the presence of free and bonded gas. In addition to the atomistic scale simulations, numerical algorithms are advanced by the development of a novel statistical mechanical model. This model promises to speed up significantly the computation of the Minkowski coefficients. Unlike existing mean-field models, fluctuations are taken into consideration, to give a more accurate description of critical points shifts under tight confinement.

2-C-6: FUNDAMENTAL INSIGHTS INTO WATER DIFFUSION IN AQUEOUS POLYMER SOLUTIONS AT MICROSCOPIC TO MACROSCOPIC LENGTH SCALES

[EFRC – M-WET] Joshua D. Moon, Thomas Webber, Dennis Robinson-Brown, Peter Richardson, Thomas Casey, Rachel A. Segalman, M. Scott Shell, Songi Han
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Polymeric water purification membrane performance is governed by macroscopic and molecular-scale interactions of water with polymer surfaces. Preparation of highly selective, permeable membranes requires fundamental understanding of water dynamics near polymer chains. Even for poly(ethylene oxide) (PEO), a ubiquitous hydrophilic component of membranes, there are considerable basic science gaps regarding the most appropriate model for water diffusion in PEO solutions and the structure of water near PEO surfaces. This study employs M-WET's unique combination of synthesis, characterization, and simulation tools to study both bulk and local water dynamics and structure in dilute and concentrated aqueous PEO solutions. Overhauser Dynamic Nuclear Polarization (ODNP) and Pulsed-Field Gradient NMR probe water dynamics at length scales from sub-nanometer to microns and timescales from tens of picoseconds to sub-seconds, respectively. Based on these composite studies, conventional models, such as Stokes-Einstein, do not fully capture bulk water diffusion across a wide range of PEO concentrations, but a new free volume model which accounts for changes in water structural properties does. Molecular dynamics simulations reveal that reduced water translational diffusivity relative to pure water accompanies enhanced tetrahedral water structure near PEO chains. ODNP experiments confirm that water diffusivities near PEO surfaces are slower than in bulk for dilute solutions but converge to near bulk water diffusivity above the polymer chain overlap concentration. Thus, PEO does not act as a simple physical obstruction to water, but it modifies water's structural and dynamic properties, which directly influences water transport and selectivity in structurally complex water purification membranes.

2-C-7: ANOMALOUS FREEZING BEHAVIOR OF CONFINED WATER IN ARCHITECTED SILICEOUS MATERIALS

[EFRC – MUSE] Yiqing Xia[1], Subhash Risbud,[1] Sabyasachi Sen,[1] Hassnain Asgar,[2] Sohaib Mohammed,[2] Greeshma Gadikota[2], Ahmed Elnashar[3], Milind Deo[3], and Michael Bartl[3, 4]

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One of the challenges in developing predictive controls on the freezing behavior of confined fluids in natural siliceous materials is their morphological heterogeneity. We have developed synthesis approaches that allow us to achieve unprecedented control on the structure of siliceous materials including the ability to architect crystalline phases with ordered pore structures. These advances in synthesis science enable us to probe the structure of confined ice and the associated changes in the freezing and melting point depressions of water in siliceous materials with unimodal and bimodal particle size distributions. Furthermore, advances in *operando* X-ray scattering and ^{2}H NMR measurements now enable us to probe the dynamic evolution of the structure of confined water in well-defined pores as the structural basis for observed freezing point depressions of confined fluids. These experimental studies are used to validate molecular scale models of water and ice in confinement. Key findings include the co-presence of hexagonal and cubic ice in silica nanopores with diameters of 4 nm as opposed to cubic ice in silica nanopores with pore diameters of 6 nm and 8 nm. These experimental observations align with modeling predictions using the TIP5P model for water. Layer-by-layer freezing behavior of confined water is noted. For the first time, we demonstrate two glass transition temperatures in siliceous materials with bimodal pore architectures. These studies show the mechanistic connections between the local structure of confined fluids and freezing behavior of nanoconfined fluids.

2-C-8: SELECTIVE FILLING AND REVERSIBLE FLUID PHASE TRANSITIONS IN CARBON NANOTUBES

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The interaction of fluid molecules with pores comparable to their size is of immediate relevance to filtration and separation technologies. Carbon nanotubes (CNT) are single digit nanopores that serve as model systems in this space, yet challenges in probing individual diameter species have hampered understanding the selectivity and thermodynamics governing fluid adsorption in these. Through photoluminescence spectroscopy we demonstrate selective encapsulation of n-hexane from a mixture with cyclohexane by 0.42 nm diameter single-walled CNTs. Surprisingly, both molecules are found to enter nanotubes with a pore size only 0.01 nm larger. These results were unexpected given that the minimal projection diameter for the molecule is larger than the pore size. Ab initio molecular dynamics (MD) simulation reveals that the molecule stretches by 11.2% to enter the pore, generating a radial strain on the nanotube. This strain induces a characteristic photoluminescence response that we spectrally resolve along the length of a single nanotube by hyperspectral imaging. Furthermore, we use Raman spectroscopy and MD simulations to investigate fluid adsorption in individual CNTs through frequency shifts of their characteristic radial breathing mode. Through local laser heating, we observe and measure reversible adsorption isobar-like behavior for a number of different fluids on the interior and exterior of individual CNTs. Using a Langmuir adsorption model we extract estimates of the enthalpy of adsorption as well as the fluid-wall interaction. The demonstration of molecular sieving and understanding of reversible fluid phase change provides critical new insights on fluid behavior in single digit nanopores.

2-C-9: STRUCTURAL AND ELECTRONIC PROPERTIES OF WATER SOLUTIONS

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Modeling aqueous solutions at the atomistic scale has long been a challenge for computational chemical science. Here we follow a first-principles quantum mechanical approach. For high concentration sodium chloride solutions, we carried out comparative studies on the predicted molecular structure using various functional approximations within density functional theory and including nuclear quantum effects. To expand the accessible simulation system size, we have employed deep learning based molecular dynamics to model the structures of sodium chloride solutions at various concentrations. The predicted reciprocal-space structure factors agree quantitively with those obtained via neutron diffraction experiments. Notably, we provide clear evidence in real space that the observed structural changes in solutions are attributed to the effects of the ionic first solvation shells intruding into the hydrogen bond network, beyond which the liquid structure does not undergo major change relative to neat water. Based on the simulated structures, we have also compared the relative energetics of the solvated chloride anion to water by employing the GW quasiparticle approach to both bulk water and sodium chloride solutions. The results are in good agreement with a recent photoemission experiment. By collaborating with another DOE center led by Steven G. Louie at UC Berkeley, we have recently established a rigorous and accurate method to calculate the X-ray absorption spectra in liquid water using the advanced GW plus Bethe-Salpeter-equation approach. We are currently applying this new technique to predict the X-ray absorption spectra in sodium chloride solutions, which will be compared with experiments.

2-C-10: 2D TO 3D TRANSLATION OF IMAGES VIA DEEP LEARNING INTEGRATED WITH PHYSICALLY ROBUST ESTIMATION OF NANOPOROUS MEDIA TRANSPORT PROPERTIES

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Characterization of rock samples at the pore-scale is relevant to hydrocarbon production, geothermal energy, and subsurface storage including waste, carbon dioxide, and hydrogen. Shale systems, however, are complex and the pore-scale images required to estimate petrophysical properties are limited. Deep learning-based methods have shown promising results to improve image resolution and to provide a methodology for 3D volume reconstruction from 2D images. We have developed a methodology to translate 2D images with pore-scale features into accurate estimates of transport properties and quantified the resulting uncertainty. Importantly, fluid transport in unconventional geological rocks exhibits different transport mechanisms depending on the Knudsen number (ratio of mean free path to pore diameter) and the pore pressure. As pores are in the nano-size range, continuum-based approaches progressively break down in these systems. Molecular dynamics (MD) simulations are a tool capable of capturing the relevant microscale physics. However, their relatively high computational expense restricts MD simulations to small systems and domains. This limitation creates a gap between computational need of macroscale systems and capabilities of MD simulations. A suitable candidate to bridge the gap between atomistic and continuum scales is the lattice Boltzmann method (LBM). This poster includes (i) the acquisition of Scanning Transmission Electron Microscopy (STEM) in high angle annular dark field (HAADF) mode to image three-dimensional (3D) networks, (ii) the integration of DL based methods to generate 3D images, and (iii) implementation of LBM to understand the flow mechanism in these systems. Results include gas flow in different regimes as slip, transitional, and Knudsen.

2-C-11: FUNDAMENTALS OF SELECTIVE ION TRANSPORT IN CHARGED POLYMERS

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Highly selective, rapid ion transport across membranes is essential in biological ion channels as well as electrochemical and water purification membranes. Ion exchange membranes (IEMs) are commonly used in water/energy applications because charged groups tethered to the polymeric chains enable selective permeation of ions based on their charge/valence. Despite a rich literature across various fields, many fundamental molecular interactions underpinning ion selectivity in IEMs are poorly understood. M-WET's experimental and computational expertise was used to study electrostatic interactions (e.g., ion-ion and ion-polyion) affecting ion sorption, diffusion, and selectivity in IEMs. Macroscopic ion solubility measurements demonstrate the importance of counter-ion condensation and ion speciation (a topic rarely considered in hydrated membranes) on ion partitioning in IEMs. A thermodynamic model we developed, which accounts for these phenomena, predicted ion sorption in IEMs with no adjustable parameters. Characterization of membrane-electrolyte solution interfaces using ambient pressure X-ray photoelectron spectroscopy (APXPS) allowed measurement of the Donnan potential, which governs ion selectivity in charged polymers. This represents the first direct measurement of the Donnan potential, which is traditionally considered to be unmeasurable, and provides a new bridge linking thermodynamic theories to membrane selectivity. Complementary ionic conductivity measurements and atomistic simulations emphasized the importance of ion valence (i.e., ion-polyion interaction strength) on counter-ion diffusion and selectivity in IEMs. This analysis moves beyond conventional heuristics used to describe ion transport in membranes (i.e., free volume and hydrated ion size). Together, these results provide critical fundamental insights for designing highly selective membrane materials.

2-C-12: INSIGHTS ON PRESSURE-DRIVEN FLOW UNDER CONFINEMENT IN SILICA NANOCHANNELS

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We present experimental and computational results to show that fluid-solid interactions for confined flow in silica nanopores govern the extent of flow deviation from continuum models. In silica nanotubes molecular dynamics (MD) simulated *flow reductions* were observed in comparison to Haagen-Poiseuille (HP) flow for water, hexane and methanol due to a stabilized interfacial molecular layer at the surface. The effect of confinement faded as pore diameter increased. These results are consistent with negative slip lengths that other researchers have observed experimentally. We upscaled the MD simulations to flow through sintered silica nanoparticle packings using dissipative particle dynamics and observed similar flow reductions.

We also probed the effects of pore wettability and interfacial water features. Compared to Couette flow, the simulated flow in slit-pores of the hydrophobic talc (001) and silane modified silica surfaces exhibited water flow enhancement and a positive slip length (~0.5 nm), whereas water flow velocities at the hydrophilic quartz (001) and amorphous silica surfaces were zero. These observations were explained from MD simulation results of interfacial water structure and experimental sum-frequency vibrational spectroscopy (SFVS) results. Water flow experiments in capillaries packed with uniform sized colloidal particles revealed moderate enhancements (~20). The simulated slip lengths at the hydrophobic surfaces were significantly less than our experimental slip lengths (>40 nm) and those from the literature. This difference appears to be due to nanobubbles expected to be present at hydrophobic surfaces, in the case of experimental results, or because of the uncertainties in the application of the Kozeny-Carman equation.

2-C-13: AB INITIO STUDIES OF WATER'S PHASE BEHAVIOR VIA DEEP POTENTIAL MOLECULAR DYNAMICS

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Princeton University

Since the first molecular simulations of water ~50 years ago, developing a model that can reproduce water's thermophysical properties while providing a molecular-level picture of water's structure and dynamics has been a grand challenge for the computational chemical sciences. One route toward predictive computational studies of water is ab initio molecular dynamics based on density functional theory. However, this technique is traditionally too computationally expensive for exhaustive studies of water's properties, particularly at conditions far from ambient temperature and pressure. Herein, we show several examples of how a neural network-based simulation technique, namely deep potential molecular dynamics, enables *ab initio*-level computational studies of water's properties and phase diagram. From first principles, we determined water's equilibrium phase diagram, including difficult-to-capture superionic phases

at high pressures. We also investigated in detail the phase equilibrium of water with hexagonal and cubic ice, and computed ice nucleation rates. Furthermore, we found/provided evidence for water's theorized liquid-liquid transition under deeply supercooled conditions. Finally, we discuss related results obtained via empirical models that explored the links between the liquid-liquid transition and the structure of amorphous ice phases prepared under different conditions. Overall, these efforts combine our varied expertise in electronic structure methods, statistical thermodynamics, enhanced-sampling molecular simulations, and machine learning and artificial intelligence, to push the boundaries of the problems accessible via computational chemistry.

2-C-14: INTEGRATORS WITH IMPROVED STABILITY AND STATISTICAL ACCURACY FOR RING-POLYMER MOLECULAR DYNAMICS

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Ring-Polymer Molecular Dynamics (RPMD) and Thermostatted RPMD (T-RPMD) are established path-integral methods to compute numerically exact quantum thermal statistics and approximate real-time quantum dynamics of atomic nuclei in condensed phases. However, standard numerical integrators for RPMD and T-RPMD are susceptible to resonance-induced instability at time-steps proportional to the oscillation period of high-frequency ring-polymer modes; therefore, such integrators require highly conservative time-steps to stably integrate the dynamics of finely discretized ring polymers and recover accurate quantum thermal expectation values. This poster presents new integrators for RPMD and T-RPMD that are free from resonance-induced instability and provide exceptional statistical accuracy for position-dependent quantum observables at time-steps up to ten-fold larger than previously possible, at no added computational cost relative to standard schemes. The new integrators are obtained via spectral modification of the free ring-polymer sub-step in standard schemes, and they come with theoretical stability and statistical accuracy guarantees for harmonic systems that are qualitatively manifest in numerical simulations of strongly anharmonic model systems and real-world applications like liquid water. Extensive numerical evidence and theoretical analysis suggests that a modification of the standard Leimkuhler scheme based on the Cayley transform of the free ring-polymer propagator exhibits optimal stability and statistical accuracy among the new integrators.

2-C-15: UNCOVERING THE MOLECULAR MECHANISM OF SALT ION ADSORPTION AT PLANAR INTERFACES AND UNDER CONFINEMENT INSIDE SINGLE DIGIT NANOPORES

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At any solid/water interface, the electric fields exerted by polar molecules like water, and charged species such as salt ions, can significantly polarize the charge distribution in the solid. Yet, a long-standing question is how electronic polarization effects, which are many-body in nature, influence the ion adsorption behavior at solid/water interfaces. In this study, by carrying out molecular simulations of chaotropic (e.g., SCN^-, NO_3^-) and kosmotropic (e.g., F^-, SO_4^{2-}) ions comprising the Hofmeister series, we first show that interfacial water molecules significantly screen the ion-solid polarization energy (more than 85% screening) at solid/water interfaces. This results in the ion adsorption behavior at solid/water interfaces to be significantly different from the intrinsic ion-solid interactions in vacuum. We also uncover a water-mediated molecular mechanism of ion adsorption involving an interplay between the ion-water and water-water interactions, which we demonstrate to be universally applicable at all solid/water interfaces. Further, the pronounced influence of the hydration shell of salt ions in dictating ion adsorption phenomena is also reinforced through molecular simulations of cations (e.g., Li^+, Na^+, K^+) using a hybrid quantum-continuum framework. Finally, our molecular simulations bring out the stark contrast in the chemical physics of salt ion adsorption at planar interfaces versus under extreme confinement inside single digit nanopores (SDNs). Specifically, we show that the well-known Nernst-Einstein relation breaks down in SDNs due to the fundamentally different molecular mechanism of diffusive and electrophoretic ion transport, which is also validated through concurrent experimental measurements.

2-C-16: PROBING THE ELECTRIC FIELD DYNAMICS AT THE SOLID-ELECTROLYTE INTERFACE WITH 2D IR SPECTROSCOPY AND MOLECULAR DYNAMICS SIMULATIONS

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The electrical double layer that forms at the interface between solids and liquid electrolytes is important for the electrical properties, molecular interactions, and chemical reactivity at the interface. Although theories describing the structure of the double layer have existed for decades, little is understood about its dynamics on the natural time- and length-scales of molecular motion, or their importance in the functioning of electrochemical devices in large part because there are few experimental tools to probe these properties. We use molecular vibrations that are sensitive to their surroundings to probe fluctuations in the water and ion configurations within the first nanometer of the interface using ultrafast 2D IR spectroscopy of surfaces engineered to project the vibrational probes a known distance into the solution from the electrode. Interpretation of the 2D IR results critically relies on atomistic modeling from molecular dynamics simulations, which allow us to determine the role of each component of the solution in generating the local electric fields sensed by the probes. Combining our techniques from bulk solution with advanced surface preparation to fabricate the functionalized interfaces, together with a new surface-sensitive 2D IR spectrometer, we successfully extend these studies to the interface. We demonstrate the impact of ionic composition and concentration on the local solution heterogeneity and reveal the importance of the interface in changing the local structure and dynamics of the solution. This approach allows us to probe solution dynamics at the solid-liquid interface revealing new information about the fluctuations intrinsic to these systems.

2-C-17: FIRST-PRINCIPLES SIMULATIONS OF WATER AT SOLID INTERFACES

[CCS – CSI] Zachary Goldsmith[1], Marcos Calegari Andrade[1], Linfeng Zhang[1], Mark DelloStritto[2], Lesheng Li[1], J.M.P. Martirez[1,3], Emily A. Carter[1,3], Michael Klein[2], Annabella Selloni[1], Roberto Car[1]
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Aqueous interfaces play a central role in transport and reactive processes such as photoelectrochemistry for fuel production and environmental recovery and water treatment membranes for electrochemical desalination. Projects in our thrust encompass characterization of the structure and reactivity of prototypical water-metal oxide interfaces of photocatalytic and environmental relevance (e.g., titania and hematite), as well as understanding the properties of the electrical double layer at aqueous interfaces of electrode materials under voltage bias. In particular, we performed *ab initio* molecular dynamics (AIMD) simulations of hole-doped hematite in contact with water to characterize catalytically-relevant electronic states near working conditions. Using AIMD we also obtained the differential capacitance of aqueous Au (111) under applied voltage in good agreement with experiment. However, the time and length scales sampled by AIMD are often insufficient to characterize the structure of interfacial water on solid materials. For example, the water-TiO_2 interface has been intensely studied for decades, yet the extent of water dissociation at this interface is still experimentally unclear. To address this issue, we simulated the anatase TiO_2–water interface using molecular dynamics with an *ab initio*-based deep neural network potential. Our simulations provide a new picture of this interface, revealing a dynamical equilibrium of molecular and dissociated water on the anatase surface. A similar deep potential molecular dynamics approach is now being used to investigate the aqueous interfaces of other relevant materials, such as TiS_2, a capacitive deionization electrode material for water desalination, and Al_2O_3, a model system of naturally abundant phases of Al-containing (hydr)oxides.

2-C-18: INVESTIGATING ELECTRONEUTRALITY BREAKDOWN IN DISCRETE ION ARRANGEMENTS AT LIQUID-SOLID INTERFACE

[EFRC – CENT] Haokun Li[1], Kyle Sendgikoski[2], Ze Zhang[1], Joel Martis[1], Matthias Kuehne[3], Xiyuan Cheng[2], James Wu[2], Wilfred Russel[4], Yun-Chiao Yao[5], Archith Rayabharam[6], Cheng Zhan[5], Tuan Anh Pham[5], Eric Schwegler[5], Narayana Aluru[6], Aleksandr Noy[5], Zuzanna Siwy[4], YuHuang Wang[2], Michael Strano[3], John Cumings[2], Arun Majumdar[1]

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The individual and collective behavior of ions near electrically charged interfaces is foundational to a variety of electrochemical phenomena encountered in biology, energy, and the environment. While many theories have been developed to predict the interfacial arrangements of counterions, direct experimental observations and validations have remained elusive. Utilizing cryo-electron microscopy, we directly visualize individual counterions and reveal their discrete interfacial layering. We also uncover correlated ionic structures under extreme confinement, with the channel widths approaching the ionic diameter (~1 nm). Comparison with simulations suggests the strong effects of finite ionic size and electrostatic interactions. Further extension with the use of cryogenic off-axis electron holography has shown that the electric field measurements of solvated ions near a charged surface is possible. Our work reveals the roles of ionic size, valency, and confinement in determining the structures of liquid-solid interfaces and opens up new opportunities to study such systems at the single-ion level.

2-C-19: INTERDISCIPLINARY EXPLORATION OF POLYMER CONFORMATION AND SEQUENCE ON WATER AND SOLUTE BEHAVIOR

[EFRC – M-WET] Audra DeStefano[1], Sally Jiao[1], Ben Pedretti[2], Jacob Monroe[1], Joshua D. Moon[1], Nate Lynd[2], M. Scott Shell[1], Songi Han[1], Rachel Segalman[1]

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Highly selective and permeable next-generation polymeric water purification membranes demand materials with precisely tuned functionality. However, a fundamental nanoscopic understanding of the influence of membrane surface structure and chemistry on water and solute transport remains elusive. Current practices to mitigate pernicious challenges such as membrane fouling largely rely on heuristics. While the behavior of water and solutes near idealized (i.e., smooth and homogeneous) surfaces is well-characterized by theory and computation, realistic surfaces possess chemical and structural heterogeneities that perturb local water and solutes in cooperative and complex ways. Elucidation of such interactions requires a synthetically realizable materials platform to systematically tuning surface structure and chemistry, coupled with experimental and computational characterization to detect, quantify, and rationalize trends. Here, we present such a platform comprising poly(ethylene oxide) (PEO) surfaces functionalized with sequence-defined polypeptoids. Solution-state characterization using state-of-the-art magnetic resonance techniques and molecular dynamics simulations demonstrates the effect of PEO and polypeptoid length and sequence on polymer conformation and water dynamics. Simulations clarify the relationship between water structure and water dynamics in these sequence-defined polymer systems. Additionally, changes in water behavior are linked to solute affinity for a polymeric surface and solute transport. Finally, PEO micelles functionalized with polypeptoids are model systems for similar relationships to be uncovered for patterned, membrane-mimetic surfaces. These relationships enable formulation of design rules for hydrated, heterogeneous surfaces, which can be applied to a number of applications beyond water purification materials, such as marine antifouling and environmental coatings.

2-C-20: ELUCIDATING CHEMICAL EVENTS AT COMPLEX MULTICOMPONENT GEOCHEMICAL INTERFACES THROUGH COMBINED SIMULATION AND EXPERIMENTS

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Multi-component chemical transformations are ubiquitous in the natural environment. However, developing experimentally validated predictive controls over these transformations has been a long-standing challenge in geoscience. To address this challenge, we have through a joint experimental/computational effort, developed validated atomistic-scale simulations tools that can now handle multi-component minerals – including a wide range of aluminosilicates, clays, and mixed carbonate/aluminosilicate phases – and the chemical dynamics of their surface interactions with aqueous electrolytes along with key organic components. We have used Density Functional Theory calculations on small, representative mineral and molecular systems to develop ReaxFF reactive force fields – enabling relatively large-scale (>>10,000 atoms) over relatively long-time (> 10 ns.) fully dynamic and reactive simulations at the geomineral interfaces. These ReaxFF simulations were validated against rich sets of experimental data – describing the dynamics of the surface chemistry through state-of-the-art Point of Zero Charge, surface leaching, IR and in-operando X-ray scattering experiments. These joint experimental and theoretical efforts have enabled us to provide insights into diverse geochemical processes ranging from CO_2 mineralization chemistry to crack initiation and propagation and the interplay with surface chemistry, surface leaching, and its impact on the mineral structure. These closely integrated experimental and simulation studies provide the basis for extending this approach to include other highly complementary but distinct mineral interfaces to probe complex geochemical interactions.

2-C-21: INTEGRATING MULTI-SCALE EXPERIMENTAL DATA TO UNDERSTAND THE PHYSICS AND CHEMISTRY OF HYDRAULIC FRACTURING, STIMULATION, AND PRODUCTION

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Hydrocarbon production from unconventional reservoirs is an immense multi-scale problem, in which mechanical, hydrological, and chemical processes are coupled over timescales from seconds to years. During hydraulic fracturing, large volumes of reactive fluid and fluid pressure are transmitted to reservoir rocks with variable properties, resulting in variable stimulation of the fracture network. Physical and chemical changes of fracture-matrix interface impact the distribution and timescales of hydrocarbon diffusion. Understanding where stimulation occurs and how it alters rock properties is critical for both efficiency and environmental controls. Current models of hydraulic fracturing are only informed by log and geophysical data. Here, we construct a model that integrates multi-scale measurements on core to predict variations in rock properties. Our study area is the Hydraulic Fracture Test Site-1 in the Midland Basin, TX. After fracturing, a deviated well was drilled through the stimulated volume and core was recovered. Our Center has conducted a battery of measurements on the core from the meter to sub-nanometer scale, including strength, elasticity, permeability, porosity, diffusion, imbibition, and reactivity. This dataset enables us to construct stratigraphic models for mechanical, hydrological, and chemical properties that can be upscaled to augment existing data. We employ the multi-scale model to model fracture growth and pressure transmission. We compare the results against the spatiotemporal distribution of microearthquakes induced by stimulation to assess where fluid pressure was raised. We also use the diffusivity, imbibition, and reactivity data to predict quasi-quantitatively how fracture area is altered over time and where production is promoted or inhibited.

2-C-22: LINKING MEMBRANE PERFORMANCE TO FOULING MECHANISMS USING SYNCHROTRON TECHNIQUES

[EFRC – M-WET] Matthew R. Landsman[1], Mostafa Nassr[1], Cameron McKay[1], Desmond F. Lawler[1], Benny D. Freeman[1], Gregory M. Su[2], Lynn E. Katz[1]
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Membrane fouling limits the ability of current membranes to address water/energy challenges, since the attachment/deposition of (in)organic solutes, microbes, and particles on membrane surfaces and in membrane pores reduces flux over time. Design of next-generation membranes to remediate complex waters containing high concentrations of foulants requires advanced characterization capabilities. While synchrotron techniques can provide molecular-level insight regarding specific fouling mechanisms, such tools are rarely applied to water purification membranes. M-WET uses theory-driven X-ray absorption spectroscopy (XAS) and small/wide angle X-ray scattering (SAXS/WAXS) techniques to investigate fouling. By combining XAS and emerging capabilities in energy-resolved WAXS at the calcium K-edge through resonant tender X-ray scattering (i.e., TReXS), we determined the spatial distribution of calcium-carboxylate interactions in organic fouling layers on reverse osmosis membranes. Complementary density functional theory simulations to predict XAS spectra for specific calcium-organic interactions support these analyses. M-WET is also harnessing SAXS to differentiate internal (i.e., inside pores) and external (i.e., surface) particle fouling mechanisms of porous microfiltration membranes.

Relating foulant distribution in/on membranes to mathematical fouling models developed by M-WET provides a comprehensive understanding of the influence of individual fouling mechanisms on membrane performance (e.g., permeate flux), thereby informing future materials design/synthesis. Additionally, we are currently developing pressurized crossflow operando cells to visualize fouling. These multidisciplinary studies demonstrate the power of novel synchrotron techniques to shed new light on the interplay between water chemistry, membrane operational parameters, and fouling layer composition to guide fundamental research and establish materials design rules to prepare advanced membranes for water purification.

2-C-23: FUNCTIONALIZING THE INTERFACES OF POROUS METAL-OXIDE FILMS WITH MOLECULAR COMPLEXES YIELDS ATOMICALLY PRECISE HYBRID MATERIALS FOR ELECTROCHEMICAL WATER REMEDIATION

[EFRC – AMEWS] Xiang He[1], Aaron Taggart[1], Zifan Ye[2], Giulia Galli[2], Alex Martinson[1], Karen Mulfort[1], David Tiede[1]

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One key goal of the AMEWS EFRC is to develop atomically precise catalyst materials and understand the principles of electrical field and nano-confinement on the interfacial reactivity that is critical to electrocatalytic water remediation. We have demonstrated that anchoring a molecular Ru(II)poly(pyridyl) catalyst on metal-oxide thin films changes molecular electronic structure and affects interfacial ion distribution, factors which synergistically increase catalytic kinetics by 400% as compared to metal oxide alone. Using first principles molecular dynamics simulations, we have studied the capacitive and Faradaic currents at electrified solid/water interfaces, generating a realistic microscopic model of the interfacial structure that can be validated by pulsed chronoamperometry. Calculations of the absorption spectra of silicon/water interfaces having either hydrophilic or hydrophobic surface termination groups were accomplished by combining machine learning with electronic structure calculations. Toward the evaluation of nano-confinement on interfacial reactivity, we are using sequential infiltration synthesis (SIS) to produce hierarchically porous thin films composed of In_2O_3 nanocrystals with resistivities $< 10^{-2}$ Ω*cm obtained through annealing in H_2, where the carrier mobility was demonstrated to be related to the nanocrystal volume fraction and grain size. High-energy X-ray scattering and pair distribution function (HEXS/PDF) analysis of the In_2O_3 SIS films enables atomic-level insight into the step-by-step growth mechanisms that impact film properties. This work is anticipated to advance the fundamental understanding of electrified interfaces involving atomically precise molecular catalysts and the impact of nanoconfinement on molecular activity to enable highly reactive and selective hybrid materials for electrochemical water remediation.

2-C-24: MULTISCALE AND MULTIDIMENSIONAL VISUALIZATION OF TRANSPORT AND REACTIVITY IN FRACTURED UNCONVENTIONAL ROCKS

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Understanding chemical and physical interactions within fractured unconventional rocks is fundamental to successful implementation of subsurface energy production and waste storage technologies. However, unconventional geological systems are very complex because they are inherently multiphysics, nonequilibrium, with matrix/fracture networks that can yield very heterogeneous distributions of reactivity and transport. Here, our goal is to better understand how physical and chemical properties of rocks affect transport and evaluate how these properties change under chemical alterations. We develop a series of experimental and modelling frameworks that allow us to observe directly transport behavior through fractures and matrix, and fracture-matrix interactions across scales. At the pore-scale, a reactive transport model was developed to predict local mineral precipitation, dissolution, and clogging through synthetic microcrack networks. This model is effectively upscaled at little computation cost. To validate the model, a microfluidic set-up that accommodates fractured shale samples was developed. At the core-scale, we applied three non-invasive techniques, including X-ray computed tomography, synchrotron X-ray fluorescence, and positron emission tomography to characterize the dynamics of fracture-matrix interactions during imbibition and diffusion processes. We uncover 3D imbibition and concentration fields from fractures of variable apertures and demonstrate the paramount role of sub-micron fractures on the overall transport process. When subject to acidic stimulating fluids, it is shown that reactive imbibition causes mineral dissolution, thereby rapidly opening porosity near the fluid-rock interface. These experiments provide unparalleled insights into complex fracture-matrix interactions and are among the most useful tools for characterizing micro-fractured unconventional rocks.

2-C-25: LOCALLY SCALED SELF-INTERACTION-CORRECTION METHOD FOR REMOVING SELF-INTERACTION-ERROR IN DENSITY FUNCTIONAL APPROXIMATIONS

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We present a locally scaled self-interaction correction (LSIC) method that removes one electron self-interaction-error on an orbital by orbital fashion by identifying single-electron regions in many-electron systems using iso-orbital indicators [1]. The iso-orbital indicators are used as a weight to scale the self-Coulomb and self-exchange energy densities. Unlike the widely used traditional Perdew-Zunger method, LSIC provides consistent performance for both equilibrium (e.g. atomization energies, bond distances) as well as stretched bond (e.g. reaction barrier heights) cases. It provides atomization energies better than the PBE-GGA functional while retaining comparable accuracy of Perdew-Zunger SIC for barrier heights. We provide the details of its implementation and its assessment using standard benchmark datasets. We also present its application to different types of systems such as excess electron bound to water clusters, polarizability of water clusters and polyacenes, binding energy of water clusters, reaction barrier heights, and magnetic exchange coupling. We also present alternative selective scaling methods for SIC and their performance[2,3].

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2-C-26: HYDROPHOBIC GATING WITH LARGE POLARIZABLE ANIONS, VOLTAGE, AND SALT CONCENTRATION

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Hydrophobic interactions under nano-constriction can control the transport of water and all dissolved species. Nanopores with hydrophobic walls, absent any external stimuli, are filled with water vapor even when in contact with salt solutions. When an external stimulus, e.g. voltage or pressure, is increased, the pore will wet once reaching a threshold stimulus magnitude. Thus, hydrophobic nanopores are ideal valves, stopping all transport, including diffusion, in the absence of stimuli or presence of sub-threshold magnitude stimuli. This poster shows voltage-induced wetting of single silicon nitride nanopores containing a hydrophobic/hydrophilic junction. Transport through such nanopores is gated by voltage, ion size, and ionic concentration. For example, in 1M KCl the pores were nearly completely closed for all positive voltages but opened for large negative voltages. The same pore, when tested in salt solutions containing large, polarizable anions, opened for all examined voltages. The open state was found more probable in higher electrolyte concentrations. Molecular dynamics simulations predicted accumulation of large polarizable anions near a hydrophobic surface and provided mechanistic insights on the effects of voltage and ion concentration on pore wetting. We also show how hydrophobic interactions can be further manipulated by using multi-atom hydrophobic quaternary ammoniums. The experiments used a membrane containing 10^8 well defined nanopores per cm^2 and showed large ions can wet the pores. Cation transport efficiency decreased with increasing hydrophobicity of the quaternary ammonium. As the more hydrophobic ammoniums adsorbed to the polymer surface, the negative membrane surface charge decreased, resulting in a loss of membrane permselectivity.

2-C-27: MEASURING AND UNDERSTANDING pH IN LOCAL MICROENVIRONMENTS

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pH is a critical parameter influencing catalytic microenvironments, the chemical state of CO_2, and reactions pertinent to solar fuel synthesis. The Liquid Sunlight Alliance (LiSA) has undertaken co-development of measurement and theory to fully characterize pH across length and timescales. A pH task force was charged with (1) designing probes that measure but don't alter pH, (2) defining techniques compatible with existing standard cells and designing a new generic standard cell if needed, and (3) identifying probes relevant to an important LiSA microenvironment. Presented here are task force findings, including experimental findings and probing techniques, a customized flow cell to measure the pH gradient in the electrolyte above a gas diffusion electrode (GDE) using atomic force microscope- scanning electrochemical microscopy (AFM-SECM), and a method to measure pH within the cracks of a GDE using a photoactive dye. These dyes also act as photoacid/base generators, enabling local generation pH gradients to modify the catalytic microenvironment. Also presented are theory and multiscale reaction-diffusion simulation techniques to characterize local details such as the pKa of water at a scale not accessible by experiments, and to help interpret experimental observations. The influence of water pool size on pKa, water ion lifetime, and water ion generation frequency is examined using both theory and reaction-diffusion kinetics simulations, providing information on the stochastic nature of pH in confined microenvironments.

2-C-28: MODELING ELECTRON TRANSFER DYNAMICS IN SOLVATED ENVIRONMENTS

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Electron transfer processes in solution phase are ubiquitous in nature, and as such, understanding these intrinsic dynamics is of fundamental importance across a range of interdisciplinary fields, and especially in biological environments. Nevertheless, a wide range of challenges exist. The electronic structure of large systems has to be well described, while dynamics beyond the Born-Oppenheimer approximation are needed to calculate the nuclear motion and coupling between nuclear and electronic degrees of freedom. To address these challenges initial work has been made in three directions. In one direction, we have focused on applying ab initio molecular dynamics and high-level electronic structure theory to describe electron attachment to uracil in solution, a problem that is related to radiation damage in DNA/RNA. It was found that electron transfer to uracil occurs ultrafast and is dominated by solvent reorganization followed by relaxation of the uracil core. In a second direction, to address the description of nonadiabatic dynamics in such processes, first we made a detailed study analyzing and benchmarking the decoherence correction derived from the rigorous exact factorization approach on small gas-phase molecules. The effect of this correction on trajectory surface-hopping methods was shown to operate on individual trajectories very differently from the ad hoc corrections traditionally used. Finally, progress has been made in understanding the evolution of charge delocalization provided by adiabatic exchange and correlation functionals and their connection to the proton transfer process in liquid water. Work is underway now to apply the exact-factorization-corrected surface-hopping method to study charge-transfer processes in solutions.

2-C-29: PHASE DISCOVERY AND PHOTOACTIVITY FOR NI-SB-O FOR OXYGEN EVOLUTION REACTION CATALYSIS

[Hub – LiSA] Karun K Rao[1,2], Lan Zhou[1,3], Matthias Richter[1,3], Elizabeth Peterson[1,4], Sijia Ke[1,4], Jeffrey B. Neaton[1,4], Xiang Li[1,4], Junko Yano[1,4], Sage Bauers[1,5], Andriy Zakutayev[1,5], Joel A. Haber[1,3], John Gregoire[1,3], Michal Bajdich[1,2]
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High throughput exploration of the Ni-Sb-O system for stable solar fuels photoanodes revealed maximum photoactivity at Ni/(Ni+Sb) = 0.50. X-ray diffraction patterns of materials with Ni concentrations greater than 0.33 did not match any previously known phase. In this work, we explore this new phase space by a combination of experimental characterization and theoretical calculations. By a symmetry analysis of the observed XRD peaks, we suggest a disordered crystal structure in the *P63-mmc* spacegroup. Cross sectional TEM measurements confirm the stoichiometry of $M_4O_{7\pm1}$, which is oxygen-deficient compared to the rutile $NiSb_2O_6$ observed in an adjacent phase field. XAS measurements suggest the antimony to be in a +5 oxidation state in samples ranging from 0.66 to 0.33 Ni, whereas the oxidation states of Ni appear lower in the new phase compared to $NiSb_2O_6$. These semiconductors are n-type with ~0.1 cm2/Vs mobility according to Seebeck and Hall effect measurements. We identify a family of structures near the convex hull of the *ab initio* phase diagram motivating further characterization of these new metastable structures. The observation of dispersive bands in the electronic structure of the known rutile $NiSb_2O_6$ phase necessitates further study of where this desirable property also exists in the family of new structures and will be pursued via theory and experiment. Overall, the Ni-Sb-O system serves as a good test system for designing bulk and surface compositions for co-design of materials for operational stability, oxygen evolution activity, and light harvesting.

2-C-30: PHASE II OF THE CENTER FOR SCALABLE PREDICTIVE METHODS FOR EXCITATIONS AND CORRELATED PHENOMENA

[CCS – SPEC] Niranjan Govind[1], Edoardo Aprà[1], Anne Chaka[1], Karol Kowalski[1], Ajay Panyala[1], Bo Peng[1], Sotiris S. Xantheas[1], Wibe de Jong[2], Chao Yang[2], Xiaosong Li[3], John J. Rehr[3], Thom H. Dunning, Jr.[3], So Hirata[4], Dominika Zgid[5], Jiří Brabec[6], Libor Veis[6], Ors Legeza[7]
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Phase II of the Center for Scalable Predictive methods for Excitations and Correlated phenomena (SPEC) will develop open-source, scalable software libraries of high-level electronic structure methods for excited states that run efficiently on hardware architectures in Leadership Computing Facilities (LCFs). Continuing to develop the SPEC libraries will enable transformational scientific discoveries in areas such as light-harvesting systems, artificial photosynthesis, carbon-based materials, solvation chemistry, catalysis, geochemistry, and novel ultrafast femtosecond techniques.

The Center objectives are to (i) develop new theoretical approaches that extend highly accurate methods to the frequency and time domains for describing the valence- and core-level excited states of complex, highly correlated molecular systems and their local environment, (ii) implement these methods to fully utilize the unique hardware architectures at DOE's Supercomputer User Facilities (NERSC's Cori and Perlmutter) and LCFs (ORNL's Summit, ALCF's Aurora) and deliver scalable, efficient software libraries to enable scientific discovery at Basic Energy Sciences Program's light sources, neutron facilities, and NSRCs and (iii) organize the BES community to provide input on the use and further development of open- source libraries of high-level electronic structure methods and associated experimental data that can be used to validate them.

Our approach is based on the synergy between PIs in domain science (electronic structure theory), computer science, and applied mathematics fields under the following tasks: (i) Novel Many-Body Formulations, **(**ii) Hierarchical Many-Body Response Formulations in the Frequency and Time Domains, (iii) Highly Correlated Methods (CASSCF, CI, DMRG), (iv) Embedding Formalisms and (v) Computer Science Tools and Applied Mathematics Algorithms.

D. MATERIALS/CHEMISTRY BY DESIGN AND SYNTHESIS (ROOM: *2D*)

2-D-1: TOWARD RATIONAL DESIGN OF BOROSILICATE GLASS BASED NUCLEAR WASTE FORM: FROM STRUCTURAL MODELS TO CORROSION RATE PREDICTION

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Borosilicate glass is a well-accepted waste form to immobilize nuclear wastes. The design of borosilicate glass compositions for new waste streams would be dramatically enhanced by improvements in the fundamental understanding of the atomic structures and structure-property relations of these glasses for key properties such as long-term chemical durability. WastePD, an EFRC center for corrosion of materials for nuclear waste applications, performed multidisciplinary, multiscale studies to understand the composition effect on the short and medium range structures and their impact on corrosion rates, corrosion mechanisms, and other properties. A complementary suite of experimental methods has been utilized to characterize the glass structures. Concurrently, a set of self-consistent interatomic potentials were developed to perform atomistic computer simulations of the multicomponent borosilicate waste glasses. Simulated structures were validated against the experimental results and, based on the structural features from simulations, the properties of borosilicate waste glasses are predicted using the Quantitative Structure-Property Relationship (QSPR) method with a range of selected structural descriptors. Other methods such as topological constraint theory (TCT) and machine learning based approaches have also been utilized to find correlations between composition and chemical durability. Promising results to predict corrosion rate was found but some glasses with preferential dissolution posed challenges to the current models. This approach, integrating experimental and simulation, provides a systematic and rational way to design and optimize nuclear waste glasses to address the challenges posed by complex waste streams.

2-D-2: DEVELOPMENT OF NOVEL RARE-EARTH PHOSPHATES AND BORATES TO TARGET TRU-CONTAINING WASTE FORMS: A COMBINATION OF EXPERIMENT AND THEORY TO PREDICT NEW COMPOSITIONS

[EFRC – CHWM] Adrian Hines[1], Hunter Tisdale[1], Hans-Conrad zur Loye[1], Matthew Christian[1], Theodore Besmann[1], Jake Amoroso[2], Travis Deason[2], David DiPrete[2], Gary Was[3], Kai Sun[3] Lumin Wang[3]
[1]University of South Carolina; [2]Savannah River National Laboratory; [3]University of Michigan

The need to remediate nuclear waste has prompted extensive research into the development of new waste forms. One goal of our EFRC is to computationally predict and to experimentally prepare new materials that can hold transuranic (TRU) elements. To that end, we are performing calculations to predict the stability of TRU-containing compositions based on new rare-earth phosphate and borate compositions. As general classes of materials, both phosphates and borates are of interest as crystalline waste forms. Several compositions, such as monazite (LnPO4) have been extensively evaluated as waste-form. We have prepared single crystals of new rare earth containing phosphates and borates via flux crystal growth and have determined the structures by single crystal X-ray diffraction. Using these determined structures, we perform DFT calculations to predict the stability of TRU containing analogs, which in turn is used to inform syntheses. Furthermore, to investigate the likely stability toward exposure to radiation over time, we have used ion and electron irradiation to investigate the stability of select compositions. Based on these experiments containing radiological surrogates, predictions as to the likely stability of these structure types containing TRU elements can be made. Finally, through this iterative approach, a select few of the most promising radiological materials can be synthesized for comparison.

2-D-3: TOWARD A MECHANISTIC UNDERSTANDING OF GIBBSITE NUCLEATION AND GROWTH

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Gibbsite [$Al(OH)_3$] is a common mineral that is a useful model for (1) developing wastewater treatments, (2) determining Al behavior during processing of nuclear waste, and (3) establishing chemical controls on soil pH and water composition. In most cases, these applications require nano-sized gibbsite, which is precipitated at neutral-to-low pH values. Synthesis of $Al(OH)_3$ nanoplates under these conditions occurs as a multi-step process from metastable intermediates and in the presence of several competing oligomeric Al-hydroxide species. Our recent study determined that flat-Al_{13}-like clusters can sorb to growing $Al(OH)_3$ nanoplates at low pH and persist as interlayer defects inside the growing particles. This raises the question whether other metastable intermediates to $Al(OH)_3$ growth exist in solution that could actively sorb to the growing nanoplates. In a second study, we further analyzed solutions that were used to precipitate $Al(OH)_3$ nanoplates and isolated previously unknown $Al_{N>30}$ clusters. Preliminary results indicate that growth of $Al(OH)_3$ from $Al_{N>30}$ clusters also increases the incorporation of trace metals, such as Fe(III) and Cr(III), when compared to $Al(OH)_3$ grown from amorphous aluminum hydroxide intermediates. Detailed characterization using nuclear magnetic resonance techniques, X-ray scattering, electrospray ionization mass spectrometry, and scanning probe/electronical microscopies indicate the $Al_{N>30}$ cluster resembles a highly disordered single $Al(OH)_3$-like sheet. Current efforts focus on modeling this dynamic structure using ab initio molecular dynamics. A large oligomeric intermediate to $Al(OH)_3$ has been identified for the first time, holding great promise for the modeling of $Al(OH)_3$ growth, and reactivity with otherwise incompatible elements, at the molecular-scale.

2-D-4: CHEMICAL DURABILITY OF $A_2B_2O_7$ PYROCHLORE AND FLUORITE STRUCTURE TYPES AND MACHINE-LEARNING PREDICTION

[EFRC – WastePD] Kun Yang[1], Bowen Gong[1], Jianwei Wang[2], Jie Lian[1]
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Pyrochlore-structure type and its derivatives with a general formula $A_2B_2O_7$ (A = rare earth elements and actinides; B = Ti, Sn, Zr, Hf, Pb, Si *etc.*) display excellent structural flexibility and rich crystal chemistry and are promising nuclear waste form materials capable of immobilizing actinides and fission products. However, it is a formidable grand technological challenge to evaluate their chemical durability and optimize materials design given the hundreds of thousands of possibilities resulting from their extreme compositional complexities due to cation substitutions at both A and B-sites. In this work, chemical durability of 30 $A_2B_2O_7$ compositions from single component rare earth (Sm to Yb) titanates, zirconates and stannates to multiple component solid solutions and high entropy ceramics were evaluated as functions of various materials parameters and structure characteristics. Two machine learning models, linear regression, and Kernel ridge regression models, were developed to elucidate the key materials parameters and structural characteristics governing the leaching behaviors from a small set of selected compositions as model systems, enabling a science-based prediction of their chemical durability that can be extended to a wide range of chemical compositions. The combination of four key structural characteristics and materials parameters including ionic radius size difference r_{A-B}, ionic potential difference E_{B-A}, electronegativity difference $\chi_{\mathrm{B-A}}$, and lattice parameter α, creates features an optimized prediction of the chemical durability. The predicted leaching rates from both machine learning models show an excellent agreement with the experimental data, demonstrating the feasibility of rapidly evaluating the material properties of new compositions.

2-D-5: THERMAL EFFECTS ON CESIUM ADSORPTION AND IMMOBILIZATION PERFORMANCE INTO ZEOLITE-/GEOPOLYMER-BASED COMPOSITE

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The growing quantity of nuclear waste and the emergence of threats associated with storing this material, pose challenges for scientific researchers to develop new waste form technologies. In the past decades, considerable effort has been devoted to developing highly selective sorbents that can be safely disposed of with the assurance of chemical stability and robust retention performance. Zeolite-containing geopolymers are regarded as a possible multi-functional material that is able to both capture and sequester elements such as Cs. These composite materials show promise for combining zeolite's tunable pore size and composition, to realize high-capacity Cs incorporation, with the geopolymer's monolithic structure and chemical and thermal stability.

For the development of materials devoted to Cs immobilization, CHWM has initially focused on the design of a composite consisting of a dispersion of crystalline zeolite particles in an amorphous and mesoporous geopolymer matrix. After incorporation of Cs, the focus changed to improving the ability to crystallize the Cs containing composite using hydrothermal techniques and calcination. The hydrothermal process provides the benefit of being a low temperature method that helps reduce shrinkage and cracking by generating a higher degree of cross-linking and prepares the matrix for higher temperature treatments. Such heat treatments can simultaneously lower the geopolymer mesoporosity as well as limit the migration of Cs from the zeolite particles to the matrix's surface.

2-D-6: CONNECTING MOLECULAR AND NANOSCALE DETAILS OF THE BOEHMITE–WATER INTERFACE TO PARTICLE INTERACTIONS, DIFFUSIVITY, AND AGGREGATION

[EFRC – IDREAM] Elias Nakouzi[1], Lili Liu[1], Benjamin A. Legg[1], Larry A. Anovitz[2], Shawn L. Riechers[1], Xin Zhang[1], Dongsheng Li[1], Jaeyoung Heo[1], Greg A. Kimmel[1], Kevin M. Rosso[1], Sebastien Kerisit[1], Gregory K. Schenter[1,3], Jaehun Chun[1], James J. De Yoreo[1,4], Andrew G. Stack[2]
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Suspensions of highly faceted nanoparticles in extreme environments of ultra-high ionic strength and pH, as found in legacy radioactive waste, challenge traditional models for colloidal behavior. Using the case study of boehmite aggregation and a suite of cutting-edge techniques, we aim to connect the molecular and nanoscale details of the boehmite–water interface to particle interactions, diffusivity, and aggregation. Interfacial solution structure is determined using 3D fast force mapping (FFM) and molecular dynamics simulations. We observe multiple layers of laterally structured water, whose pattern depends on ion concentration and is templated by the boehmite lattice. Complementary force spectroscopy measurements indicate that boehmite–boehmite adhesion forces are affected by nanoscale surface roughness, thus motivating us to probe local changes in interfacial chemistry around steps and surface defects with 3D FFM. Interestingly, the adhesion force is also strongly influenced by X-ray irradiation, as demonstrated by in situ measurements using our novel rad-atomic force microscopy capability. Furthermore, by directly imaging boehmite aggregation using in situ transmission electron microscopy, we extract information on particle interactions, which reveal radiolytically driven pH-dependent modes of aggregation. These results are coupled to simulations of rotational and translational diffusivities, providing a unique correlation between energetics and dynamics for boehmite platelets. Finally, the collective dynamics of boehmite aggregation are measured using ultra-small angle neutron scattering, which shows a non-monotonic dependence of the aggregation rate on ionic strength. By correlating these observations across multiple length scales, we will advance a predictive understanding of particle aggregation in extreme chemical and radioactive environments.

2-D-7: PASSIVITY AND PITTING CORROSION BEHAVIOR OF NON-EQUIATOMIC NIFECRMNCO MULTI-PRINCIPAL ELEMENT ALLOYS

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Multi-principal element alloys (MPEAs) have demonstrated excellent corrosion resistance in chloride environments compared to stainless steel. These alloys have exhibited large ranges of passivity and high pitting potentials. However why these MPEAs exhibit such corrosion resistance is not well understood. Due to their multi-element composition, it is difficult to predict the passivity of these alloys. These multi-element alloys can form many different types of oxides such as complexed oxides, non-stoichiometric solid solutions, or stoichiometric oxides. The focus of this poster will be to investigate alloy passivation and pitting as a function of Cr concentration in solid solution $Ni_{38}Fe_{20}Cr_xMn_{21-0.5x}Co_{21-0.5x}$ MPEAs and compared to binary alloys. The MPEAs Cr content was varied systematically by adjusting the sum of Co and Mn concentrations. Results showed equal or superior passivity compared to the model Ni-Cr, Fe-Cr, and Co-Cr binary alloys in dilute slightly acidic sodium chloride. The possible origins of this behavior are discussed. Pitting corrosion behavior of these alloys was characterized in 0.6 M NaCl at room temperature. All these MPEAs exhibited pitting, as implied by positive hysteresis loop and low repassivation potential in the potentiodynamic polarization tests. Pitting resistance increased with increase in the chromium content. Interestingly, even the MPEAs with low chromium content exhibited passivity. Crystallographic pit morphology was observed in $Ni_{38}Fe_{20}Cr_6Mn_{18}Co_{18}$, $Ni_{38}Fe_{20}Cr_{10}Mn_{16}Co_{16}$, and $Ni_{38}Fe_{20}Cr_{14}Mn_{14}Co_{14}$, indicating that pit growth was under activation-controlled mechanism. A 3D phase field model was developed to simulate the crystallographic pit morphologies for various substrate orientations.

2-D-8: ACTINIDE-BASED METAL-ORGANIC FRAMEWORKS (MOFS)

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Detailed study demonstrates that metal-organic frameworks (MOFs), composed of metal nodes connected by organic linkers, are an excellent platform for selective radionuclide affinity and sequestration, and therefore provide novel pathways for transforming nuclear waste management. Due to their porosity, high surface area, and tunability, MOFs can be considered excellent contenders capable of a high uptake capacity of radionuclides through three mechanisms: integration as a part of a framework skeleton (metal nodes); chelation to organic linkers; and immobilization as guests within pore voids. Moreover, post-synthetic modification of prepared materials through installation of additional capping linkers can add additional methods for radionuclide sequestration and incorporation. For instance, the modularity of robust zirconium-based frameworks allows for control over leaching kinetics of radionuclide species. Exposure to gamma radiation revealed that frameworks are also a robust platform with respect to radiation damage. Overall, preparation of actinide-containing frameworks, fundamental understanding of their thermodynamic aspects, and radionuclide leaching kinetics discussed in the presented work are essential steps for understanding the potential of MOFs as viable radionuclide wasteform materials.

2-D-9: NOVEL METHODS AND ALGORITHMS ADVANCING MATERIALS COMPUTATION

[CMS – C2SEPEM] Aaron Altman[1], Nadine Bradbury[2], Yang-Hao Chan[3,4], Ming Chen[3,4], Jack R. Deslippe[3], Wenjie Dou[3,4], Felipe H. da Jornada[1], Wenfei Li[2], Daniel Neuhauser[2], Minh Nguyen[2], Diana Y. Qiu[5], Eran Rabani[3,4], Mykola Sereda[2], Chao Yang[3], Jia Yin[3], Steven G. Louie[3,4]

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We present methods developed to reduce the computational complexity and improve the accuracy of describing excited states within many-body perturbation techniques. We focus on three main threads: (a) *Noise reduction schemes*: Controlling the statistical error and bias is central to all stochastic orbital techniques. We present two approaches that reduce the noise by an order of magnitude, a combined real- and energy-space fragmentation approach and a range-separated stochastic resolution of identity approach, which is implemented within second order Green's function (GF) approaches. (b) *Dynamic mode decomposition* (DMD): Describing the dynamics of quantum driven systems is challenging since the nonequilibrium GF depends on two times. We demonstrate how to use the DMD for characterizing and predicting the long-time dynamics from a limited number of snapshots and point out a potential pitfall of the standard DMD caused by insufficient spatial/momentum resolution which can be eliminated by using a higher-order variant of the DMD method. (c) *Downfolding methods*: In solving the Bethe-Salpeter equation (BSE) numerically for correlated electron-hole excitations, it is necessary to truncate the Hilbert space to a subspace consisting of a smaller, finite basis set. When the Hilbert space is truncated, one can then screen the electron-hole exchange with electron-hole polarization propagators from outside of the truncated subspace, known as the "S-approximation". We show that it is formally equivalent to downfolding the full Hilbert space and develop a method for

accelerating convergence of the BSE that can be separated into well-defined subspaces either spatially or energetically.

2-D-10: FIRST-PRINCIPLES MOLECULAR DYNAMICS: NEW DEVELOPMENTS AND APPLICATIONS

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First-Principles Molecular Dynamics (FPMD) has emerged as an accurate simulation tool for investigations of the electronic and structural properties of molecules, liquids, and solids. The MICCoM center supports the development of Qbox, a high-performance implementation of this method, and its deployment on DOE Leadership Computing facilities. We present simulations of the Al_2O_3/water interface and of its X-Ray reflectivity spectra, which are compared with measurements performed at the Advanced Photon Source to obtain a quantitative validation of simulation parameters and approximations. We extend the range of applications of FPMD simulations by coupling the method with other software, giving access to physical quantities that are not provided by the conventional FPMD approach. In a first example, we present results of path-integral molecular dynamics simulations in which FPMD is coupled to the i-PI path-integral sampling software. When applied to diamond and amorphous carbon, this approach reveals the importance of nuclear quantum effects on electronic properties such as the electronic band gap. When coupled with the SSAGES advanced sampling software suite, FPMD simulations provide accurate free energy surfaces, an essential prerequisite for investigations of chemical reaction paths. This approach was used to map the free energy surface of the alanine dipeptide, using a hierarchy of electronic structure approximations of increasing accuracy. Coupling FPMD with the SSAGES software was also used to compute the free energy landscape of a prototypical heterogeneous catalysis reaction, the dissociation of molecular nitrogen on ruthenium. This simulation was made possible by exploiting new sampling algorithms based on neural networks.

2-D-11: QUANTUM MONTE CARLO DATABASE FOR MACHINE LEARNING ACCURATE INTERATOMIC POTENTIALS OF DENSE HYDROGEN

[CMS – QMC-HAMM] Scott Jensen[1], Yubo Yang[2], HongWei Niu[3], Markus Holzmann[4], Carlo Pierleoni[5], Matt Turk[1], David Ceperley[1]

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Machine-learned interatomic potentials trained on Ab initio data have been applied in large-scale molecular dynamics simulations to approach the accuracy of the Ab initio methods. Typically, these relied on density functional theory to generate the training data. Here we present the first large-scale publicly accessible database of quantum Monte Carlo (QMC) force calculations for dense hydrogen enabling more accurate machine-learned potentials. As a first study with this data, we determine the melting temperature of molecular hydrogen as a function of pressure in the range 50-200 GPa. While at lower pressure our result agrees with previous theory and experiment, we find a substantially higher melting temperature for higher pressures.

2-D-12: ADVANCES IN MANY-BODY EXCITED-STATE COMPUTATIONAL THEORIES

[CMS – C2SEPEM] Yang-Hao Chan[1,2], Jonah B. Haber[1,2], Felipe H. da Jornada[3], Zhenglu Li[1,2], Mit H. Naik[1,2], Jeffrey B. Neaton[1,2], Diana Y. Qiu[4], Chao Yang[1], Steven G. Louie[1,2]
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Developing predictive, parameter-free methods to understand the science of novel energy conversion and transfer devices is a challenging endeavor since in general excited states are involved and accurate treatment of many-body interactions are essential. Here, we present some recent advances developed in our Center (C2SEPEM) to address these challenges. We developed a new time-dependent GW method to understand nonequilibrium and nonlinear excited-state phenomena of materials including excitonic effects. We showcase applications of this formalism to understand excitonic effects in the shift-current conductivity of low-dimensional materials, a novel Floquet-like band renormalization phenomenon driven by excitonic field, and many-electron effects on second-harmonic generation. We developed new formalisms to describe exciton-phonon interactions that are applicable to both band-like and activated transport regimes. We show that off-diagonal terms in the exciton-phonon coupling matrix elements are essential for predicting accurate exciton linewidth in monolayer MoS_2. We present a method called GW perturbation theory (GWPT) that computes electron-phonon interactions including self-energy effects and show how it is essential for correlated materials. We further showcase a first-principles formalism to compute multiparticle excitations, such as trions and biexcitons. Our calculations reveal a rich physics in the valley and momentum distribution of the electrons and holes constituting these multiparticle excitations. Finally, we present formalisms to compute excitons in moiré superlattices. By developing the ab initio GW plus Bethe-Salpeter equation with a pristine-unit-cell-basis expansion (PUCBE) approach, we predict moiré excitons that have a previously unidentified charge-transfer character.

2-D-13: SPEED UP DFT+GRISB CALCULATIONS WITH MACHINE LEARNING AND ANALYTICAL JACOBIANS

[CMS – Comscope] Yong-Xin Yao
Ames National Laboratory

Recent algorithmic and code development to speed up large-scale Density Functional Theory plus Gutzwiller Rotationally Invariant Slave-Boson (DFT-GRISB) calculations are reported. An efficient machine learning approach based on kernel ridge regressions with n-mode expansions to solve the Gutzwiller embedding Hamiltonian is developed with implementation and demonstration for the actinide compounds. Analytical Jacobians to solve the Gutzwiller nonlinear equations are derived and implemented. This, in combination with ongoing force development, prepares the DFT-GRISB approach for large-scale material simulations.

2-D-14: MACHINE LEARNING DRIVEN AUTOMATED SCANNING PROBE MICROSCOPY FOR FERROELECTRICS

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Piezoresponse Force Microscopy has emerged as the technique of choice for the visualization of domain structures and their evolution under external fields, such as electric bias applied through tip and electrodes, strain, light illumination, and heating. However, the behaviors of interest are mostly related to specific elements of domain structures or materials microstructure, and concentrated in a small number of a prior unknown spatial locations. Here, we developed machine learning driven automated experiments (AE) scanning probe microscopy (SPM) workflows for investigating ferroelectric materials and devices fabricated within the 3DFeM center. To date, three AE-SPM workflows have been implemented: (1) AE feature-discovery& exploration (FDE); (2) deep kernel learning (DKL) piezoresponse force microscopy (PFM); (3) FerroBot. Specifically, AE-FDE allows us to discover and locate specific features in materials and subsequently explore the dynamics of discovered features. Using AE-FDE, we explored the behavior of conductive hotspots in $Hf_{1-x}Zr_xO_2$ (HZO), which provide insights into the leakage behavior of HZO devices. Using DKL-PFM, we actively discover relationships between local domain structure and physical properties (*e.g.,* switching dynamics, nonlinearity), which allows us to explore domain walls dynamics and nonlinearity in HZO thin films and $CuInP_2S_6$, respectively. Lastly, FerroBot is capable of poling specific features in materials in a customized manner, which enables investigations of domain wall dynamics in $CuInP_2S_6$ and edge structures in InSe. These AE workflows can be further adapted to investigate a broader range of behaviors of ferroelectric materials and devices.

2-D-15: FIRST PRINCIPLES COMPUTATIONAL SPECTROSCOPY AT FINITE TEMPERATURE

[CMS – MICCoM] M. Govoni[1,2], S. Dong[3], F. Gygi[4], M. He[2], J. Heremans[1], Y. Jin[2], N. Sheng[2], S. Sullivan[1], C. Vorwerk[2], H.Yang[1], G .Galli[1,2]

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Computational tools enabling the simulation of spectroscopic properties of materials and molecules at finite temperature, from first principles, are critical components of the predictive simulation framework developed by the MICCoM center. Through the calculation of response functions and electronic excited states, these tools constitute predictive probes of the atomic structure of complex systems simulated with first principles molecular dynamics, including defects in solids, solid/solid and solid/liquid interfaces, and amorphous materials. Here we describe recent progress in the development of the WEST code (http://www.west-code.org/) that implements GW, electron-phonon calculations and solves the Bethe Salpeter Equation (BSE) for solids and molecules without explicit evaluation of virtual electronic states and inversion of dielectric matrices and using full-frequency integration. We present results for the photoluminescence spectra of defects in semiconductors and for finite temperature absorption spectra of water and aqueous interfaces. The latter have been obtained with a method to solve the BSE for electron–hole pairs based on the calculations of perturbations in finite electric field, by coupling the WEST and Qbox (http://qboxcode.org/) codes, and on a machine learning approach to evaluate the dielectric screening. In addition, we discuss a recently developed quantum embedding theory (QDET) to describe active regions in condensed systems and results for the electronic structure of highly correlated states of spin defects in semiconductors and insulators, obtained on classical and quantum computers.

2-D-16: TOWARDS ATOMIC-SCALE CONTROL OF PHOTON-EMISSION IN 2D MATERIALS

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2D van-der-Waals materials with high exciton binding energy, versatility, and tunability are promising platforms to create near-ideal photon emitters. Here, we study and enhance these exceptional properties in various 2D systems. First, we study quantum emitters in 2D hexagonal boron nitride using optically-coupled transmission electron microscopy and discuss the role of substitutional carbon atoms. Concurrent ab-initio theory and spectroscopy reveals the effect of spectral inhomogeneity, spectral diffusion, and thermal phonon broadening at various temperatures of these quantum emitters. Excitonic emission in 2D transition metal dichalcogenides (TMDCs) has been another focus of our work. We demonstrate that the photoluminescence of monolayer TMDCs is highly strain-tunable up to about 5% of biaxial strain. We show that both the emission energy and linewidth can be strain-tuned owing to the modification of the bandgap and intervalley scattering. We further integrate TMDCs with nanophotonic platforms to control the emission intensity and polarization. Using strain tuning of the of excitons energy in WS_2 we control the coupling of the emission with the resonant modes of gold plasmonic nano-antennas. Integration with dielectric silicon nanostructures at the first Kerker condition, where the electric dipole mode and magnetic dipole modes overlap, results in strong near-field enhancement at the A-exciton energy of MoS_2 and provides a pathway toward enhancing the circularly-polarized emission of valley-polarized excitons. Together, our studies show how the emission of 2D material excitons can be tuned mechanically and tailored in the photonic near-field of plasmonics and metasurfaces, providing a foundation for complete control of the electronic, photonic, and phononic density of states.

2-D-17: STACKING-DEPENDENT BINDING ENERGY CURVE OF BILAYER GRAPHENE FROM DIFFUSION MONTE CARLO

[CMS – QMC-HAMM] Kittithat Krongchon, Naheed Ferdous, Gabriel H. Brown, Elif Ertekin, Harley T. Johnson, Lucas K. Wagner
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Layering van der Waals (vdW) materials has shown the capability to create new functional materials, such as small-twist-angle bilayer graphene with strongly correlated phases. These phases as determined by the electronic properties are sensitive to geometry relaxations, the determination of which requires an accurate description of the vdW interaction between bilayers. However, there does not exist enough accurate data to fully parameterize the dependence on registry between the bilayers.

In this work, we use diffusion Monte Carlo (DMC) to parameterize the interaction between layers of graphene. The DMC method is able to compute the vdW energy accurately [1] and is efficient enough that we can use the Summit supercomputer to compute the binding curve for multiple different stacking types. We present the DMC data set and compare it to other approximations for the binding curve of graphene. We anticipate this data will be used to develop accurate classical potentials and total energy tight binding models, which then can be used to study the long-wavelength relaxations in bilayer graphene.

[1] Mostaani, Drummond, Falko. PRL 115 115501 (2015).

2-D-18: SOFTWARE DEVELOPMENT AND USER COMMUNITY

[CMS – C2SEPEM] James R. Chelikowsky[1], Mauro Del Ben[2], Jack R. Deslippe[2], Jonah B. Haber[2,3], Felipe H. da Jornada[4], Zhenglu Li[2,3], Kai-Hsin Liou[1], Jeffrey B. Neaton[2,3], Daniel Neuhauser[5], Minh Nguyen[5], Diana Y. Qiu[6], Eran Rabani[2,3], Chao Yang[2], Steven G. Louie[2,3]

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This poster presents progress in the development, testing and release of the production quality and highly scalable software deployed by our Center C2SEPEM. We discuss new features and improvements made in our recent software public releases. Our software packages are designed to be highly modular and scalable, targeting the world's largest supercomputers as well as local workstations. We present progress towards GPU support for the Summit and Frontier systems at ORNL, Perlmutter at NERSC, and Aurora at ALCF. We demonstrate the capability of scaling unprecedented GW calculations to over 10,000 electrons utilizing the entire Summit supercomputer at OLCF (more than 27,000 GPUs) achieving over 100 PFLOP/s of double-precision performance and time to solution to the order of minutes. These results set an important milestone for computational materials science applications on next generation exascale high-performance computing systems. In this poster, we also showcase the engagement with the vast and vibrant users' and developers' community of the Center. We annually organize users' tutorial workshops as well as the developers' workshops. Since 2019, we moreover launched the annual Berkeley Excited States Conference (BESC) series, featuring invited talks by expert scientists in the field, and focusing on forefront research that involves advanced many-body approaches studying excited-state phenomena in materials.

2-D-19: TOWARDS EXASCALE SIMULATION OF STRONGLY CORRELATED MATERIALS

[CMS – Comscope] Corey Melnick[1], Gabi Kotliar[1,2]

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Strongly correlated materials offer exciting functionalities like topological insulation for quantum computing, unconventional superconductivity for high-temperature superconductors, or massive thermopower for thermoelectric generators. Unfortunately, the standard theories of condensed matter physics fail to predict or explain the exciting behavior of strongly correlated materials. At the same time, experimental efforts are slow, costly, and hampered by the failure of these standard theories. Recently developed theoretical frameworks like dynamical mean field theory (DMFT) provide sorely needed insight into this important class of materials. However, simulating materials within these frameworks requires massive computational effort, particularly for high-fidelity and *ab initio* theories like GW+DMFT. We have implemented massively parallelizable physics codes (scaling up to machine size on leading supercomputers) which leverage GPU acceleration (by a factor of up to 225) and cutting-edge algorithmic optimizations to overcome this barrier. Recent INCITE and ALCC awards allow us to leverage these capabilities on the nation's leading supercomputers Summit (at ORNL) and Theta (at ANL) and simulate previously inaccessible materials (α-Pu) and properties (spin and charge response functions). These petascale projects offer new insight into strongly correlated materials and their functionalities and prepare us for exascale simulations on the next generation of supercomputers.

2-D-20: SYNTHESIS AND STRUCTURAL, MAGNETIC, AND DFT CHARACTERIZATION OF FE22 AND FE24 COMPLEXES

[CCS – FLOSIC] Ashyln R. Hale[1], Megan E. Lott[1], Khalil A. Abboud[1], Juan E. Peralta[2], George Christou[1]
[1]University of Florida; [2]Central Michigan University

The current quest for synthetic routes to monodisperse (single-size) magnetic nanomaterials is motivated by the increasing demand for miniaturization of components in devices of various kinds. Molecular ‘bottom-up’ synthesis approaches bring the advantages of true monodispersity, crystallinity, and true solubility, all highly desirable properties for practical applications. Fe-oxo clusters are highly coveted in this context since iron is one of the Earth’s most abundant and hence cheapest metals. However, despite efforts towards this end, there is still a need to devise systematic synthetic schemes and develop characterization protocols to families of discrete high nuclearity Fe-oxo clusters, as there are only a few isolated reports in the literature for Fe-oxo clusters of nano-scale size. Here we elucidate the synthetic parameters for the growth of Fe_{22} and Fe_{24} clusters to map out the path for the targeted synthesis of increasingly higher nuclearity Fe-oxo clusters. The exchange coupling parameters have also been investigated via complementary use of a magnetostructural correlation for high nuclearity Fe^{III}/O systems and computational methods. Calculations based on density functional theory for both Fe_{22} and Fe_{24} clusters show quantitative agreement with magnetostructural correlations, and suggest a zero spin ground-state in both complexes, in agreement with the experimental observations.

2-D-21: LOW-TEMPERATURE EMERGENT NEUROMORPHIC NETWORKS WITH CORRELATED OXIDE DEVICES MODIFIED WITH LIGHT ION IRRADIATION

[EFRC – Q-MEEN-C] Uday S. Goteti[1], Ivan A. Zaluzhnyy[1], Shriram Ramanathan[2], Robert C. Dynes[1], and Alex Frano[1]
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Neuromorphic systems that emulate the biological brain’s behavior require networks of electronic devices with emergent properties that can process information across large spatial and temporal scales. We propose a novel approach to such systems using disordered networks of correlated oxide devices. These exhibit an emergent complexity of stable conductivity configurations in response to spiking voltage inputs. First, we survey the experiments performed to attain local control of the electronic behavior in two archetypal correlated systems, $YBa_2Cu_3O_7$ (YBCO) and $ReNiO_3$ (Re=Sm,Pr). He-damage on YBCO can create Josephson loops and in $ReNiO_3$ it can create conductive domains. H-implantation of $ReNiO_3$ devices yields the ability to use electrical fields to yield tree-like conductance behavior. Consequently, at the network level, disordered device arrays can be randomly coupled to obtain multi-terminal networks with emergent complexity in their overall memory configurations. Spatial information is stored in the form of dynamic flux states that affect the superconducting current flow in YBCO, and in the positions of dynamic H-induced insulating clouds or in static He-damaged conducting domains in nickelates. Together, these systems exhibit exponential scaling of memory capacity with size, while temporal information is encoded in the time scales at which memory states evolve. The dynamics of flux states occur at frequencies as high as ~THz while H-ion configurations can be retained for very long times. Combining these two systems will result in a highly scalable neuromorphic system with emergent complexity in spatial information and a wide bandwidth of temporal information processing.

2-D-22: APPLICATION OF ADVANCED COMPUTATIONAL METHODS AND THEIR VALIDATIONS WITH EXPERIMENTS

[CMS – C2SEPEM] Antonios M. Alvertis[1,2], Aurélie Champagne[1,2], James R. Chelikowsky[3], Weiwei Gao[3], Naomi S. Ginsberg[1,2], Jonah B. Haber[1,2], Felipe H. da Jornada[4], Zhenglu Li[1,2], Mit H. Naik[1,2], Jeffery B. Neaton[1,2], Diana Y. Qiu[5], Eran Rabani[1,2], Trevor D. Roberts[1,2], Feng Wang[1,2], Yoseob Yoon[1,2], Steven G. Louie[1,2]

[1]Lawrence Berkeley National Laboratory; [2]University of California at Berkeley; [3]University of Texas at Austin; [4]Stanford University; [5]Yale University

Applying new computational frameworks for modeling excited-state phenomena to real materials and experimental conditions is critical for validating novel theoretical approaches. Here we highlight recent experimental comparisons and collaborations to validate some of the latest theoretical and computational advances made in C2SEPEM. We showcase developments in computing electron- and exciton-phonon interactions from first principles. We study the photoemission kinks in cuprates and find that self-energy effects greatly enhance the electron-phonon coupling and improves agreement with experiments. We model phonon mediated exciton transport and compare it against time-resolved ultrafast microscopy measurements of the exciton diffusion constant. Furthermore, we combine first-principles calculations and optical experiments to identify excitons in WS_2/WSe_2 moiré superlattices and discover their distinct characters, and to reveal a strong effect by the moiré potential on interlayer shearing and phonons of the heterostructure. We also find that the biexciton Auger recombination lifetime increases with total nanocrystal volume for quasi-type II CdSe/CdS quantum dots and is independent of the shell thickness for type I CdSe/ZnS dots. We explain the experimentally-observed narrowing of the lowest exciton PL linewidth in gated $MoTe_2$ with increasing carrier concentration, and reveal that oxygen substitutions at the chalcogen site are the most common defects in quasi two-dimensional (2D) transition metal dichalcogenides, introducing defect engineering as a way of tuning valley polarization in 2D materials. Finally, we find that the low-energy excitonic states of a divacancy defect in 3C-SiC are made primarily of transitions from occupied defect states to continuum conduction states of SiC.

2-D-23: KITAEV INTERACTIONS IN CO BASED QUANTUM MAGNETS

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Kitaev quantum spin liquids (QSLs) are exotic states of matter that are predicted to host Majorana fermions and gauge flux excitations. However, so far, all known Kitaev QSL candidates are known to have appreciable non-Kitaev interactions that pushes these systems far from the QSL regime. Co-based magnets have been proposed to be perhaps a more ideal platform for realizing Kitaev QSLs. We show evidence for Kitaev interactions in both the quasi-one-dimensional ferromagnet $CoNb_2O_6$ [1] as well as the hexagonal magnet $BaCo_2(AsO_4)_2$ [2]. $CoNb_2O_6$ was believed to be the best material realization of a 1D Ising chain, showing evidence for a 1+1 D quantum critical point and Kramers-Wannier duality. We have recently shown that $CoNb_2O_6$ has bond-dependent interactions and forms a 'twisted Kitaev chain', as these interactions are similar to those of the honeycomb Kitaev spin liquid. The ferromagnetic ground state of $CoNb_2O_6$ arises from the compromise between two axes. Owing to this frustration, even at zero field, domain walls have quantum motion, which is described by the celebrated Su–Schriefer–Heeger model of polyacetylene and shows rich behavior versus field. Most recently, we have shown that the honeycomb cobalt-based Kitaev QSL candidate, $BaCo_2(AsO_4)_2$, has dominant Kitaev interactions

so a magnetic continuum consistent with Majorana fermions and a Kitaev QSL can be induced in a field. The possibility of controlling them with ultrafast THz pulses opens possibilities for quantum information processing and control.

[1] C.M. Morris et al. Nature Physics 17, 832–836 (2021).
[2] X. Zhang, et al., https://arxiv.org/abs/2106.13418.

2-D-24: UNDERSTANDING CORRELATED QUANTUM MATERIALS: THE INSIGHT FROM *AB INITIO* DYNAMICAL MEAN FIELD THEORY

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Quantum information science is a surging frontier of physical science. By creating quantum states and utilizing them as quantum bits, it promises vastly improved performance in computing, sensing, communication, and cryptography. Quantum Materials are a class of materials that have the potential to be the “semiconductors” of quantum information science. One of the biggest challenges in this field is to understand and predict quantum materials properties, especially when the material is correlated, and its quantum nature is many-body. Correlated quantum materials preclude simple explanations and computationally simple methods based on Landau’s Fermi liquid theory, such as density functional theory and Hartree-Fock. To this end, Comscope has been focused on developing and validating methodologies (theory, algorithm, and codes) based on *first principles* approaches and dynamical mean field theory (ab initio DMFT). In this poster, we will introduce three *ab initio* DMFT flavors in Comsuite, an *ab initio* package targeting correlated quantum materials. We will also show our recent validation results on various classes of correlated quantum materials: paramagnetic Mott insulator La_2CuO_4, Hund metal FeSe, correlated narrow-gap semiconductor $FeSb_2$, and Ni-based superconductor $LaNiO_2$.

2-D-25: STRUCTURE-PROPERTY CONTROL FOR ENHANCED SPIN-SPLITTING IN 2D HYBRID PEROVSKITES

[EFRC – CHOISE] Ruyi Song[1], Yi Xie[1], Manoj K. Jana[1], Rundong Zhao[1], Peter C. Sercel[2], Dipak Rajkhanal[3], Evan Lafalce[3], Brian Fluegel[4], Nicholas Weadock[5], Leah Kelly[6], Michael Toney[5], Matt Beard[4], Valy Vardeny[3], Volker Blum[1], David B. Mitzi[1]
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Two-dimensional hybrid organic-inorganic perovskite (2D HOIP) semiconductors with giant Rashba/Dresselhaus (R/D) spin-splitting offer outstanding potential for spin manipulation in future spintronic applications, and efforts have been devoted to realizing, understanding, and controlling this electronic feature in the 2D HOIPs. One of our previous works from CHOISE (*Nat. Commun.* 11, 4699, 2020) demonstrated that organic-inorganic “chirality transfer” provides one synthetic design strategy to break the inversion symmetry and promote spin-splitting in 2D HOIPs. However, a quantitative microscopic understanding of what controls the spin-splitting magnitude is generally lacking. Through crystallographic and first-principles studies on a broad array of chiral and achiral 2D perovskites, we find (*Nat. Commun.* 12, 4982, 2021) that a specific bond angle disparity connected with asymmetric tilting distortions of the metal halide octahedra breaks the local inversion symmetry and strongly correlates with the computed spin-splitting. This distortion metric can serve as a crystallographic descriptor for the rapid discovery of potential candidate materials with strong spin-splitting. Additionally, we are developing HOIPs that offer temperature-induced structural transitions, as an innovative approach for enabling switching among different symmetry breaking and chirality transfer states for the inorganic layers, which in turn enables control over R/D splitting in the 2D HOIPs. These tunable structural and electronic properties, achieved via selecting appropriate organic cations and associated temperature-induced structural transitions, show the potential for using 2D HOIPs as promising candidates for future spin-related, optoelectronic, and ferroelectric applications.

2-D-26: OPERANDO STUDIES OF RESISTIVE SWITCHING IN VO_2 FOR NEUROMORPHIC COMPUTING

[EFRC – Q-MEEN-C] Shaobo Cheng[1], Min-Han Lee[2], Lorenzo Fratino[3], Richard Tran[2], Anatoly G. Shabalin[2], Javier del Valle[2], Nelson Hua[2], Mathew J. Cherukara[4], Martin V. Holt[4], Marcelo J. Rozenberg[3], Shyue Ping Ong[2], R. C. Dynes[2], Ivan K. Schuller[2], Oleg G. Shpyrko[2], Yimei Zhu[1]
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Emulating the functionality of the human brain using neuromorphic computing systems has been proposed as the next generation computing architecture, because of its low energy consumption, plasticity, and high proficiency at complex tasks, such as pattern recognition. Quantum materials undergoing Metal-Insulator transition, specifically VO_2, which has near room temperature metal-insulator transition, have emerged among prominent candidates for neuristor platforms in bio-inspired devices. However, many fundamental questions related to the mechanisms of resistive switching behavior, stochastic electric response, and the balance between volatile and non-volatile switching, remain an obstacle to the practical use of these devices in neuromorphic computing. Here, taking advantage of operando transmission electron microscopy, operando X-ray diffraction and theoretical calculations, we have systematically studied the nanoscale evolution of electronic and structural phases during the resistive switching of metal-insulator devices in both in-plane and out-of-plane geometries. The inherent stochasticity related to the transition pathways between rutile and monoclinic VO_2 phases has been uncovered. The Magnéli phase $VO_{2-\delta}$ has been identified as the filament phase for non-volatile switching. Our findings not only facilitate the fundamentally deeper understanding of materials physics of Metal-Insulator transition, but also accelerate the development of neuromorphic computing techniques.

2-D-27: PHASE TRANSITIONS AND WAKE-UP IN FERROELECTRIC HAFNIUM ZIRCONIUM OXIDE FILMS

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$Hf_{1-x}Zr_xO_2$ (HZO) is an enabling material for next generation computing, including 3-D architectures, because it exhibits robust ferroelectricity at the nanometer scale and is compatible with silicon microprocessor platforms. Our interdisciplinary 3DFEM team is addressing three specific challenges that must be understood and controlled: 1) the mechanisms leading to the ferroelectric phase transition, which is necessary to overcome wake-up effects, 2) the role of defects on phase stability, wake-up, and fatigue, and 3) engineered design of the material to enable promising memory devices. To understand the ferroelectric phase transition and polarization reversal process, theoretical symmetry analysis and density functional theory calculations show that tetragonal "chiral variants" could be induced by the cubic-to-tetragonal transition. These calculations suggest the possibility of additional orthorhombic chiral variants.

Nudged elastic band calculations simulated the transition between different symmetry variants featuring the same and the opposite chirality. The low-energy transition pathways for each are different and present new possibilities to understand (and engineer) the atomistic mechanisms of ferroelectric polarization reversal. Non-ambient piezoresponse force microscopy (PFM) shows for the first time that capacitor wake-up is accompanied by a reversible exchange of atmospheric oxygen, demonstrating the importance of point defects. Silicon CMOS compatibility and novel ferroelectric field-effect transistors would be further enhanced if remanent polarization values are reduced. To do so, new formulations involving 20-30% Ta substitution were developed and prepared by laser ablation and chemical solution deposition. Current analysis reveals the desired polar symmetry and a 40% reduction in the spontaneous polarization.

2-D-28: SUPPRESSION OF LONG-RANGE ORDER BY LATTICE DEFECTS IN A FRUSTRATED TRIANGULAR ANTIFERROMAGNET

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High degeneracy of the ground state in a frustrated magnet can be lifted by a lattice distortion through spin-lattice coupling [1,2]. The frustrated antiferromagnet on a triangular lattice $NiGa_2S_4$ escapes this fate and remains in a state with only short-range correlations down to the lowest temperatures[3]. We explore theoretically and experimentally a scenario proposed by Stoudenmire et al. [4], in which the valence-bond order is suppressed by disorder from lattice defects such as vacancies. Shear strain induced by randomly situated vacancies acts like the random field of Imry and Ma.

Raman scattering spectroscopic experiments [5] reveal a major role of an Eg phonon that creates in-plane shear strain and couples to valence-bond order. The detection of Raman-forbidden phonons reveals a local symmetry breaking by vacancies. A combination of analytical arguments and numerical simulations confirmed that the ordinarily negligible lattice disorder breaks an ordered state into domains whose size scales exponentially with the inverse spin-lattice coupling. A spin correlation length of a few lattice spacings is achieved with 1 percent of vacancies and moderate spin-lattice coupling.

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2-D-29: RECENT DEVELOPMENTS AND APPLICATIONS OF THE FLAPWMBPT CODE

[CMS – Comscope] Andrey Kutepov
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The poster will give a brief account of new advances in the FlapwMBPT code such as elimination of the linearization error in relativistic (Dirac equation based) LAPW basis set [1,2] and changes in how the input information for calculations is provided. New applications of vertex corrected GW approach as implemented in the FlapwMBPT code will be presented. They include the comparative study of correlation effects in $LaNiO_2$ and $CaCuO_2$ [3], research on the electronic structure and on the importance on non-local physics in the van der Waals ferromagnet CrI_3 [4], establishing the spatial non-locality of diagrams beyond GW (NiO, α-Ce, LiFeAs) [5], and the investigation into importance of full self-consistency (instead of quasi-particle self-consistency) in diagrammatic approaches which go beyond GW [6].

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[3] Phys. Rev. B 104, 085109 (2021)
[4] Phys. Rev. Materials 5, 083805 (2021)
[5] J. Phys.: Condens. Matter – Accepted, in press (2021) [6] arXiv: 2109.01021 2 Sep 2021

F. QUANTUM SCIENCE AND MICROELECTRONICS (ROOM: *2F*)

2-F-1: EVIDENCE FOR A TUNABLE MAGNETIC WEYL SEMIMETAL: CEBI

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We present a multi-faceted study of CeBi, of interest for its multiple magnetic phases, and its corresponding potential as a magnetically tunable Weyl semimetal. Our density functional theory calculations in the ferromagnetic phase predict two pairs of Weyl nodes within 100 meV of the Fermi level, and two corresponding Fermi arcs on the (010) surface. In the ferrimagnetic phase, our DFT predicts additional tunability, with up to seven pairs of Weyl nodes near E_F. To verify these predictions, we synthesize CeBi single crystals with Bi self-flux, and use magnetization and transport measurements to detail the rich temperature-field (T-B) magnetic phase diagram. Our neutron diffraction data show magnetic Bragg peaks consistent with the two previously reported zero-field phases. ARPES shows significant band reconstruction upon cooling into the zero-field antiferromagnetic phases, and presence of three different domains with distinct band structure due to orientation of magnetic moments with respect to sample surface. Finally, we present spin-polarized scanning tunneling microscopy and spectroscopy to directly image the surface states in the antiferromagnetic, ferrimagnetic, and ferromagnetic phases, and to quantify the magnetic band splitting necessary for Weyl point formation. In all three phases, we observe a Fano line shape in the conductance spectra, suggesting the Bi p-states partially Kondo screen the 4f magnetic moments, and this p−f hybridization causes strong Fermi-level band renormalization. The p-band flattening is supported by our quasiparticle interference measurements, which paint a consistent picture of a strongly interacting magnetic Weyl semimetal.

2-F-2: Novel Spin and Charge Excitations in the Antiferromagnetic Weyl Semimetal Mn_3SN

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[1]Johns Hopkins University; [2]University of Tokyo

Topological magnets produce gigantic electric and magnetic responses that are useful for spintronics and energy harvesting [1]. In particular, exotic transport has been found in Mn_3Sn due to Weyl fermions on a kagome lattice [2]. A coherent team effort involving half of IQM has provided evidence for (i) THz Hall conductivity [3,4], (ii) a chiral magnetism and the associated excitations [5], (iii) strong magnetoelastic coupling and (iv) omnidirectional control of electric output [6]. We discuss our discovery of the topological phase transition between a Weyl

semimetal and a spin/charge density wave phase. The non-coplanar magnetic structure arises from the interplay between geometrical frustration and electronic correlations [5]. Given the prospects for ultrafast AFM spintronics, the understanding of their spin and charge dynamics in thin film configurations is highly important. Our fabrication of high-quality thin films unveils transmission THz Hall conductivity at 300K [3,4] and its near absence of dissipative transport, essential for AF spintronics. We also discuss our discovery of additional novel topological magnets [7,8].

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2-F-3: KRAMERS-WEYL FERMIONS IN THE CHIRAL CHARGE DENSITY WAVE MATERIAL (TASE4)2I

[EFRC – QSQM] Soyeun Kim[1], Robert C. McKay[1], Nina Bielinski[1], Chengxi Zhao[1], Meng-Kai Lin[2], Joseph A. Hlevyack[1], Xuefei Guo[1], Sung-Kwan Mo[3], Peter Abbamonte[1], Tai-Chang Chiang[1], André Schleife[1], Daniel P. Shoemaker[1], Barry Bradlyn[1], and Fahad Mahmood[1]
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The quasi-one-dimensional chiral charge density wave (CDW) material $(TaSe_4)_2I$ is a type of topological crystalline insulator that has recently been predicted to host Kramers-Weyl (KW) fermions which should exist in the vicinity of high symmetry points in the Brillouin zone in chiral materials with strong spin-orbit coupling. However, direct spectroscopic evidence of KW fermions is limited. Here we use helicity- dependent laser-based angle resolved photoemission spectroscopy (ARPES) in conjunction with tight-binding and first-principles calculations to identify KW fermions in $(TaSe_4)_2I$. We find that topological and symmetry considerations place distinct constraints on the (pseudo-) spin texture and the observed spectra around a KW node. We further reveal an interplay between the spin texture around the chiral KW node and the onset of CDW order in $(TaSe_4)_2I$. Our findings highlight the unique topological nature of $(TaSe_4)_2I$ and provide a pathway for identifying KW fermions in other chiral materials.

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2-F-4: NON-RECIPROCAL HEAT AND LIGHT PROPAGATION USING MAGNETIC WEYL SEMI METALS AND HIGH-QUALITY-FACTOR METASURFACES

[EFRC – PTL] Arun Nagpal[1], Jefferson Dixon[2], Harsha Eragamreddy[2], Chris Ciccarino[3], Prineha Narang[3], Jennifer Dionne[2], Harry Atwater[1]
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The control of infrared radiation, particularly in the thermodynamic limit, is of significant interest in the development of thermal emitters. Non-reciprocal control of such emission allows for the separate tuning of the emissivity and absorptivity characteristics of a device, breaking Kirchhoff's Law. However, previous experiments involving Kirchhoff's Law violations involved magnetooptical devices that incorporated bulky external magnets in their steady-state operation. Here, we show the development of nonreciprocal emitters in the absence of an externally applied magnetic field, leveraging two unique phenomena: 1) the topological properties of the magnetic Weyl semimetal $Co_3Sn_2S_2$, and 2) spin-polarizing optical metasurfaces. First, using ab-initio methods, we develop models of the electron-phonon scattering and the temperature-resolved dielectric function of $Co_3Sn_2S_2$ in its Weyl phase. We further experimentally characterize the crystallinity of our single crystals through X-ray diffractometry, and the dielectric tensor elements through generalized ellipsometry. We further theoretically propose the expected non-reciprocal response of an optical metasurface incorporating $Co_3Sn_2S_2$. In parallel, we also discuss the design and development of non-reciprocal metasurfaces incorporating spin-polarized non-linearities. Our design relies on nanoscale silicon meta-molecules with three-dimensional chiral symmetry. When these chiral meta-molecules are arranged in a periodic two-dimensional subwavelength lattice, they constitute a metasurface with distinct spin-dependent transmission and reflection properties. Using spin-polarized Stimulated Raman Scattering (SRS) together with our chiral metasurface, we computationally demonstrate Raman lasing in the forward direction, while the lasing action is suppressed by over an order of magnitude in the backward direction. We will discuss these computational findings and our recent efforts to experimentally realize the proposed devices.

2-F-5: Manipulating electronic symmetry in Weyl semimetal TaAs using ultrafast photocurrents

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Ultrafast manipulation of symmetry and topology is a key element of future technologies that exploit topological phenomena such as quantization and protection of electronic transport. Topological semimetals are particularly sensitive to the breaking and restoring of time-reversal and crystalline symmetries, which affect both bulk and surface electronic states. Using second harmonic generation spectroscopy as a sensitive probe of electronic symmetry, we here demonstrate transient breaking of time-reversal and spatial symmetry on picosecond timescales in the type-I Weyl semimetal TaAs following femtosecond optical excitation. A detailed theoretical symmetry analysis together with terahertz emission experiments reveals an underlying all-electronic mechanism based on photocurrent generation. We demonstrate that the direction of transient photocurrents can be controlled via the light polarization of the pump pulse: while helicity-independent photocurrents are excited along the polar c-axis in the non-centrosymmetric material, photocurrents in the ab-plane depend on the helicity of the light. This allows manipulation of the degree of symmetry lowering via the pump polarization direction, as we explicitly demonstrate. This collaborative work involving theorists and experimentalists from different CATS institutions reveals that optically driven photocurrents can be tailored to break electronic symmetry in a generic fashion, opening up the possibility to driving phase transitions between symmetry-protected states on ultrafast timescales.

2-F-6: TUNABLE TOPOLOGY AND ELECTRONIC SPECTROSCOPY

[EFRC – Pro-QM] Ana Asenjo-Garcia[1], D.N. Basov[1], Cory Dean[1], James Hone[1], James Shuck[1], Michal Lipson[1], Andrew Millis[1], Abhay Pasupathy[1,3], Xavier Roy[1], Xiaoyang Zhu[1], David Cobden[2], Daniel Gamelin[2], Jiun-haw Chu[2], Di Xiao[2], Xiaodong Xu[2], Matt Yankowitz[2], Valentina Bisogni[3]
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Topological phases in quantum materials are defined by non-zero topological indices associated with the electronic structure. Discovering pathways to realize topological and exert control over them is currently a central goal of physical sciences. In this poster, we will present a UW-Columbia collaboration in creating, visualizing, and manipulating topological states in low-dimensional quantum materials. We have investigated the interplay between topology and magnetism in two distinct systems. The first is spin-based - newly discovered topological antiferromagnet $MnBi_2Te_4$, in which we unraveled a series of Chern insulating states, tightly coupled to the magnetic order with electrical control. The second is based on emerging orbital magnetism in twisted graphene. For a twisted monolayer-bilayer graphene, we observe the emergence of electrically tunable ferromagnetism with an associated anomalous Hall effect and switchable magnetization by electrostatic doping. Topology is also intimately linked to atomic structure via orbital overlaps, and moiré systems offer a facile route to achieve new atomic and hence electronic structures. We investigate this in two platforms. First, we study twisted trilayer graphene by scanning tunneling microscopy where superconductivity has been recently discovered, and find that the atomic structure displays a moiré of moiré patterns. Secondly, we illustrate our recent progress in revealing the gate-tuned electronic structure in moiré superlattice systems formed in twisted van der Waals heterostructures using angle-resolved photoemission spectroscopy with sub-µm spatial resolution.

2-F-7: INVESTIGATION OF MAGNETOELECTRIC COUPLING IN MULTINUCLEAR SPIN-FRUSTRATED CLUSTERS AND SPIN-STATE SWITCHING MOLECULES

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Triangular configurations of antiferromagnetically coupled spins provide a new approach to spin-electric coupling (SEC). Such systems react to the external magnetic field by changing spin orientations and developing a non-zero electric dipole. Theoretical investigation of a tetrahedral cluster $Mn_4Te_4(PEt_3)_4$ suggests a potential for SEC driven by Dzyaloshinskii-Moriya interaction. Preliminary studies of an octahedral cluster $[Fe_6O_2(O_2CBu^t)_6(hmp)_6](NO_3)_2$ show that the dielectric constant follows the changes in magnetic properties, hinting at potential SEC effect. A combined theoretical-experimental study reveals strong spin frustration in a heptanuclear cluster $Cr_7S_8(en)_8Cl_5(H_2O)$. Theoretical approaches have been extended to giant clusters, Mn_{84} and Mn_{70}, allowing computation of magnetic parameters and Monte-Carlo simulation of macroscopic physical properties. A high sensitivity cryogenic tunnel diode oscillator has been developed to search for SEC, with the sensitivities as high as 0.1 ppm, 2-120 K temperature range, and applied electric fields up to 300 kV/m. Magneto-electric (ME) coupling afforded by spin crossover (SCO) can be leveraged to control properties of magnetic molecular materials. SCO allows cross-coupling between magnetic and electric properties, and local molecular and global crystal structures. We are exploring four Mn and Fe compounds where the SCO, induced by changes in temperature and

magnetic field, alters the electric polarization of the material, creating ME coupling. As a next step we are investigating Co(Cat)(SQ)(4-CNpy)$_2$, in which the SCO occurs due to the change in the valence of the Co ion. An electron toggles between the metal ion and ligand orbitals, thereby altering the molecular electric dipole, which might lead to the ME effect.

2-F-8: DEFECT CENTERS IN DIAMOND FOR QUANTUM SENSING APPLICATIONS

[EFRC – NPQC] Prabudhya Bhattacharyya[1,2], Satcher Hsieh[1,2], Nikola Maksimovic[1,2], Bryce Kobrin[1,2], Maxwell Block[1], Weijie Wu[1], Yuanqi Lyu[1], Benchen Huang[3], Nazar Delegan[3,4], James G. Analytis[1,2], Joel E. Moore[1,2], Martin V. Holt[4], F. Joseph Heremans[3,4], Giulia Galli[3,4], Norman Y. Yao[1,2]
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The Nitrogen-Vacancy (NV) center in diamond has cemented its role as a robust and versatile quantum sensor capable of operating in a wide range of modalities with nanoscale spatial resolution. Our present work on quantum sensing encompasses a two-pronged approach. On the one hand, we use widefield and confocal NV sensing to explore a rich landscape of condensed matter phenomena ranging from imaging of individual superconductor vortices to spatially-resolved quantum phase transitions. On the other hand, we present ongoing efforts to probe, both experimentally and computationally, the spectroscopic response of NV centers to tensorial crystallographic strain over several orders of magnitude (10^{-6} to 10^{-1}). Our work enables new routes for strain control of defect centers and opens the door to hitherto unexplored regimes of quantum sensing using pressure as a thermodynamic tuning parameter.

2-F-9: ACCURATE AND TRANSFERABLE MOLECULAR-ORBITAL-BASED MACHINE LEARNING FOR MOLECULAR MODELLING

[CCS – NGMD] Thomas F. Miller III[1], Frederick R. Manby[2], J. Emiliano Deustua[1], Lixue Cheng[1], Jiace Sun[1]
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Quantum simulation is a powerful tool to understand chemistry and other physical processes. Current state-of-the-art electronic structure methods based on the wavefunction offer great accuracy, but unfortunately incur in tremendous computational costs that drive most interesting problems out of reach. In this work, we introduce an accurate and transferable molecular modelling framework, known as Molecular Orbital Based Machine Learning (MOB-ML), which provides quantum descriptions similar to those provided by high-quality, wavefunction-based methods, while keeping the computational cost low, at the level of Hartree—Fock computations. Preserving all the physical constraints, MOB features can represent the chemical space properly, even when small datasets are used for training. They can be used to prepare models leading to almost exact predictions of energies and other observables, whilst providing useful insights within the chemical space by exploiting unsupervised learning approaches. As a general new tool to tackle various problems in chemistry, we show that MOB-ML offers great accuracies in predicting total energies of organic and transition-metal containing molecules as well as providing high-level descriptions of non-covalent interactions such as those governing backbone-backbone interactions in proteins. In addition to this, we demonstrate how MOB-ML can be used for the computation of high-quality potential energy surfaces, such as those required by Diffusion Monte Carlo simulations of the water and CH_5+ molecules.

2-F-10: MAGNETIC MOLECULES AS A ROUTE TO MULTI-QUBIT SYSTEMS AND OTHER IMPORTANT QUANTUM PROPERTIES

[EFRC – M^{2}QM] ChristiAnna Brantley[1], Alexander Diodati[1], Shuanglong Liu[1], Tuhin Ghosh[1], Khoa Dong[1], Jiexiang Yu[1], Daphné Lubert-Perquel[2], We-Hao Chou[2], Robert Stewart[2], Jonathan Marbey[2], Zahra Hooshmand[3], Miguel Gakiya-Teruya[2], Ping Wang[2], Jia Chen[1], Silas Hoffman[1], Hai-Ping Cheng[1], Stephen Hill[2,] Mark Pederson[3], Michael Shatruk[2], George Christou[1]
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The synthetic control provided by molecular chemistry represents a powerful resource in the use of magnetic molecules to investigate quantum properties important to next-generation technologies. The molecular nature also allows their study by EPR spectroscopy and other techniques in phases spanning single crystals, microcrystalline powders, and glasses. Multiple approaches have been developed to generate families of molecular multi-qubit systems exhibiting quantum superposition/entanglement states. One approach is the synthesis of homo- and heterometallic dinuclear complexes with controllable permutations of metal ions and spin. Another is the controlled linkage of magnetic molecules into exchange-coupled molecular dimers and higher oligomers. The latter approach has spanned both Mn3 single-molecule magnets with S = 6 and smaller Mn2 complexes with S = ½, and different linkers that allow control of the magnitude and size of the exchange coupling between them. Molecular crystals and metal-organic frameworks that contain lanthanide ions in high-symmetry environments matching the expected ground-state mJ doublet for the particular ion are predicted to exhibit robust clock transitions that are insensitive to the surrounding spin bath, thus dramatically increasing the spin coherence time. EPR spectroscopic study of several hexagonal complexes of Tb3+ (expected |mJ| = 6) and tetragonal complexes of Ho3+ (possible |mJ| = 4) has revealed two such complexes that exhibit low-field resonances indicative of clock transitions. DFT calculations predict unquenched orbital moment in quasi-octahedral Co single-ion magnets and in Co2 dimers with an unusual reordering of electronic levels in the latter as a function of spin ordering.

2-F-11: PERMANENT POROSITY IN MOLECULE-BASED ROOM TEMPERATURE MAGNET VANADIUM TETRACYANOETHYLENE (V[TCNE]$_2$)

[EFRC – CMQT] Jesse Park[1], Kennedy McCone[1], Huma Yusuf[2], Donley Cormode[2], Qin Xu[4], Yueguang Shi[3], Dmitriy Lebedev[3], Iqbal Utama[5], Jeffrey Long[1], Ezekiel Johnston-Halperin[2], Michael E. Flatté[3], Gregory D. Fuchs[4], Mark C. Hersam[5]
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One of the fundamental goals of quantum information science is to achieve the ability to relay, process and store information by manipulating qubits. Magnons coupled with the atomic-scale structural and spatial control of molecular systems have the potential to achieve this goal via pairwise interactions to other molecular degrees of freedom such as phonons, photons and excitons. In this context, porous magnets that combine permanent porosity and long-range magnetic order provide the molecular architecture for exploring quantum transduction in distributed molecular systems through intercalation of molecular qubit candidates. However, in order to fulfill this potential, materials with ultralow magnetic damping or low-loss magnons are required. Molecule-based V[TCNE]$_2$ is a room-temperature ferrimagnet with single-peaked, narrow magnetic resonance feature (less than 1 G at 10 GHz) and a Curie temperature of over 600 K. Additionally, the ability to pattern and deposit high-quality V[TCNE]$_2$ films on a wide range of substrates with different morphologies makes V[TCNE]$_2$ a promising candidate for incorporation into magnetoelectric devices conducive to applications in quantum information science and engineering. Here, we present a systematic evaluation of porosity and intercalation in bulk V[TCNE]$_2$ obtained through an activation of the parent V[TCNE]$_2$·0.95CH$_2$Cl$_2$. Notably, the activated V(TCNE)$_2$ is permanently porous to the insertion of various gas molecules and exhibits ferrimagnetic order beyond room-temperature. Theoretical calculations show that certain gas molecules, such as ethylene, can be easily incorporated into the V[TCNE]$_2$ matrix and be used to tailor behavior of magnon modes by modifying the spin-polarized density of states in V[TCNE]$_2$.

2-F-12: MANY-BODY PHYSICS WITH COLOR CENTERS IN DIAMOND: HYDRODYNAMICS AND MANY-BODY NOISE

[EFRC – NPQC] Emily J. Davis[1], Francisco Machado[1,2], Chong Zu[1,2,3], Bingtian Ye[1], Simon A. Meynell[4], Thomas Mittiga[1,2], William Schenken[4], Maxime Joos[4], Lillian Hughes[4]. Bryce Kobrin[1,2], Yuanqi Lyu[1], Dolev Bluvstein[5], Satcher Hsieh[1,2], Prabudhya Bhattacharyya[1,2], Matthew Markham[6], Dan Twitchen[6,] Andrey Jarmola[1,7], Dmitry Budker[1,8], Soonwon Choi[1], Chris R. Laumann[9], Joel E. Moore[1,2], Ania C. Bleszynski Jayich[4], Norman Y. Yao[1,2]

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Spin defects in solid state materials have emerged as a promising platform for quantum science, providing long-lived and coherent qubits at ambient temperatures and pressures. The ability to directly control the defect density when growing a material creates the possibility to engineer highly coherent, strongly-interacting spin ensembles for use in quantum simulation. We highlight these opportunities in two different studies on hybrid spin defect ensembles in diamond. First, we consider the dynamics of a strongly interacting ensemble of substitutional nitrogen (P1) centers. Using the optically polarizable nitrogen-vacancy (NV) center to initialize and probe the P1 spin ensemble, we prepare inhomogeneous spatial profiles of spin density and observe its spreading through the system. We verify the emergence of an unorthodox hydrodynamical description for diffusion in the three-dimensional strongly disordered many-body system. Second, harnessing novel growth techniques for diamond, we prepare a sample constraining the spins to a thin layer; controlling the ratio of the defect density to the layer thickness directly affects the dimensionality of the defect ensemble. Using the coherence dynamics of the coexisting NV probe spins, we measure the dimensionality of the P1 ensemble and observe results consistent with a two dimensional sample. Our work also addresses a persistent debate about the microscopic nature of spin dynamics in strongly-interacting dipolar systems — our observations are consistent with continuous Gaussian noise, despite a naive expectation of discrete telegraph-like noise.

2-F-13: PHONON- AND DEFECT-LIMITED MOBILITY OF DIAMOND AND CUBIC BORON NITRIDE

[CSM – EPW] Nocona Sanders, Emmanouil Kioupakis

University of Michigan at Ann Arbor

Diamond and cBN are two of the most promising ultra-wide bandgap semiconductors for applications in high-power high-frequency electronic devices. Despite extensive studies on carrier transport in these materials, there are large discrepancies in their reported carrier mobilities. In this poster we report an atomic-scale investigation of the phonon- and dopant-limited carrier mobilities of cBN and diamond, based on the *ab initio* Boltzmann transport equation. We found that, although the phonon-limited electron mobilities are comparable between cBN and diamond, the hole mobility is significantly lower in cBN due to its heavier hole effective mass. Moreover, although lattice scattering dominates the mobility at low doping, neutral impurity scattering becomes the dominant scattering mechanism at higher dopant concentrations due to the high ionization energy of the dopants. The present analysis provides critical insights into the transport properties of ultra-wide bandgap semiconductors and reveals the intrinsic upper limits to the carrier mobilities of diamond and cBN as a function of doping and temperature. Our findings carry important implications for the use of these semiconductors in high-power electronics.

2-F-14: DISLOCATIONS, DEFECTS, AND DOPING IN DIAMOND

[EFRC – ULTRA] Timothy Grotjohn[1], Robert Nemanich[2], Fernando Ponce[2], Mary Ellen Zvanut[3], Arunima Singh[2], Srabanti Chowdhury[4], Richard Wilson[5], Alexander Balandin[5]

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Diamond for power electronics is grown by plasma-assisted CVD and dopants are incorporated during the growth. The EFRC work on diamond is to understand and reduce dislocation defects and to get uniform and controlled doping levels that lead to diamond with high thermal conductivity, high carrier mobilities and high electric field breakdown strength. The technical goals driven by the co-design effort include deposition of undoped and doped diamond with no new dislocations created and controlled, uniform doping levels of desired thickness. To achieve these goals and because measured values are less than expectations due to dislocations and defects of various types, a deeper understanding is needed to advance the technology beyond that achieved through past research. The work on diamond reported in this poster extends across materials synthesis, computational material discovery, and materials characterization. Synthesis of diamond is performed with advances being explored in dislocation reduction and doping control. The structural properties and origin of dislocations are being investigated with nano-scale cathodoluminescence and TEM microscopy. The nature of point defects is measured with electron paramagnetic resonance. Vibrational and thermal transport properties are being measured as a function of dopant concentration using Raman and Brillouin spectroscopy, and time-domain thermoreflectance. Photoconductive and electrical properties are being measured at high electric fields and fast time scales to understand breakdown in diamond. Lastly, these efforts are supported by computational materials science to both add understanding to the phenomenon measured and to direct further improvements in diamond for the ultra-conditions of future power electronic systems.

2-F-15: MULTI-MESSENGER NANO-IMAGING OF QUANTUM MATERIALS

[EFRC – Pro-QM] D.N. Basov[1], Cory Dean[1], James Hone[1], James Shuck[1], Michal Lipson[1], Andrew Millis[1], Abhay Pasupathy[1,3], Xavier Roy[1], Xiaoyang Zhu[1], David Cobden[2], Daniel Gamelin[2], Xiaodong Xu[2], Matt Yankowitz[2], Valentina Bisogni[3]

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As a central cross-cutting effort, Pro-QM is developing advanced capabilities and techniques that enable one to visualize and correlate complex QM phenomena at their native length and time scales, redefining the cutting edge of characterization. The length scales of many critical processes within the materials and devices developed by Pro-QM – such as exciton Bohr radii, plasmon-polariton wavelengths, and Moiré lattice spacings – are at the nanoscale, well below the diffraction limit of light. Since the inception of the Pro-QM grant, co-PIs have expanded the range of scanning probe and nano-imaging modalities, providing unique access to QM properties and (programmable) functions. An important development milestone is our realization of a *universal cryogenic platform (UCP)*. The UCP has been designed, modeled, fabricated, assembled, tested, and commissioned by Pro-QM and now enable multi-scale, multi-modal, multi-messenger nano-imaging of complex quantum materials and their heterostructures. The UCP offers more than a dozen nano-imaging contrasts including nano-IR, nano-THz scattering, emission, photoconductivity and others. Major effort has also been dedicated to pushing the spatial resolution of nano-optical scan-probe measurements below 10 nm – into the single-digit-nanometer regime. By developing new gap-mode nano-photoluminescence (nano-PL) and ultra-PL methods, we have demonstrated <5 nm hyperspectral optical mapping. Combined with STM, nano/ultra-PL experiments uncovered quantum-dot-like exciton states in 2D semiconductors that are localized by strain alone at room temperature. In addition, Pro-QM has investigated and developed nonlinear nano-optical techniques that have unveiled how programmable symmetry.

2-F-16: MOLECULAR RUBIES FOR OPTICAL READOUT OF SPIN-STRAIN COUPLING

[EFRC – CMQT] Stephen von Kugelgen[1], Brendan McCullian[2], Jeremy Amdur[1], Chloe Washabaugh[2], Subhajyoti Chaudhuri[3], George C. Schatz[3], Gregory D. Fuchs[3], Danna E. Freedman[1]
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Transduction of quantum information from one quantum degree of freedom (DOF) to another is a key requirement for building from single qubits into an integrated quantum ecosystem. Chemical synthesis of molecular qubits uniquely enables the design and integration of multiple local DOFs into a single system with atomistic control over their interaction. The coupling of a molecular electron spin DOF to quantized mechanical DOF of a resonator is one such interaction, mediated by strain, that is well suited to design from the bottom-up in molecular solids. A canonical example of a strain-responsive solid state color center is the Cr(III) dopant in ruby, whose strain-dependent emission spectrum is used to calibrate high-pressure experiments. Drawing inspiration from this dopant ion, here we present our combined synthetic, spectroscopic, and theoretical approach to controlling this spin-strain coupling in octahedral molecular Cr(III) complexes. Chromium-doped single-crystals of tris(3-bromo-2,4-pentanediono) aluminum recapitulate the electronic structure of ruby, featuring long (~ms) emission lifetimes. The zero-field splitting of the 4A ground state is much larger than the lifetime-limited linewidth, which will enable observing perturbations to the ground state spin manifold as a function of applied strain. To inform the mechanism of spin-strain coupling, we have synthesized a series of Cr(III) derivatives that feature progressively larger distortions from perfect octahedral geometry. Guided by theory, these structures provide static snapshots of specific strain-induced deformations to understand their impact on the molecular spin DOF.

2-F-17: COUPLED QUANTUM SOLUTIONS FOR MOLECULAR MAGNETIC QUBITS AND COHERENCE (CROSSCUTTING THEORY)

[EFRC – M^{2}QM] Garnet Chan[1], Magdalena T. Owczarek[2], Minseong Lee[2], Vivienne Zapf[2], Karma Dema[3], Zahra Hooshmand[3], Mark R. Pederson[3], Steven Hill[4], Michael Shatruk[4], Eric Switzer[5], Talat Rahman[5], Dian-Teng Cheng[6], Ashlyn Hale[6], Shuang-Long Liu[6], Angel Martin Albavera Mata[6], Yue Yu[6], Maher Yazback[6], Xiaoliang Zhang[6], George Christou[6], Richard Hennig[6], John Stanton[6], Sam Trickey[6], Xiaoguang Zhang[6], and Hai-Ping Cheng[6]
[1]California Institute of Technology; [2]Los Alamos National Laboratory; [3]The University of Texas at El Paso; [4]Florida State University; [5]University of Central Florida; [6]University of Florida

Quantitative partially automated computational prediction of field-induced entanglement, or dis-entanglement, of physical spins in molecular-magnetic qubits is required to realize the center's goal of controlling quantum states associated with magneto-electrics, field-induced quantum tunneling in anisotropic macro-spins, or more generally, producing or managing coherent superpositions of states. Achieving this goal efficiently requires myriad quantum computational approaches with the full range of correlated vs mean field treatments and, at least as importantly, methodologies that predict couplings arising from vibrational-, spin-, orbit- excitonic-, and electronic degrees of freedom and substrate dependencies. M^2QM identified three-center molecular magnetic monomers and dimers as systems that exhibit ligand-dependent magneto-electric or magnetic-tunneling behaviors and further realized, since trimers seem to have a propensity toward Hund's-rule ambivalence, that spin-crossover and spin-flip excitons can further enrich the diversity of behaviors in these quantum systems. To validate our predicted pressure-assisted Hunds-rule-violating spin-flips in Mn-based trimers we have used high-level quantum methods and new DFT-parameterizations which has led to better understanding of ligated spin-crossover Mn monomers and concomitant structural features. We extend these investigations to low-energy field-dependent or polarization-dependent magnetic order switching in M_3-monomers, with M=Ni, Cr, Co, Ln (Shatruk *et al*) and Fe_3-dimers (Zapf *et al*) respectively. To address the recent synthesis of even stronger ligation-induced dipole-containing quantum trimers, M^2QM uses a full range of methods to understand a new class of Cu_3 spin systems (Christou *et al*). This poster illustrates our rational team-based technical workflow to describe perfect and defective quantum trimers and step toward a coupled theory of (de)coherence.

2-F-18: DISTINGUISHING FINITE MOMENTUM SUPERCONDUCTING PAIRING STATES WITH TWO-ELECTRON PHOTOEMISSION SPECTROSCOPY

[EFRC – QSQM] Fahad Mahmood[1], Thomas Devereaux[2], Peter Abbamonte[1], and Dirk K. Morr[3]
[1]University of Illinois, Urbana-Champaign; [2]SLAC National Accelerator Laboratory; [3]University of Illinois, Chicago

We show theoretically that double photoemission (2*e*-ARPES) may be used to identify the pairing state in superconductors in which the Cooper pairs have a nonzero center-of-mass momentum, $\mathbf{q}_{cm}$. We theoretically evaluate the 2*e* ARPES counting rate, $P^{(2)}$, for the cases of a d_{x2-y2}-wave superconductor, a pair-density-wave (PDW) phase, and a Fulde-Ferrel-Larkin-Ovchinnikov (FFLO) phase. We show that $P^{(2)}$ provides direct insight into the center-of-mass momentum and spin state of the superconducting condensate, and thus can distinguish between these three different superconducting pairing states. In addition, $P^{(2)}$ can be used to map out the momentum dependence of the superconducting order parameter. Our results identify 2*e*-ARPES as an ideal tool for identifying and probing $\mathbf{q}_{cm} \neq 0$ superconducting pairing states in superconductors.

Reference: F. Mahmood, T. P. Devereaux, P. Abbamonte, D. K. Morr, Distinguishing finite momentum superconducting pairing states with two-electron photoemission spectroscopy, arXiv:2108.04260

2-F-19: PROBING ULTRAFAST CURRENTS IN SOLIDS: APPLICATION TO FERROELECTRIC WTE2 AND BIFEO3

[CMS – NPNEQ] Aaron Lindenberg[1,2], Das Pemmaraju[2], Liang Tan[3]
[1]Stanford University; [2]SLAC National Accelerator Laboratory; [3]Lawrence Berkeley National Laboratory

We discuss recent coupled experimental and theoretical efforts to probe light-driven dynamical currents in ferroelectric materials. In $BiFeO_3$ we use THz emission spectroscopy coupled to first principles methods to directly and quantitatively probe the intrinsic charge separation mechanisms in both monodomain and stripe domain samples. We find evidence for charge separation driven by ferroelectric domain walls acting as nanoscale junctions and compare quantitatively the measured currents to theory [1]. In the 2D ferroelectric WTe_2, we present experimental efforts to probe light-induced currents and associated structural deformations via ultrafast electron scattering and show how these modulations, in the form of sub-terahertz interlayer shear modes, lead to new ways for controlling the topological and ferroelectric properties of this and related materials [2,3].

[1] B. Guzelturk, "Light-Induced Currents at Domain Walls in Multiferroic $BiFeO_3$", Nano Lett. **20**, 145 (2020).
[2] E. J. Sie et al., "An ultrafast symmetry switch in a Weyl semimetal", Nature **565**, 61 (2019).
[3] J. Xiao et al., "Berry curvature memory through electrically driven stacking transitions", Nat. Phys. **16**, 1028 (2020).

2-F-20: INTEGRATION OF DIVERSE FUNCTIONAL DEVICES ON 3D FERROELECTRIC PLATFORM

[EFRC – 3DFeM] Kai Ni[1], Shan Deng,[1] Yi Xiao[2], Quyen Tran[2], Xiaojun Zheng[2], Thomas Jackson[2], Chengyang Zhang[3], Shriram Ramanathan[3], Amin Nozariasbmarz[2], Wenyi Zhu[2], Sanju Gupta[2], Shashank Priya[2], M. David Henry[4], Giovanni Esteves[4], Ying Liu[2], Autumn Heltman[2], Ryan Hawks[2], Qi Li[2], Susan Trolier-McKinstry[2], Takanori Mimura[5], Jon Ihlefeld[5], Vijaykrishnan Narayanan[2]
[1]Rochester Institute of Technology; [2]The Pennsylvania State University; [3]Purdue University; [4]Sandia National Laboratories; [5]University of Virginia

The development of back-end-of-line (BEOL) compatible ferroelectric materials brings exciting opportunities for novel devices. The 3DFeM team is exploiting this to address major challenges in 3D integrated systems. BEOL-compatible ferroelectric field effect transistors (FeFET) based on $Hf_{1-x}Zr_xO_2$, $Al_{1-x}B_xN$, $Al_{1-x}Sc_xN$, and $Zn_{1-x}Mg_xO$ ferroelectrics and ZnO and IZO channels were fabricated and characterized. A memory window around 1 V for ±3 V operating voltages was demonstrated in a $Hf_{1-x}Zr_xO_2$/IZO FeFET. We discovered that channel percolation due to the spatial distribution of ferroelectric domains disappears when the domain size is small compared with the carrier diffusion length. Device optimization in ferroelectric thickness scaling (<10nm), operation voltages (<1.8 V) and channel mobility enhancement (~100 $cm^2/V{\cdot}s$) are underway for high performance BEOL FeFETs. In addition, we are exploring ferroelectric semiconductors, like In_2Se_3, as channel materials. Ferroelectric tunnel junctions (FTJ), as two-terminal devices, are of great interest for high density memory and in-memory computing in crossbar array structures. We have developed a new predictive model of FTJs, incorporating multi-band transport and dynamic polarization switching to guide the design space exploration of FTJs for memory and neuromorphic applications. Fabrication of $TaN/Hf_{1-x}Zr_xO_2$, $Nb\text{-}SrTiO_3/PbZr_{1-x}Ti_xO_3$ and $Nb\text{-}SrTiO_3/Hf_{1-x}Zr_xO_2$ based structures is underway. Novel phase transition switches have been synthesized on conducting oxides that can be monolithically integrated with ferroelectric layers for solid state electrocaloric cooling. For large thermal flux on-chip cooling (>100 W/cm^2), a thermal heat pump utilizing ferroelectric–electrocaloric-thermoelectric stacks has been designed and is being investigated.

2-F-21: INQ, A SOFTWARE FRAMEWORK FOR FIRST PRINCIPLES ELECTRON DYNAMICS FOR HPC AND GPU SYSTEMS

[CMS – NPNEQ] Xavier Andrade[1], Das Pemmaraju[2], Aaron Lindenberg[2,4], Liang Tang[3], Tadashi Ogitsu[1], Alfredo A. Correa[1]
[1]Lawrence Livermore National Laboratory; [2]SLAC National Accelerator Laboratory; [3]Lawrence Berkeley National Laboratory; [4]Stanford University

We introduce the INQ project, a software framework for first principles electron dynamics for HPC and GPU systems. INQ is developed in modern C++ with emphasis in portability and performance in a variety of present and future hardware architectures. By designing the code around algorithms, rather than against specific implementations and numerical libraries, we aim to provide a concise and community-maintainable modular code. The INQ code can be used as a library driven by user code or as a standalone application. INQ leverages C++ syntax and high-level objects to specify simulation options instead of relying on ad-hoc scripting language or input formats. At the moment, INQ provides essential components to run a typical DFT (ground state) or TDDFT (electron dynamics) simulation in finite or infinite (supercell-periodic) system.

By enforcing an open software crafting process using development branches and version control, unit testing and continuous integration we aim to foster a dynamic community of users and developers. The goal of the project is to model ultrafast experiments performed at SLAC and other facilities that access the femto to picosecond time resolution and as part of the efforts of the NPNEQ center.

The work was supported by the U.S. Department of Energy, Office of Science, Materials Sciences and Engineering Division. Computing support for this work came from the Lawrence Livermore National Laboratory Institutional Computing Grand Challenge program.

2-F-22: ALN-BASED HETEROSTRUCTURES: EPITAXY AND PROPERTIES

[EFRC – ULTRA] H. Grace Xing[1], Yuji Zhao[2], Debdeep Jena[1], David J. Smith[2], Fernando Ponce[2], Mary Ellen Zvanut[3], Martin Kuball[4]
[1]Cornell University; [2]Arizona State University; [3]University of Alabama, Birmingham; [4]University of Bristol

AlN is an ultrawide-bandgap semiconductor with a high thermal conductivity and high piezoelectricity. The combination of a wide bandgap, high piezoelectricity, and a large thermal conductivity makes AlN a critical material for advancing applications in micro electro-mechanical systems, ultraviolet photonics, and high-power electronics. Furthermore, various heterostructures can be developed on an AlN platform, including BAlN, ScAlN, AlGaN etc.; these polar heterostructures allow a unique doping science: polarization-induced doping, which eliminates the need for impurity dopants with shallow enough activation energies as the conventional doping science dictates. The ULTRA EFRC is aiming to advance epitaxial growth and understanding of defect formation and doping control in AlN-based heterostructures, their electronic and thermal properties with an application focus on power electronics. High-quality AlN homoepitaxy by molecular beam epitaxy was recently enabled by an in-situ Al-assisted deoxidation method of AlN substrates, leading to both 2D hole gases and 2D electron gases with unprecedented properties. AlN and AlGaN are developed on cost effective sapphire substrate by metalorganic chemical vapor deposition. Structural, optical, electronic, dopants, and thermal properties are being examined by a suite of techniques: X-ray diffraction, transmission electron microscopy, spatial resolved cathodoluminescence, electron paramagnetic resonance, Hall effect measurements, transient thermoreflectance measurement and Raman thermography.

2-F-23: METASTABLE SLIDETRONIC SWITCHING IN BULK 1T-TAS$_2$

[EFRC-NPQC] Eran Maniv[1,2], Vishal Ravi[1,2], Shannon C. Haley[1, 2], Josue Rodriguez[1,2]; Sophie F. Weber[1,2], Jeffrey B. Neaton[1,2,3], James G. Analytis[1,2]
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The introduction of highly correlated electron physics in 2D like systems creates novel possibilities for phase engineering of new electronic states. The ability to control and manipulate these phases by application of external pressure, gate voltage, twist-angle and optical stimulation enables vast opportunities for modern applications and basic research. Electronic charge order reconstruction is a fascinating direction towards manipulation of exotic phases. One example is the ultra-fast nonvolatile switching between the insulating commensurate charge density wave (CDW) and the metallic phase of 1T-TaS$_2$. Recent theoretical and experimental work showed the connection of the resistance state and its band structure to the c-axis stacking sequence of the CDW, opening a new path for controlling the CDW phase through sliding of domains. In this work, we show for the first time that DC electrical pulses of the order of 1-10 KA/cm^2 can switch the resistance of micrometer Bulk TaS$_2$. Two components compose this nonvolatile resistance switching; the first is the known insulating to metallic metastable transition which doesn't depend on the current direction, while the second is a new directional coupled resistance switch formed by pulsing in various crystallographic directions. We connect this directional switching to the formation of various stacking configurations which opens a path for controlled slidetronics in vdW-based materials.

2-F-24: EMBEDDING FOR AB INITIO QUANTUM CHEMISTRY

[CCS – NGMD] Garnet Kin-Lic Chan, Tianyu Zhu, Zhi-Hao Cui
California Institute of Technology

Quantum embedding theories have emerged as an important class of methods in both quantum chemistry and materials science. In this poster, we present a series of conceptual and technical advances to enable efficient quantum embedding calculations in ab initio quantum chemical simulations of correlated electron systems. In the context of density matrix embedding, we extend the original theory to realistic condensed phase problems, as demonstrated across a variety of semiconducting and insulating materials. Within the framework of dynamical mean-field theory, we introduce the coupled-cluster Green's function approach as an impurity solver and demonstrate its accuracy in a variety of models. To capture long-range electron correlation in embedding theories, we also describe an all-electron G0W0 method with k-point sampling in a crystalline Gaussian basis. We showcase these theories in several challenging condensed phase chemistry problems, including for both ground-state and spectroscopic quantities.

2-F-25: ULTRAFAST NONLINEAR ELECTRON DYNAMICS IN CONDENSED MATTER FROM REAL-TIME TDDFT

[CMS – NPNEQ] Das Pemmaraju[1], Ming-Fu Lin[1], Alfredo A. Correa[2], Xavier Andrade[2], Aaron Lindenberg[1,3], Liang Tan[4], Tadashi Ogitsu[2]
[1]SLAC National Accelerator Laboratory; [2]Lawrence Livermore National Laboratory; [3]Stanford University; [4]Lawrence Berkeley National Laboratory

Velocity-gauge real-time TDDFT provides a convenient framework for accessing both linear and nonlinear optical response in solids across near-infrared to soft X-ray energy ranges. Of particular interest in ultrafast materials science is the description of nonlinear electron dynamics under strong laser fields. We recently used RT-TDDFT to explore the excitation of electrons in liquid water under strong IR fields to make direct contact with experimental efforts aimed at characterizing photo-ionization induced radiolysis [1]. We estimated the photo-ionization fraction in liquid water for experimentally relevant laser pulse parameters. Our simulations revealed a non-linear multi-step photo-ionization process under strong IR pumping in liquid water which is distinct from the response of ordered crystalline ice. In recent work we have also investigated band edge nonlinear optics under illumination and provided a protocol for simulating the AC stark shift in excitonic systems such as hexagonal BN with RT-TDDFT. In future we will extend our studies to magnetic systems and explore spin dynamics in layered anti-ferromagnets within the (Fe,Ni,Mn)PS_3 family as well as nonlinear response in spin-orbit coupled topological materials such as WTe_2.
[1] Ming-Fu Lin et. al., Imaging the solvated hydronium cation and hydroxyl radical in the ionized liquid water", under review.

2-F-26: ROBUST, NON-PERTURBATIVE INCLUSION OF SPIN-ORBIT EFFECTS INTO QMC

[CMS – CPSFM] Cody Melton[1], Raymond Clay[1], Luke Shulenburger[1], M. Chandler Bennett[2], Abdulgani Annaberdiyev[3], Guangming Wang[4], Lubos Mitas[4]
[1]Sandia National Laboratories; [2]Oak Ridge national Laboratory; [3]North Carolina State University

This poster highlights the development of a non-perturbative many-body treatment of spin-orbit coupling effects in Quantum Monte Carlo and QMCPACK. Spin-orbit effects are incorporated directly into the QMC Hamiltonian via a relativistic effective core potential (ECP). We generalize the trial wave function to be constructed from spinors and introduce a spin degree of freedom in the sampling for both variational and diffusion Monte Carlo methods. The implementation allows for both open and periodic boundary conditions, which allows spin-orbit effects to be included in both quantum chemistry and solid-state applications where relativistic effects may be competitive with electron correlation. Additionally, we build upon our previous work in developing high accuracy correlation consistent ECPs to include these spin-orbit terms. We apply this new methodology to generate new potentials for Pd, Ag, I, W, Ir, Au and Bi demonstrating their accuracy over traditional mean-field constructed ECPs. Together, these developments broaden the applicability of accurate QMC methods to heavy element materials.

G. SOLAR ENERGY (ROOM: *2AG*)

2-G-1: BIO-INSPIRED LIGAND LIMITS CHARGE RECOMBINATION WITH AN IRIDIUM PHOTOREDOX CATALYST

[EFRC – BioLEC] Hannah J. Sayre[1], Hunter H. Ripberger[1], Emmanuel Odella[2], Anna Zieleniewska[3], Daniel A. Heredia[2], Garry Rumbles[3], Gregory D. Scholes[1], Thomas A. Moore[2], Ana L. Moore[2], Robert R. Knowles[1]
[1]Princeton University; [2]Arizona State University; [3]National Renewable Energy Laboratory

Charge recombination upon photoinitiated electron transfer limits the quantum efficiency of photocatalyzed reactions. Inspired by proton-coupled electron transfer (PCET) in Photosystem II, a PCET-based ligand, benzimidazole phenol (BIP), was coordinated to an Ir(III) photocatalyst. The rate constant for charge recombination following photoinitiated electron transfer to methyl viologen dication was decreased by an order of magnitude compared with the control Ir(III) photocatalyst. The benefit of limiting charge recombination was demonstrated by a two-fold quantum yield increase in a photocatalyzed phthalimide ester reduction.

2-G-2: EXPANDING THE PURVIEW OF ORGANIC ADDITIVES IN SOLAR FUELS SYNTHESIS

[Hub – LiSA] Yungchieh Lai[1,2], Nicholas B. Watkins[1,2], Alonso Rosas-Hernández[1,2], Arnaud Thevenon[1,2], Gavin P. Heim[1,2], Lan Zhou[1,2], Yueshen Wu[1,2], Christopher Muzzillo[1,3], Andriy Zakutayev[1,3], Joel A. Haber[1,2], Jonas C. Peters[1,2], John M. Gregoire[1,2], Theodor Agapie[1,2]
[1]Liquid Sunlight Alliance; [2]California Institute of Technology; [3]National Renewable Energy Laboratory

Motivated by product selectivity modulation with organic additives on Cu or Ag electrodes, we explore broader uses of organic additives in solar fuel synthesis. We commence with binary Cu alloy catalysts where high throughput experiments reveal that different alloying elements and concentrations result in a broad range of partial current densities for many products with an important exception. The data reveal an unforeseen scaling relationship between the partial current densities of CH_4 and C_{2+} products. While organic additives have been shown to suppress CH_4 formation on Cu, our findings show the effect of the additives is quite profound for the entire family of bimetallic Cu alloys, where the N,N′-ethylene-phenanthrolinium dibromide additive disrupts the CH_4 - C_{2+} scaling relationship, opening a new window of opportunity for development of hybrid catalysts. Emboldened by this success we proceeded to evaluate use of organic additives as coatings for chalcogenide photocathodes. $CuGa_3Se_5$ with a 1.8 eV band gap is a promising absorber for solar photoreduction and has been demonstrated for H_2 evolution with a CdS coating. We find that under CO_2RR conditions the photocathode suffers from both Cd corrosion, which consequently compromises charge separation, and from poor selectivity toward CO_2RR. Coating the photocathode with N,N′-(1,4phenylene)bispyridinium salt lowers the corrosion of Cd at least 10-fold and increases the CO:H_2 product ratio more than 10-fold. This initial demonstration opens a host of opportunities for further development and understanding of how to co-optimize activity, selectivity, and durability in solar fuel photocathodes.

2-G-3: QUANTUM DOT-SENSITIZED PHOTOREDUCTION OF CO2 IN WATER WITH TURNOVER NUMBER >80,000

[EFRC – CBES] Francesca Arcudi, Luka Đorđević, Samuel I. Stupp, Emily A. Weiss
Northwestern University

Climate change and global energy demands motivate the search for sustainable transformations of carbon dioxide (CO_2) to storable liquid fuels. Photocatalysis is a pathway for direct conversion of CO_2 to CO, one step within light-powered reaction networks that could, if efficient enough, transform the solar energy conversion landscape. To date, the best performing photocatalytic CO_2 reduction systems operate in nonaqueous solvents, but technologically viable solar fuels networks will likely operate in water. Here we demonstrate catalytic photoreduction of CO_2 to CO in pure water at pH 6-7 with an unprecedented combination of performance parameters: turnover number >80,000, quantum yield >5%, and selectivity >99%, using $CuInS_2$ colloidal quantum dots (QDs) as photosensitizers and a Co-porphyrin catalyst. The performance of the QD-driven system greatly exceeds that of the benchmark aqueous system (926 turnovers with a quantum yield of 0.81% and selectivity of 82%), due primarily to: electrostatic attraction of the QD to the catalyst, which promotes fast multielectron delivery and co-localization of protons, CO_2, and catalyst at the source of photoelectrons, and termination of the QD's ligand shell with free amines, which capture CO_2 as carbamic acid that serves as a reservoir for CO_2, effectively increasing its solubility in water, and lowers the onset potential for catalytic CO_2 reduction by the Co-porphyrin. The breakthrough efficiency achieved in this work represents a non-incremental step in the realization of reaction networks for direct solar-to-fuel conversion.

2-G-4: PHOTOELECTROCHEMICAL REDUCTIVE N-METHYLATION WITH CO2 ENABLED BY A MOLECULAR CATALYST

[HUB – CHASE] Conor Rooney[1], Chungsuk Choi[1], Jeffrey E. Dick[2], Zahra Fakhraai[4], Alexandre Genoux[1], Patrick L. Holland[1], Paul A. Maggard[5], Scott McGuigan[5], Magnus Pauly[5], Hailiang Wang[1]
[1]Yale University; [2]University of North Carolina at Chapel Hill; [4]University of Pennsylvania; [5]North Carolina State University

The Center for Hybrid Approaches in Solar Energy to Liquid Fuels (CHASE) seeks to develop solar-energy-powered hybrid photoelectrodes competent of the reduction of CO_2, as a one-carbon building block, and N_2 for the sustainable production of liquid fuels. The photoelectrochemical reduction of CO_2 has been previously studied, but its integration with N_2 reduction has rarely been. In this poster, we present the first steps, enabled by hybrid electrodes developed by CHASE researchers, toward the integration of N_2 and CO_2 reductions to yield organonitrogen liquid fuels. We report the first electrochemical reductive N-methylation reaction with CO_2 and demonstrate its compatibility with amines, hydroxylamines, and hydrazine in aqueous media. Catalyzed by cobalt phthalocyanine molecules supported on carbon nanotubes, the N-methylation reaction is proposed to proceed via the chemical condensation of an electrophilic formaldehyde intermediate, formed from the four-electron reduction of CO_2, with nucleophilic nitrogen-containing reagents and subsequent reduction. By comparing various amines, CHASE research discovered that the nucleophilicity of the amine reactant is a descriptor for the C-N coupling efficacy. By using hydrazine as the nitrogen source, it is possible to produce methylhydrazine, which is a high energy density rocket fuel, from CO_2 reduction. Because hydrazine is a known product or intermediate of N_2 reduction with certain catalysts, this finding suggests a plausible approach to using N_2 as the nitrogen precursor for liquid fuels using electrons from sustainable energy sources. The importance of these advances to CHASE goals and the realization of liquid fuels from CO_2 and N_2 will be discussed.

2-G-5: 3D-D EXCITED STATES OF NI(III) COMPLEXES RELEVANT TO PHOTOREDOX CATALYSIS: SPECTROSCOPIC IDENTIFICATION AND MECHANISTIC IMPLICATIONS

[EFRC – BioLEC] Stephen I. Ting[1]; Sofia Garakyaraghi[1], Chelsea M. Taliaferro[2], Benjamin J. Shields[1], Gregory D. Scholes[1], Felix N. Castellano[2], Abigail G. Doyle[1]
[1]Princeton University; [2]North Carolina State University

Synthetic organic chemistry has seen major advances due to the merger of nickel and photoredox catalysis. A growing number of Ni-photoredox reactions are proposed to involve generation of excited nickel species, sometimes even in the absence of a photoredox catalyst. To gain insights about these excited states, two of our groups previously studied the photophysics of Ni($^{t\text{-Bu}}$bpy)(*o*-Tol)Cl, which is representative of proposed intermediates in many Ni-photoredox reactions. This complex was found to have a long-lived excited state (τ = 4 ns), which was computationally assigned as a metal-to-ligand charge transfer (MLCT) state. This work evaluates the computational assignment experimentally using a series of related complexes. Combined spectroscopic, organometallic and computational studies indicated that a MLCT state is generated initially but decays to a long-lived state that is ^{3}d-d in character. The ^{3}d-d state features a weak Ni–aryl bond, such that excited Ni(II) complexes can undergo Ni–aryl homolysis to generate aryl radicals and Ni(I), both of which are supported experimentally. Thus, photoinduced Ni–aryl homolysis offers a novel mechanism of initiating catalysis by Ni(I).

2-G-6: DEVELOPMENT OF AN ATR-IR SPECTROELECTROCHEMICAL CELL FOR THE CHARACTERIZATION OF MOLECULES ON SILICON PHOTOELECTRODE SURFACES

[HUB – CHASE] Samuel R. Bottum[1], James F. Cahoon[1], Javier J. Concepcion[2], Carrie L. Donley[1], David C. Grills[2], Qi Han[1], Matthew R. Lockett[1], Kristina P. Martinez[2], André D. Orr[1], Dmitry E. Polyansky[2]
[1]University of North Carolina at Chapel Hill; [2]Brookhaven National Laboratory

The mission of the Center for Hybrid Approaches in Solar Energy to Liquid Fuels (CHASE) is to develop molecule/material hybrid photoelectrodes for cooperative sunlight-driven generation of liquid fuels from CO_2, N_2, and H_2O. Specifically, we are pairing light-absorbing semiconductor materials with surface-attached, fuel-producing molecular catalysts that will operate in tailored microenvironments using a multi-catalyst cascade approach to access liquid fuels. Since CHASE is using visible light-absorbing semiconductor substrates (e.g., Si), mid-IR spectroscopy will be an important technique for characterizing the functionalized surfaces, determining catalytic mechanisms, and monitoring the progress of catalysis by detecting intermediates/products. Transmission IR spectroscopy of a catalyst monolayer will result in extremely weak signals. CHASE is therefore using multiple reflection Attenuated Total Reflection (ATR) IR spectroscopy of catalysts directly attached to a Si ATR crystal to achieve improved IR signals. This has involved the design and fabrication of a new ATR-IR spectroelectrochemical (SEC) cell in which a functionalized, surface-doped Si ATR crystal is the working (photo)electrode. Here, we present our recent work on (i) the development of electrochemically reversible probe molecules containing strong IR reporter groups (e.g., M–CO) and surface anchoring groups, (ii) the diffusional surface *n*- and *p*-doping of Si ATR crystals, (iii) the design and fabrication of a new ATR-IR-SEC cell, and (iv) ATR-IR-SEC spectra of surface-bound molecules under applied bias.

2-G-7: ENGINEERING A NON-NATURAL PHOTOENZYME FOR IMPROVED PHOTON EFFICIENCY

[EFRC – BioLEC] Bryce T. Nicholls[1], Daniel G. Oblinsky[2], Sarah I. Kurtoic[2], Daria Grosheva[2], Yuxuan Ye[1], Gregory D. Scholes[2], Todd K. Hyster[1]

[1]Cornell University; [2]Princeton University

Photoenzymes are biological catalysts that use light to convert starting materials to products. These catalysts require photon absorption for each catalyst turnover, making quantum efficiency an important optimization parameter. Flavin-dependent 'ene'-reductases (EREDs) display latent photoenzymatic activity for synthetically valuable hydroalkylations; however, protein engineering has not been used to optimize this non-natural function. Here, we describe a protein engineering platform for the high throughput optimization of photoenzymes. A single round of engineering results in improved catalytic function toward the synthesis of γ, δ, ε-lactams, and acyclic amides. Mechanistic studies indicate that key mutations can alter the enzyme's excited state dynamics, enhance its photon efficiency, and ultimately increase catalyst performance. Transient absorption spectroscopy reveals that engineered variants display dramatically decreased radical lifetimes – indicating an evolution toward a concerted mechanism. Overall, this platform enables the development and optimization of photoenzymes for tailored applications in chemical synthesis.

2-G-8: ZNTE-BASED PHOTOCATHODES

[Hub – LiSA] Andriy Zakutayev[1,2], Sage Bauers[1,2], Theodore Culman[1,2], Guiji Liu[1,3], Guosong Zeng[1,3], Chanyeon Kim[1,4], Alexis Bell[1,3], Martin Siron[1,4], Oxana Andriuc[1,4], Hanzhe Liu[1,5], Lily Shiau[1,5], Kevin Kan[1,5], Dan Guevarra[1,5], Lan Zhou[1,5], Scott Cushing[1,5], Francesca Toma[1,3], Kristin Persson[1,3,4], Joel Haber[1,5], John Gregoire[1,5], Harry Atwater[1,5]

[1]Liquid Sunlight Alliance; [2]National Renewable Energy Laboratory; [3]Lawrence Berkeley National Laboratory; [4]University of California, Berkeley; [5]California Institute of Technology

Generating liquid solar fuels from sunlight, carbon dioxide (CO_2) and water (H_2O) is a promising basic research direction to transition away from fossil fuels towards a more sustainable planetary carbon cycle. Co-designing new photoactive materials and stable catalysts is particularly important for the CO_2 reduction reaction process at the photocathode. The Liquid Sunlight Alliance (LiSA) Solar Fuels Hub is developing high-performance photocathodes for CO_2 reduction based on wide band gap II-VI semiconductors such as ZnTe and related compounds, using several complementary experimental and computational methods. The ZnTe and related materials with zincblende-derived crystal structure (e.g., ZnSe, $ZnGa_2Se_4$, $ZnGa_2Te_4$) are theoretically predicted to be stable under operating conditions and to have band edge positions suitable for this application. Our surface adsorption calculation results on ZnTe are consistent with previously published experimental data. Experimental measurements are performed on a broad range of ZnTe samples tuned for practical applications or fundamental investigations and synthesized by various methods: electrodeposition with and without a Cu-Sn-Fe-based electrocatalyst coatings, co-sputtering with ZnSe and Ga_2Te_3, and molecular beam epitaxy with Cu and N doping. Measured optoelectronic and electrocatalytic properties are compared to transient spectroscopy measurements on ZnTe single crystals. Overall, these ZnTe results illustrate a co-design approach to photocathode design for CO_2 reduction.

2-G-9: IMPLEMENTATION OF MANY-BODY PERTURBATION THEORY, FIRST PRINCIPLES MOLECULAR DYNAMICS AND ADVANCED SAMPLING METHODS ON HETEROGENEOUS ARCHITECTURES

[CMS – MICCoM] W. Yu[1], M. Puligheddu[1], P. Zubieta[2], F. Gygi[3], J. J. de Pablo[1,2], J. K. Whitmer[4], G. Galli[1,2], M. Govoni[1,2]
[1]Argonne National Laboratory; [2]University of Chicago; [3]University of California Davis; [4]University of Notre Dame

The development of efficient and scalable simulation software is facing the challenge of a rapidly changing high-performance computing landscape. Current trends show that efficient implementations on heterogeneous architectures (e.g., CPU+GPU) will be required to take full advantage of current pre-exascale and announced exascale machines, where GPU accelerators deliver the main contribution to the computational performance. We discuss the porting to GPUs of codes for many-body perturbation theory (WEST), first-principles molecular dynamics (Qbox), and advanced sampling simulations (SSAGES), carried out within the MICCoM center. We use optimized GPU libraries, new algorithms, and strategies that minimize data transfer operations. We present a series of performance benchmarks that demonstrate good strong and weak scaling of WEST on Summit, and the efficient use of pySAGES coupled with the HOOMD-blue library for biased classical molecular dynamics on GPUs. We showcase the capability of the newly developed GPU codes, demonstrating large-scale GW full frequency calculations of realistic nanostructures and interfaces with up to ten thousand electrons, and biased molecular dynamics simulations with up to 1,000,000 Lennard-Jones.

2-G-10: ULTRA-HIGH EMISSION QUANTUM YIELD NANOPARTICLES FOR PHOTONIC THERMODYNAMIC CYCLES

[EFRC – PTL] Dipti Jasrasaria[1], Benjamin L. Cotts[2], John P. Philbin[3], Ethan Curling[1], Burak Guzelturk[2], David A. Hanifi[2], Brent K. Koscher[1], A. Paul Alivisatos[1], Alberto Salleo[2], Prineha Narang[3], Aaron M. Lindenberg[2], Eran Rabani[1]
[1]University of California, Berkeley; [2]Stanford University; [3]Harvard University

Semiconductor nanocrystals with ultra-high emission quantum yields approaching unity can enable new thermodynamic systems with use in applications ranging from radiative cooling to optical refrigeration to photonic engines. Here, we present our center's efforts to combine expertise in synthesis, spectroscopy, and theory to develop new nanocrystal systems that operate near their thermodynamic limits. Validation and optimization of near-unity quantum yield nanostructures necessitate high-sensitivity metrology. To this end, our center has developed photothermal threshold quantum yield (PTQY), a measurement technique that can detect luminescence efficiency with accuracies of 0.1%. We present our latest results on lead-halide perovskite quantum dots and how thiocyanate passivation can push the emission quantum yield towards unity. We further investigate the non-radiative pathways in near-unity quantum yield core-shell and lead-halide perovskite nanocrystals. Using ultrafast electron diffraction (UED) measurements, we probe the dynamic structural response of these nanocrystals to optical excitation. The structural changes associated with nonradiative processes, such as heating-induced disorder and polaron formation is reconciled with new theoretical models of the exciton-phonon coupling. Related theoretical studies on the effect of the nanocrystal surface identify a strong contribution to exciton-phonon coupling in smaller nanocrystals. This modeling has informed ongoing UED experiments of core-shell nanostructures as well as anisotropic nanoplatelets. Finally, close collaboration between theory and experiment has led to the rational design of nanocuboids that display new phenomena, such as room-temperature superfluorescence. This collective phenomenon had previously only been demonstrated in

nanomaterials at temperatures below 10K. The robust observation of superfluorescence in these nanocuboids paves the way for boosting the emission quantum yield based on cooperative emission.

2-G-11: CONTROLLING OF CHARGE TRANSPORT AND RECOMBINATION IN PEROVSKITES BY TAILORING DEFECTS AND DOPING

[EFRC – CHOISE] Zhenyi Ni[1], Shangshang Chen[1], Yehao Deng[1], Yuze Lin[1], Xun Xiao[1], Zhenhua Yu[1], Ye Liu[1], Fei Zhang[2], Haipeng Lu[2], Xihan Chen[2], Steven P. Harvey[2], Ji Hao[2], Jinhui Tong[2], Bryon Larson[2], Sean Dunfield[2], Chunxiao Xiao[2], Axel F. Palmstrom[2], Matthew C. Beard[2], Joseph Berry[2], Jeff Blackburn[2], Canglang Yao[3], Yanfa Yan[3], Kai Zhu[2], Jinsong Huang[1]

[1]University of North Carolina, Chapel Hill; [2]National Renewable Energy Lab; [3]University of Toledo

Many unusual charge transport, recombination, thermal relaxation, and electromechanical behaviors have been observed for metal halide perovskites, yet the origins of these phenomena remain unclear. We elucidated the structure/function properties that govern how charges interact with the defects, lattice to induce unusual optoelectronic properties by: 1) identifying defects chemistry, distribution, and their impacts on material and device efficiency and stability; 2) understanding the doping and de-doping of lead and tin-lead based perovskites with different material process and treatment; 3) understanding how the big cations and defects of different dimensionality impact the octahedral distortion and related carrier transport and recombination process in perovskites of different dimensionality. We have resolved the spatial and energy distribution of deep charge trapping point defects in real device geometry for the first time, predicting a large density of detrimental defects at both interfaces of polycrystalline films made by most existing method. Removing of these defects layer by physical and chemical approaches have been designed. Lead perovskites showed a self-dedoping process, facilitated by the ion migration, while tin based perovskites show complicated doping and de-doping phenomenon by their interaction with chemical species such as oxygen and impurity metal ions. These understandings provide us guidance in designing material processes and ink formulations that can precisely tailor the defects and doping at different locations of polycrystalline films and perovskites with different compositions, which enables record performance solar cells.

2-G-12: *IN SITU* SURFACE ENHANCED RAMAN AND VIBRATIONAL SFG SPECTROSCOPIC PROBES OF MOLECULAR CATALYSTS ON SEMICONDUCTOR PHOTOELECTRODES

[HUB – CHASE] Zihao Xu[1], Dhritiman Bhattacharyya[1], Fengyi Zhao[1], Sa Suo[1], Isaac Tangen[1], Samuel R. Bottum[2], Taylor S. Teitsworth[2], Jin-Sung Park[2], John Bost[2], Langqiu Xiao[3], Colton Sheehan[3], Hala Atallah[4], Kristina P. Martinez[5], James F. Cahoon[2], Yosuke Kanai[2], Thomas E. Mallouk[3], Felix N. Castellano[4], Javier J. Concepcion[5], Tianquan Lian[1]

[1]Emory University; [2]University of North Carolina at Chapel Hill; [3]University of Pennsylvania; [4]North Carolina State University; [5]Brookhaven National Laboratory

Hybrid photoelectrodes composed of semiconductor light absorbers and attached molecular catalysts are a promising new approach for efficient and selective generation of solar fuels. To provide mechanistic insights into their efficiency and stability limiting factors, CHASE has developed *in situ* surface sensitive and/or selective molecular spectroscopic techniques, including Vibrational Sum Frequency Generation (VSFG) and Surface Enhanced Raman (SERS) Spectroscopy to probe surface-bound molecular catalysts and their microenvironment under photo/electrochemical conditions. The VSFG spectroscopy is employed to study Rhenium CO_2 reduction catalysts with carboxylate or silatrane anchoring groups on the surface of TiO_2 single crystals and ALD TiO_2 protected p-Si electrodes. The VSFG spectra recorded at different polarization combinations will be compared with ongoing theoretical simulations to determine the catalyst surface binding geometries. SERS is employed to study Ag-decorated nanoporous black Si photoelectrodes for CO_2 reduction, probing reactive intermediates and surface bound CO and other products. For probe molecules (4-mercaptobenzonitrile, 4-MBN) with selective binding to Ag, their SERS spectra show pronounced CN stretching frequency shift as a function of the applied potential, from which the local electric field strength can be determined with the help of computational modelling. CHASE is also developing shell-isolated nanoparticle enhanced Raman spectroscopy (SHINERS) as a general *in situ* vibrational spectroscopic probe of planar and low surface area photoelectrodes (including single crystals). Finally, in ongoing work, these techniques are coupled with pulsed exciton of the photoelectrodes to allow an *in situ* time-dependent probe of the transformations of molecular catalysts and their microenvironments driven by photogenerated carriers.

2-G-13: THERMODYNAMIC PHOTONIC ENGINES

[EFRC – PTL] Bo Zhao[1], Zunaid Omair[1,2], Yubin Park[1], Eli Yablonovitch[2], Shanhui Fan[1]
[1]Stanford University; [2]University of California, Berkeley

Photons represent one of the most important heat carriers that can be utilized as working fluid in heat engines. When an emitting body is not in thermal equilibrium, the photons in the body can possess a nonzero chemical potential that can be harnessed. Our center has proposed and demonstrated several new types of photonic heat engines that can harvest nonzero photon chemical potentials. They include luminescent concentrators, thermophotovoltaics, thermophotonics, negative-illuminated power harvester, and radiatively cooled surfaces. Compared to traditional photonic energy harvesters like solar cells, these systems enable combined heat-and-power applications with high efficiency and high power density. This poster describes our work developing photonic thermodynamic cycles - and how we achieve the requisite photon management in these systems using high quantum yield semiconductors, nonreciprocal optical components, and high-reflectivity mirrors. We demonstrate the development of quantum dots with extremely high quantum efficiencies, the design and characterization of nonreciprocal semitransparent optical components, and perfect mirrors that can increase efficiencies of thermophotovoltaic systems. We also describe the implications of photonic thermodynamic cycles for power electronic applications. In particular, we demonstrate a new type of photon-based DC voltage transformer that can efficiently convert DC voltages without producing any electromagnetic interference.

2-G-14: ELECTRON-PHONON COUPLING AND CARRIER MOBILITY IN LEAD-FREE HALIDE PEROVSKITES

[CSM – EPW] Joshua Leveillee[1], George Volonakis[2], Feliciano Giustino[1]
[1]The University of Texas at Austin; [2]University of Rennes

Lead-free halide double perovskites have attracted considerable interest as a complement to lead-based perovskites in tandem solar cells and broadband light emitting devices. One of the most popular lead-free double perovskites, Cs2AgBiBr6, exhibits promising optical properties, but its electrical transport properties are comparatively poor. Recent measurements indicate carrier mobilities that are closer to organics (1-10 cm2/Vs) than inorganic semiconductors and hybrid lead-based perovskites. The origin of such low mobilities is currently unclear and calls for an atomic-scale investigation. In this poster we report state-of-the-art *ab initio* calculations of the phonon-limited mobility of charge carriers in Cs2AgBiBr6 using the ab initio Boltzmann transport equation. Our parameter-free calculations yield room-temperature electron and hole mobilities of 17/14 cm2/Vs, respectively, in line with experiments. We show that the root cause for the lower mobilities of this compound resides in the low lattice vibrational frequencies and the relatively heavier carrier effective masses, and that the electron-phonon coupling is dominated by Fröhlich polar phonon scattering. Based on our findings, we argue that, to increase the carrier mobility of lead-free halide perovskites, it will be necessary to lower the carrier effective masses by alloying Bi with Sb and Br with I, as demonstrated in recent experiments.

2-G-15: HIGHLY CORRELATED ELECTRONIC STRUCTURE METHODS FOR EXCITED STATES AND SPECTROSCOPY

[CCS – SPEC] Karol Kowalski[1], Edoardo Aprà[1], Wibe de Jong[2], Niranjan Govind[1], Sriram Krishnamoorthy[1], Xiaosong Li[3], John J. Rehr[3], Chao Yang[2]
[1]Pacific Northwest National Laboratory (lead institution); [2]Lawrence Berkeley National Laboratory; [3]University of Washington

We have developed new approaches for describing the valence- and core-level excited states of complex molecular systems and their local environment based on accurate and scalable electronic structure methods for highly correlated systems. These methods have been implemented in scalable, open-source libraries that utilize the unique computational resources at DOE's Leadership Computer Facilities.

The Green's Function Coupled Cluster library (https://github.com/spec-org/gfcc) consists of iterative formulations for the cost-effective inclusion of triple excitations. These new approximations can be categorized as GFCC-i(n, m) methods, where the excitation level of the inner auxiliary operators (m) used to describe the ionization potentials and electron affinities in the (N−1) and (N+1) particle spaces is higher than the excitation level (n) used to correlate the ground-state CC wave function for the N-electron system. Rigourous criteria, known as the "n+1" conditions, ensure the size-extensivity of the corresponding GF. The GFCC-i(2,3) formalism was found to exhibit better agreement with experimental results, particularly in terms of providing higher resolution of satellite peaks compared to the standard GFCC approximation with singles and doubles. In addition, Model-Order-Reduction (MOR) techniques were implemented in the GFCC framework. For a frequency regime of interest, instead of solving the GFCC linear equations of full dimension for every single frequency point, an efficiently solvable linear system model of a reduced dimension is built upon projecting the original GFCC linear system onto a subspace. From this a reasonable approximation to the full dimensional GFCC linear equations in both interpolative and extrapolative spectral regions was obtained.

ACRONYMS AND IDS

ENERGY FRONTIER RESEARCH CENTERS (EFRC)

[EFRC – 3DFeM] Center for 3D Ferroelectric Microelectronics
Susan Trolier-McKinstry, The Pennsylvania State University
Class: 2020 – 2024

[EFRC – AMEWS] Advanced Materials for Energy-Water Systems
Seth Darling, Argonne National Laboratory
Class: 2018 – 2022

[EFRC – BEES] Breakthrough Electrolytes for Energy Storage
Robert Savinell, Case Western Reserve University
Class: 2018 – 2022

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

[EFRC – CABES] Center for Alkaline-Based Energy Solutions
Héctor Abruña, Cornell University
Class: 2018 – 2022

[EFRC – CAST] Center for Actinide Science and Technology
Thomas Albrecht- Schoenzart, Florida State University
Class: 2016 – 2022

[EFRC – CATS] Center for the Advancement of Topological Semimetals
Robert McQueeney, Ames Laboratory
Class: 2018 – 2022

[EFRC – CBES] Center for Bio-Inspired Energy Science
Samuel Stupp, Northwestern University
Class: 2009 – 2022

[EFRC – CCEI] Catalysis Center for Energy Innovation
Dionisios Vlachos, University of Delaware
Class: 2009 – 2022

[EFRC – CENT] Center for Enhanced Nanofluidic Transport
Michael Strano, Massachusetts Institute of Technology
Class: 2018 – 2022

[EFRC – CHOISE] Center for Hybrid Organic Inorganic Semiconductors for Energy
Matthew Beard, National Renewable Energy Laboratory
Class: 2018 – 2022

[EFRC – CHWM] Center for Hierarchical Waste Form Materials
Hans-Conrad zur Loye, University of South Carolina
Class: 2016 – 2024

[EFRC – CLSF] Center for Lignocellulose Structure and Formation
Daniel Cosgrove, Pennsylvania State University
Class: 2009 – 2022

[EFRC – CMC-UF] Center for Mechanistic Control of Water-Hydrocarbon-Rock Interactions in Unconventional and Tight Oil Formations
Anthony Kovscek, Stanford University
Class: 2018 – 2022

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

[EFRC – CMQT] Center for Molecular Quantum Transduction
Michael Wasielewski, Northwestern University
Class: 2020 – 2024

[EFRC – CPI] Center for Plastics Innovation
LaShanda Korley, University of Delaware
Class: 2020 – 2024

[EFRC – CSSAS] Center for the Science of Synthesis Across Scales
François Baneyx, University of Washington
Class: 2018 – 2022

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

[EFRC – FUTURE] Fundamental Understanding of Transport Under Reactor Extremes
Blas Uberuaga, Los Alamos National Laboratory
Class: 2018 – 2022

[EFRC – GENESIS] A Next Generation Synthesis Center
John Parise, Stony Brook University
Class: 2018 – 2022

[EFRC – ICDC] Inorganometallic Catalyst Design Center
Laura Gagliardi, University of Minnesota
Class: 2014 – 2022

[EFRC – iCOUP] Institute for Cooperative Upcycling of Plastics
Aaron Sadow, Ames Laboratory
Class: 2020 – 2024

[EFRC – IDREAM] Interfacial Dynamics in Radioactive Environments and Materials
Carolyn Pearce, Pacific Northwest National Laboratory
Class: 2016 – 2024

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

[EFRC – IQM] Institute for Quantum Matter
Collin Broholm, Johns Hopkins University
Class: 2018 – 2022

[EFRC – m2M/t] Center for Mesoscale Transport Properties
Esther Takeuchi, Stony Brook University
Class: 2014 – 2022

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

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

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

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

[EFRC – NPQC] Center for Novel Pathways to Quantum Coherence in Materials
Joel Moore, Lawrence Berkeley National Laboratory
Class: 2018 – 2022

[EFRC – Pro-QM] Programmable Quantum Materials
Dmitri Basov, Columbia University
Class: 2018 – 2022

[EFRC – PTL] Photonics at Thermodynamic Limits
Jennifer Dionne, Stanford University
Class: 2018 – 2022

[EFRC – Q-MEEN-C] Quantum Materials for Energy Efficient Neuromorphic Computing
Ivan Schuller, University of California, San Diego
Class: 2018 – 2022

[EFRC – QSQM] Quantum Sensing and Quantum Materials
Peter Abbamonte, University of Illinois, Urbana-Champaign
Class: 2020 – 2024

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

[EFRC – TETI] Center for Thermal Energy Transport under Irradiation
David Hurley, Idaho National Laboratory
Class: 2018 – 2022

[EFRC – ULTRA] Ultra Materials for a Resilient, Smart Electricity Grid
Robert Nemanich, Arizona State University
Class: 2020 – 2024

[EFRC – UNCAGE-ME] Center for Understanding and Control of Acid Gas-induced Evolution of Materials for Energy
Ryan Lively, Georgia Institute of Technology
Class: 2014 – 2022

[EFRC – WastePD] Center for Performance and Design of Nuclear Waste Forms and Containers
Gerald Frankel, Ohio State University
Class: 2016 – 2022

ENERGY INNOVATION HUBS (HUB)

[Hub – CHASE] Center for Hybrid Approaches in Solar Energy to Liquid Fuels
Jerry Meyer, University of North Carolina at Chapel Hill
Started: 2020

[Hub – JCESR] Joint Center for Energy Storage Research
George Crabtree, Argonne National Laboratory
Started: 2013

[Hub – LiSA] Liquid Sunlight Alliance
Harry Atwater, California Institute of Technology
Started: 2020

COMPUTATIONAL MATERIALS SCIENCES (CMS)

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

[CMS – COMMS] Computational Mesoscale Science and Open Software for Quantum Materials
Long-Qing Chen, Pennsylvania State University
Started: 2019

[CMS – COMSCOPE] Center for Computational Material Spectroscopy and Design
Gabriel Kotliar, Brookhaven National Laboratory
Started: 2015

[CMS – CPSFM] Center for Predictive Simulation of Functional Materials
Paul Kent, Oak Ridge National Laboratory
Started: 2016

[CMS – EPW] Toward Exascale Computing of Electron-Phonon Couplings for Finite-Temperature Materials Design
Feliciano Giustino, University of Texas, Austin
Started: 2019

[CMS – MICCoM] Midwest Integrated Center for Computational Materials
Giulia Galli, Argonne National Laboratory
Started: 2015

[CMS – NPNEQ] Center for Non-Perturbative Studies of Functional Materials under Non-Equilibrium Conditions
Tadashi Ogitsu, Lawrence Livermore National Laboratory
Started: 2019

[CMS – QMC-HAMM] From Accurate Correlated Quantum Simulations to Mesoscopic Scales
David Ceperley, University of Illinois, Urbana-Champaign
Started: 2019

COMPUTATIONAL CHEMICAL SCIENCES (CCS)

[CCS – BEAST] Beyond-DFT Electrochemistry with Accelerated and Solvated Techniques
Ravishankar Sundararaman, Rensselaer Polytechnic Institute
Started: 2021

[CCS – CSI] Chemistry in Solution and at Interfaces
Roberto Car, Princeton University
Started: 2018

[CCS – ECC] Exascale Catalytic Chemistry Project
Judi Zádor, Sandia National Laboratory
Started: 2017

[CCS – ExaQC] Novel Toolkit for Harnessing the Power of Exascale Computing for Catalyst Design
Anna Krylov, University of Southern California
Started: 2021

[CCS – FLOSIC] Fermi-Lowdin Orbital Self-Interaction Correction Center
Koblar Alan Jackson, Central Michigan University
Started: 2017

[CCS – HetCat] Exascale Software for Heterogeneous and Interfacial Catalysis
Mark Gordon, Ames Laboratory
Started: 2018

[CCS – NEREST] Numerically-Exact Relativistic Many-Body Electronic Structure of Heavy Elements
Edward Valeev, Virginia Tech
Started: 2021

[CCS – NGMD] Ab initio Molecular Dynamics Beyond Density Functional Theory
Thomas Miller, California Institute of Technology
Started: 2018

[CCS – NMGC] Nanoporous Materials Genome Center
J. Ilja Siepmann, University of Minnesota
Started: 2017

[CCS – PsiXC] From Wave Functions to Exchange Correlation for Large-Scale Electronic Structure
Paul Zimmerman, University of Michigan
Started: 2021

[CCS – QuestC] Hierarchical Scalable Green's Function Modeling of Chemistry at Interfaces
Mark van Schilfgaarde, National Renewable Energy Laboratory
Started: 2021

[CCS – SPARC-X] SPARC: Simulation Package for Ab-initio Real-Space Calculations
Panish Suryanarayana, Georgia Tech
Started: 2018

[CCS – SPEC] Scalable Predictive Methods for Excitations and Correlated Penomena
Sotiris Xantheas, Pacific Northwest National Laboratory
Started: 2017

U.S. NATIONAL LABORATORIES

ANL	Argonne National Laboratory
BNL	Brookhaven National Laboratory
LBNL	Lawrence Berkeley National Laboratory
LLNL	Lawrence Livermore National Laboratory
LANL	Los Alamos National Laboratory
NETL	National Energy Technology Laboratory
NHMFL	National High Magnetic Field Laboratory
NIST	National Institute of Standards and Technology
NREL	National Renewable Energy Laboratory
ORNL	Oak Ridge National Laboratory
PNNL	Pacific Northwest National Laboratory
SLAC	SLAC National Accelerator Laboratory
SNL	Sandia National Laboratories
SRNL	Savannah River National Laboratory