



7th Annual
RESEARCH SYMPOSIUM

POSTER SESSION

Wednesday, April 24, 2024

9:00-11:45 a.m.

216 McKenna Hall

**THANK YOU TO ALL POSTER PRESENTERS FOR
SHARING THEIR RESEARCH IN
SUSTAINABLE ENERGY!**

Presentation Criteria

- Research purpose is clearly stated.
- Rationale/justification for the study is well explained.
- Methods used are clearly described and appropriate to address the research question/aim.
- Figures/tables used to present data are clear and appropriate.
- Analysis is well explained and appropriately applied.
- Presenter adequately addresses research problem/question.
- Conclusion is sufficiently supported by the results.
- Presenter summarized study clearly and answered questions well.
- Organization of information is aesthetically effective.
- Flow of information is logical and facilitates understanding.



Seventh Annual Research Symposium

Poster Session Schedule

April 24, 2024 | 9:00-11:45 a.m. | 216 McKenna Hall

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12	Matthew Egan	Promoting Sustainable Development in Northern Uganda: Empowering Households through Biogas Systems for Health, Socio-economic Empowerment, and Environmental Conservation	Corey Angst MCOB
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14	Zoë C. Emory	The Impact of Node Structure on Ionizing Radiation Stability of Thorium-Terephthalate Coordination Polymers	Peter C. Burns CEEES
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16	Daniel Kim	Exploring Chain Length and OH-Spacing Effects of Choline-Chloride Based Alkanediol Deep Eutectic Solvents Via Classical Molecular Dynamics	Edward Maginn CBE
17	Hoon Lee	Stochastic Modeling of Electron Scattering in Liquid Water	Ryan McClarren AME

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24	Agboola Suleiman	Iptycene-based Polybenzoxazole Membranes for High-temperature Hydrogen Separations	Ruilan Guo CBE
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AME	Aerospace and Mechanical Engineering
CBE	Chemical and Biomolecular Engineering
CEEES	Civil and Environmental Engineering and Earth Sciences
CHEM	Chemistry and Biochemistry
MCOB	Mendoza College of Business
RAD LAB	Notre Dame Radiation Laboratory

From Molecular Fragments to Novel High-performing Fluids: The Discovery of Green Refrigerants

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Advisor:

Edward J. Maginn, Keough-Hesburgh Professor, Department of Chemical and Biomolecular Engineering

Abstract

The Kigali Agreement of 2016 requires that environmentally harmful hydrofluorocarbons (HFCs), which are predominantly used as refrigerants but cause global warming, be phased out. The phase-out of current refrigerant compounds requires the design of green alternatives. Previous works in green refrigerant discovery have relied mainly on database screening in which it was reported that options for pure-component green refrigerants were very limited. This work presents a novel and rigorous approach to the discovery of new materials applied to refrigerant discovery. We developed a computational molecule generation tool written in Python called FineSMILES. FineSMILES collects packets of molecular fragments made up of pre-selected elements based on an understanding of the problem and literature. These packets of molecular fragments are screened using structural and chemical constraints to identify packets that could be assembled into chemically feasible molecules. FineSMILES assembles these packets into complete molecules with outputs as SMILES strings. Application of the FineSMILES code generated hundreds of thousands of molecules, of which more than fifty percent are new molecules that are not present in the PubChem database of compounds used in previous refrigerant discovery projects. A key implication is that a new world of chemical compounds not previously explored for use as green refrigerants has been discovered. We then applied a simple and novel approach that integrates group contribution models and Sigma profiles with Gaussian process regression models for accurate and reliable property prediction. The predicted properties were then used to screen the refrigerant molecules for technical, environmental, and safety performance. Based on a combined consideration of predicted thermophysical, environmental, and safety properties, tens of molecules were identified as high-potential green refrigerants, with several of them not previously reported in the open literature. Future work includes further in-depth screening of the identified molecules using molecular simulations and quantum mechanical calculations.

Computational Comparison of Zeolite and Polyoxometalate Hosts For Ni-catalyzed Ethylene Oligomerization

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Advisor:

William F. Schneider, Dorini Family Chair in Energy Studies and Department Chair, Department of Chemical Engineering

Abstract

The United States' abundant shale gas reserves present a transformative opportunity in the energy sector, particularly with the rise of shale gas as a more environmentally sustainable alternative to crude oil. Shale gas is rich in ethane, which can be used as a feedstock source to produce ethylene. In turn, ethylene can be converted into longer-chain hydrocarbons through oligomerization reactions. Catalysts are utilized to selectively transform ethylene sourced from shale gas into longer-chain hydrocarbons, which can then be utilized as raw materials for manufacturing transportation fuels. The development of efficient and selective catalysts for oligomerization of ethylene is vital as it facilitates the production of desired outputs while minimizing the generation of unwanted by-products. Current data indicates that homogeneous based catalysts commonly used in the industry for oligomerization are not environmentally sustainable and necessitate energy-intensive separation techniques for catalyst retrieval. Hence, there is a need to investigate alternative processes and innovative catalysts that are both environmentally friendly and cost-effective, while also exhibiting high selectivity for the desired end products.

Recent investigations have unveiled Ni-substituted polyoxometalate (POM) as a promising candidate for the oligomerization process. This catalyst shows promises due to its distinctive characteristics, such as adjustable acidity, redox capabilities, resistance to oxidative breakdown, and excellent thermal stability, all of which are critical in the catalytic conversion process. However, the design space for such catalysts is inherently complex, incorporating a myriad of factors that influence their performance. Therefore, theoretical tools offer invaluable insights into elucidating the complex interplay of structural and chemical properties governing catalytic behavior. In the present work, we use density functional theory as a tool to elucidate the oligomerization mechanism over Ni POMs as a means to rationally design these catalysts, improving their rate, durability, and selectivity for the intended conversion process. We compare our results to those obtained for Ni-based zeolites, which are better understood and serve as a platform to compare and contrast the Ni-based POM with. We compared the structures and coordination environment of Ni in both catalysts, as well as predicted reaction energies, electronic properties, and selectivity. Results show there exist different affinity of Ni in both frameworks with Ni having more affinity for POM. We use ethylene as a probe molecule to study and analyze their adsorption energies. Moreover, the Ni environment in both frameworks shows some similarity as they both are square planar. Ultimately, understanding the difference between Ni-hosted in zeolite and polyoxometalate will provide a direction on how to approach the mechanism of the catalytic activity for ethylene oligomerization.

Effect of ZrO₂ Surface Modification with Polyphenols on Radiolysis

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Advisor:

Jay A. LaVerne, Professor, Radiation laboratory and Department of Physics and Astronomy

Abstract

Zirconium and its alloys play a crucial role in nuclear industries, serving as fuel cladding and guide tubes. These alloys are extensively utilized due to their remarkable ability to endure harsh reactor conditions over extended periods, owing to their corrosion-resistant and radiation-tolerant properties. Despite their exceptional characteristics, the radiolysis of water adsorbed on zirconium oxide (ZrO₂) leads to a higher production of molecular hydrogen (H₂) compared to bulk water. This excessive H₂ generation presents a formidable challenge in the management of nuclear reactors and waste storage facilities. Addressing this issue requires periodic removal of H₂s to mitigate its potential consequences. Failure to address this concern could result in significant challenges for the nuclear industry. To address the problem effectively, it's crucial to delve into the underlying chemistry and explore strategies for managing H₂ production. Since H₂ production occurs at oxide surfaces, it becomes crucial to understand the radiation chemistry at these surfaces.

Surface modification with organic molecules, forming complexes with zirconium ions, emerges as a potential strategy for managing H₂ production. Polyphenol ligands, known for their diverse bonding capabilities, including hydrogen bonding and coordination, are present promising candidates. In this work, the surface of ZrO₂ was modified with various aromatic polyphenols to change the surface chemistry induced by radiolysis. Among the polyphenols, catechol (1,2-dihydroxybenzene) stands out for its ability to form coordination complexes with various metal ions including zirconium. This study explores how the γ -radiolysis of catechol and its substituents (with methyl, hydroxyl, and carboxylic groups) adsorbed on ZrO₂ nanoparticles decreases H₂ production. The mechanism of H₂ suppression probably involves the displacement of surface hydroxyl groups and the scavenging of hydrogen atoms by the aromatic rings. Electron paramagnetic resonance spectroscopy provides insights into the nature of radicals formed on catechol-modified ZrO₂, suggesting their involvement in trapping hydrogen atoms and suppressing H₂ production.

In conclusion, this study demonstrates the potential of strong coordinating aromatic ligands, such as catechol to mitigate H₂ production on ZrO₂ surfaces. Future research directions will explore the optimization of surface modification strategies and the mechanistic understanding radiolytic processes for tailored hydrogen management in radiation environments.

Experimental Study of Carbon-Carbon Composite Oxidation in Hypersonic Airflow

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Advisor:

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Abstract

Carbon-Carbon (C-C) composites are prospective materials for the fabrication of components of hypersonic vehicles such as aeroshells and leading edges. These composites possess excellent performance characteristics, including a low density ($1.60\text{-}1.98 \frac{g}{cm^3}$), a low coefficient of thermal expansion (-0.85 to $1.1 * 10^{-6} \frac{1}{K}$), a high modulus of elasticity (200 GPa), and high thermal conductivities ($\sim 4\text{-}35 \frac{W}{mK}$), while retaining mechanical properties in conditions up to $\sim 2000^\circ\text{C}$ in inert environments. However, a significant drawback of the C-C composite is its high rate of oxidation in the presence of oxygen at high surface temperatures. The mechanism and rate of oxidation are well-studied at ambient conditions, but data on the ablation and oxidation in hypersonic environments are limited. For this research project, various models made of a C-C composite were exposed to hypersonic (Mach 6) flow at controlled surface temperatures up to 1450°C . The flow total pressure was setup up to 200 psi. The surface heating was performed by a CW IR laser at power levels up to 535W. Data was collected using an IR camera to capture surface temperature dynamics and distribution, an internal thermocouple to measure the internal temperature of the model, schlieren visualization, and macrophotography to capture physical changes of the model fibers. It was found that the C-C oxidation rate significantly increased in hypersonic airflow compared to ambient conditions, up to 34 times. The mechanism of the accelerated degradation is discussed as a combination of thermal ablation, chemical oxidation, and mechanical destruction of overheated individual carbon fibers.

Directing Triplet and Singlet Energy Transfer in Halide Perovskite Nanocrystal- Rhodamine Dye Hybrids

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Advisor:

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Department of Chemistry and Biochemistry

Abstract

The rich optoelectronic properties of metal lead halide perovskites have facilitated their use in light harvesting and light-emitting devices. Cesium lead halide perovskites can capture and convert a wide range of visible to near-IR photons via charge or energy transfer mechanisms. We have demonstrated the triplet energy transfer between CsPbI₃ nanocrystals and surface-bound rhodamine acceptor dyes using a combination of steady-state and time-resolved absorption and photoluminescence (PL) experiments. The long-lived triplet excited states of rhodamine dyes observed in the CsPbI₃-acceptor system provide evidence for triplet-triplet energy transfer from selectively excited CsPbI₃ nanocrystals. The influence of acceptor functionalization on energy transfer kinetics is also established in this study. Of the three rhodamine acceptors studied, CsPbI₃-rose Bengal showed 96% energy transfer efficiency with a rate constant of $1 \times 10^9 \text{ s}^{-1}$. rhodamine B, which lacks a pendent group shows weak binding with the nanocrystals, which caused a four-fold decrease in triplet energy transfer rate. This triplet energy transfer rate constant is nearly 2 orders of magnitude slower than the singlet energy transfer observed for the CsPbBr₃-rose Bengal hybrid ($1.1 \times 10^{11} \text{ s}^{-1}$). To establish the influence of donor bandgap in directing singlet and triplet energy transfer in semiconductor-dye assemblies, we varied the bromide/iodide ratio in CsPb(Br_{1-x}I_x)₃ nanocrystals thereby tuning the bandgap. While the single-halide CsPbBr₃ and CsPbI₃ nanocrystals selectively populate the singlet and triplet excited states of rose Bengal dye, the mixed halide perovskites were able to generate a mixture of both singlet and triplet excited states. Therefore, the properties of semiconductor-molecular dye hybrids discussed here open effective design strategies for light-harvesting systems to advance their utilization in optoelectronic and up-conversion devices.

Energy Saving in Natural Gas Production: Amine Modified PIM Membrane for Propylene/Propane Separation

Bo Wei Cynthia Chen
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College of Engineering

Advisor:

Casey O'Brien, Assistant Professor, Department of Chemical and Biomolecular Engineering

Abstract

Cryogenic distillation is a common practice in the current refinery industry to purify light hydrocarbon gases from crude oil streams, but it is a thermally intensive process with overwhelming consumption of energy. In order to lower the carbon footprint associated with industrial distillation processes, literature has shown that membrane separation processes can reduce energy consumption up to 90%. However, membranes have limitations on their gas separation efficiency, as it is dependent on the intrinsic properties of the material. The gas diffusivity and solubility in a polymeric membrane can be fine-tuned by designing the structure of the polymer. Polymer of Intrinsic Microporosity (PIM-1) is well known for its bulky, ladder-shaped backbone that creates high free volume, leading to high gas diffusivity, but suffers from a low gas selectivity. By introducing amine groups into the PIM-1 backbone, the hydrogen bonding forces creates tighter packing in the membrane, creating new gas separation characteristics and efficiency. This study proposes to develop a novel membrane separation system to selectively separate hydrocarbon gases by using amine functional groups. Initial investigation of amine-modified PIM-1 (PIM-NH₂) shows higher propylene/propane separation performance than PIM-1. At the same time, PIM-NH₂ has lower propylene permeability and faster aging compared to PIM-1. The project explores the gas separation efficiency of different amine composition and future plans for aging mitigation.

Design and Optimization of Integrated Energy Systems within Wholesale Electricity Markets

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College of Engineering

Advisor:
Alexandar Dowling, Associate Professor, Department of Chemical and Biomolecular Engineering

Abstract

With renewable energy penetration increasing during the past few years, improving energy efficiency and integrating renewable energy into the grid have become increasingly important. Integrated Energy Systems (IES), which combine multiple energy inputs and technologies and provide multiple outputs to different markets, have shown great potential for achieving the decarbonization goal. However, design and operating the IES is challenging because different decisions can vary in different timescales. The challenge becomes more tricky under the complex structure of the wholesale electricity market in the U.S.

However, optimization of IES within the electricity market is not easy. One of the widely used methods in optimizing IES is called the 'price-taker' assumption. Price-taker assumes the electricity market can take all the electricity from the grid without impacting the price. However, this is an ideal assumption which ignores interactions between the market and IES.

In our work, we proposed two methods to go beyond the price-taker, multiscale optimization and surrogate-assisted optimization. In the multiscale optimization, we use rigorous product cost models (PCM) to mimic the operation of wholesale electricity market. We simulate different IES designs and operation strategies in the multiscale optimization and show that the IES impacts the market prices. In the surrogate approach, we train the surrogate models to predict the market outcomes of IES.

Computational Investigation of Mono-uranium Oxide Anions in the Gas Phase

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Peter C. Burns, Massman Professor, Department of Civil and Environmental Engineering and Earth Sciences

Abstract

The uranyl triperoxide (UT) monomer consists of a linear uranyl ion (UO_2^{2+}) coordinated equatorially to three bidentate peroxy ligands. The uranyl peroxide cage cluster (UPC) $\text{U}_{28}[(\text{UO}_2)_{28}(\text{O}_2)_{42}]^{28-}$ is a polyoxometalate composed of UT building blocks. The formation and speciation mechanisms between U_{28} and UT, along with other UPCs, are largely unknown due to the difficulty in isolating intermediates. Aqueous UPCs are observed with electrospray ionization mass spectrometry (ESI-MS), along with collision induced dissociation (CID). This area of focus in our group is used to study the speciation of UPCs in low concentration aqueous solutions. Current research shows ESI-MS of Li-UT and ESI-MS/CID/MS of Li- U_{28} produces the low mass gas phase anions UO_x^- ($x=3-8$) and UO_xH_y^- ($x=4-8$, $y=1-2$). The electronic structure of many of the observed low mass anions is unknown, and their formation likely involves short-lived reactive oxygen species. Computational efforts involving actinides are complicated by relativistic effects and near degeneracy of valence orbitals. However, modern density functional theory (DFT) has been known to produce reliable geometric optimizations, and multi-configuration calculations can aid in the resolution of spin contamination issues. Geometry optimization calculations of various isomers of UO_x^- ($x=6-8$) and UO_xH_y^- ($x=6-8$, $y=1-2$) suggest the inclusion of oxo and superoxo radical groups as well as unique hydroperoxo groups. Refined energy calculations help elucidate the relative stabilities of potential isomeric structures, and spin density and orbital population analysis help describe the character of the uranium centers and oxygen groups.

Hybrid Molybdenum Bronzes for Energy-Related Applications

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Advisor:

Adam Jaffe, Assistant Professor, Department of Chemistry and Biochemistry

Abstract

Metal oxide bronzes denoted as A_xMO_3 (A = cation, M = metal) display favorable electronic properties for applications ranging from energy storage to catalysis. These inorganic solid-state materials, however, can require high-temperature syntheses, are difficult to tune post-synthetically, and stand to benefit from molecular-level control. We recently introduced a new material platform that we call “hybrid bronzes,” where we combine the advantageous structural, redox, and electronic attributes of extended inorganic bronzes with the tunable functionality and synthetic control of the molecular species. Our primary objective is to template molecular species between two-dimensional layered hydrogen molybdenum bronzes to modulate their electronic properties. To this end, we have established a library of such materials, supported by the development of new mild, solution-state reaction conditions. We have developed control of these hybrids’ reduction levels to yield the desired hybrid bronzes, thereby tuning the electronic properties of these materials. Using powder and single-crystal X-ray diffraction, vibrational and electronic spectroscopies, and conductivity studies, we have targeted the intricate relationship between structure and property of these materials. Additionally, we have begun utilizing the unique tool of high-pressure experimentation to understand stimulus-induced changes and how structure dictates the electronic behavior of these materials. Our goal is to develop a new tunable material platform from which we can access desirable chemical and electronic properties for energy-related applications.

Characterizing Sulfur Copolymer Composite Cathodes for All-Solid Batteries

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Advisor:

Jennifer L. Schaefer, Sheehan Family Collegiate Professor, Department of Chemical and Biomolecular Engineering

Abstract

High energy density and high-performance metal-sulfur batteries are sought after as a potential improvement on the current Li-ion battery technology. The high energy density that would be achieved from metal-sulfur batteries can be used to power large vehicles, such as semi-trucks and airplanes, aiding in the global movement towards more sustainable energy. The use of sulfur as a cathode material in these devised batteries is beneficial due to the abundance of sulfur as well as its low cost. A solid polymer electrolyte will be used for the battery in this study as opposed to the standard liquid electrolyte. This is a safety benefit since the volatile, flammable liquid components would be eliminated from the batteries. Liquid electrolyte batteries are also more susceptible to the polysulfide shuttle effect where reaction intermediate metal sulfides (M_xS_y) dissolve into the electrolyte, “shuttle” to the anode, and then react with it, thus diminishing the electrochemical capacity of the cell. In this work, we investigate lithium-sulfur batteries based on solid polymer electrolytes and sulfur copolymer cathodes with built-in ion transport channels. We report on the synthesis of the crosslinked sulfur copolymer as well as the characterization of the bulk material properties of the copolymer and the overall composite cathode. These characterizations include Raman spectroscopy on the polymer materials as well as on the cathode during cycling of the battery for gaining information on the charge / discharge reaction pathways with sulfur and polysulfide speciation along with the ionic interactions that impact cation transport in the solid state.

Multiscale Optimization to Promote a Circular Economy of Critical Materials

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Advisor:
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Abstract

The design and optimization of sustainable processes to extract critical minerals (e.g., lithium) has become increasingly important as the demand for technological consumer products (e.g., lithium-ion batteries in electronic devices) increases. While membrane-based processes show promise in process intensification efforts of the current critical mineral harvesting techniques, there are still significant gaps in understanding how to scale up and integrate this technology into the current infrastructure. This poster summarizes the collaborations we have with the Bill Phillip group at Notre Dame, which specializes in membranes, and the Department of Energy-funded project PrOMMiS (Process Optimization and Modeling for Minerals Sustainability), which incorporates academic, national lab, and industry partners within process systems engineering.

We propose that process systems engineering techniques can enable the rapid design, optimization, and scale-up of membrane-based critical mineral recovery processes. On the molecular scale, machine learning techniques enable rapid screening of different materials to provide the larger-scale design with appropriate material property targets. With enhanced materials, bench-top experiments can be designed and further improved using model-based data analytics. For example, the model-based design of experiments can accelerate the information gain of filtration systems. The small-scale experiments can be scaled up and optimized using superstructure optimization, which enables the rapid design of membrane cascades for staged separations. Finally, on the infrastructure scale, process systems engineering informs how we can approach complex optimization problems (e.g., supply chain optimization with multiple stakeholders). With a multiscale approach to the design and optimization of critical mineral recovery processes, we can promote a circular economy by systematically analyzing the relationship of process intensification across all scales of process development. However, we emphasize the need to collaborate across disciplines, such as membrane, data, and computational sciences, to realize the molecular-to-systems optimization framework.

Future Reading:

Lair, L.; Ouimet, J. A.; Dougher, M.; Boudouris, B. W.; Dowling, A. W.; Phillip, W. A. Critical Mineral Separations: Opportunities for Membrane Materials and Processes to Advance Sustainable Economies and Secure Supplies. *Annu Rev Chem Biomol Eng* **2024**. [Accepted]

Promoting Sustainable Development in Northern Uganda: Empowering Households through Biogas Systems for Health, Socio- economic Empowerment, and Environmental Conservation

Matthew Egan
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Mendoza College of Business and Center for Social Concerns Collaboration

Advisor:
Corey Angst, Jack and Joan McGraw Family Collegiate Professor of IT, Analytics, and
Operations, Department of IT, Analytics, and Operations

Abstract

Unsafe cooking methods pose a significant health risk. The World Health Organization (WHO) estimates that 2.3 billion people worldwide employ cooking methods that generate substantial and harmful air pollution. This household air pollution, which is extremely prevalent in Sub-Saharan Africa, is estimated to result in over 3 million deaths per year. In the villages of Northern Uganda, families cook with firewood that has been cut down from nearby forests. Many governmental and non-governmental organizations (NGOs) have endeavored to distribute improved stoves and biogas systems to mitigate this issue. Biogas is an environmentally friendly, renewable energy source produced by the breakdown of organic matter such as food scraps and animal waste. Biogas is produced when organic matter is broken down by microorganisms without oxygen, which is called anaerobic digestion. Methane is the main, high-energy gas produced. Slurry or fertilizer is also produced, which is significantly better than manure and other natural fertilizers. Initially, the goal was to see the feasibility of any sort of biogas system in the village environment in Uganda. In the summer of 2023 this was accomplished, a 6 m³ manure-based digester bag design was installed for \$1500 with parts sourced outside of Uganda. This system has been functional for over 8 months, providing around 4 hours of cooking time per day and 10-20 L of slurry fertilizer for the Sisters of the compound. While this biogas system was successful, it is far too expensive and unreasonable for the average village household to obtain. The aim of this project then shifted to providing the benefits of biogas in an accessible form for the average Northern-Ugandan. With this in mind, the ARTI model was selected largely due to its potential for scalability and cost. It is used in many similar contexts of developing and traditional economies, including India and Tanzania. Scalability is driven by the ability to source materials locally, consistently reproduce the design quickly and accurately, and adapt the size to specific locations (households v. schools). Most importantly, its cost is around \$250-300, around a sixth of the original system cost. This spring, at Saint Bakhita's Vocational Training School of Kalongo, an ARTI system was constructed successfully for around \$450. It is extremely efficient, producing around 750-1000 L of biogas daily utilizing the food waste of the school and kitchen. The ARTI system serves as the basis for a proposal under the Poverty Initiative that aims to explore strategies for influencing household sustainable energy usage behavior so that the improved stoves can achieve the intended benefits. It is planned to conduct a controlled field experiment at a Notre Dame sponsored boarding school in rural Uganda, with the aim of assessing the effectiveness of a semester-long training course on biogas stove usage and maintenance among girls, and evaluating its impact on their families' biogas stove usage behavior after they move back home. Impact will be quantified in terms of different health, environment, and economic benefits. This narrative, biogas findings, and future research are to be presented.

Flow and Turbulence Characteristics at Hub Height for Offshore Wind Energy Production

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Advisor:

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Abstract

Interest in offshore wind has continued to grow over the last few decades as a vital component in the renewable energy landscape. The wind speeds offshore are higher and generally more consistent in magnitude and direction owing to the aerodynamically smoother surface of the ocean, and turbines can be built at a larger scale which generates greater and more reliable energy production. However, there are several risks and disadvantages including the possibility of hurricanes, higher wind speeds, and waves/swell. Thus, there is a pressing need for a comprehensive understanding of the range of conditions, such as wind speeds and turbulence levels, to inform turbine design and reduce costs by ensuring reliable energy production under variable and demanding environmental conditions. Large-eddy simulations were utilized to explore this question, as they are a tool that has the ability to simulate winds over the ocean surface. This allows one to quantify the wind fluctuations as a function of factors such as wind speed and wave properties. My goal was to gain proficiency in using this tool and to analyze turbulence patterns, particularly at a standard hub height, resulting from wind flow over surface waves. This preliminary research scratches the surface of exploration into wind-wave interactions and the turbulence characteristics induced by these interactions, which will continue to be important to investigate in order to affordably build offshore wind turbines in areas that experience higher wind speeds and even hurricanes. Future studies would involve simulating conditions similar to those in a hurricane and including a realistic representation of wind turbines themselves into the model.

The Impact of Node Structure on Ionizing Radiation Stability of Thorium-Terephthalate Coordination Polymers

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College of Science

Advisor:

Peter C. Burns, Massman Professor, Department of Civil and Environmental Engineering and Earth Sciences

Abstract

Coordination polymers comprise a large class of hybrid organic-inorganic materials. Metal organic frameworks (MOFs) are a three-dimensional subset of this class which are tunable, porous materials with high surface areas.¹ MOFs have potential applications in the nuclear fuel cycle, particularly in nuclear waste management; examples include waste separations, selective gas capture, and radionuclide sequestration, however, these proposed uses require high radiolytic stability.^{2,3} Recent studies have examined actinide MOFs, including UiO-66, which exposed these materials to ionizing radiation to probe the role of linker and metal node identities in radiation stability of these materials.^{4,5} To understand another fundamental aspect towards radiolytic stability, our study examines materials with the same metal identity and the same linker, arranged in different structural motifs. UiO-66 consists of a 12-connected hexanuclear M_6O_8 node, with the ditopic 1,4-benzene dicarboxylic acid (BDC) linker. Differing from Th-UiO-66, $Th(BDC)_2(DMF)_2$ consists of mononuclear thorium tetra-oxide nodes, which are ten-fold coordinated. Two of the ten coordination sites of $Th(BDC)_2(DMF)_2$ are occupied by carbonyl oxygen atoms from N,N-dimethylformamide (DMF) ligands. $Th(BDC)_2(DMF)_2$ is composed of neutral sheets that cannot connect the thorium node in three dimensions due to the *trans* position of DMF extending into the interlayer. The third material, $Th(BDC)_2$, consists of a mononuclear node, eight-connected with the BDC linker into three-dimensions. These materials were exposed to doses of approximately 11.37, 23, 34, 45.5, 57, 113, and 227 MGy. Material degradation was characterized using X-ray powder diffraction (PXRD), Raman spectroscopy, and diffuse reflectance Fourier Transform infrared spectroscopy. The structures containing fewer node-linker connections presented enhanced radiation resistance. $Th(BDC)_2$ showed unprecedented radiolytic resistance maintaining powder X-ray diffraction peaks up to 227 MGy, while Th-UiO66 and $Th(BDC)_2(DMF)_2$ were rendered X-ray amorphous at 86 MGy and 114 MGy, respectively.

References

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Use of Kinetic Modeling to Probe the Chemical Opportunities in an Ethane Nonthermal Plasma

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Abstract

Finding electrified routes for the valorization of ethane, usually the second most abundant hydrocarbon in natural gas, has significant environmental benefits and economic incentive. Nonthermal plasma is presented as a possible technology due to its electric-driven nature, mild operating conditions, and demonstrated ability to dehydrogenate ethane. Nonthermal plasmas are generated by applying a strong electric field to a gas in such a way that it becomes partially ionized (~1% ionization) and electrically conductive. This creates a highly reactive environment that is in a non-equilibrium state, with radical, excited, and neutral species near ambient temperatures and free electrons in excess of 10,000 K. Due to the complexities of nonthermal plasma chemistry, most studies using nonthermal plasmas with ethane have focused on demonstrating ethane conversion within a limited range of reaction and plasma conditions. Therefore, we present an investigation of the chemical opportunities within an expanded range of conditions through the use of time-dependent kinetic modeling. We apply a kinetic modeling software (ZDPlasKin) developed for the unique combination of thermally- and electron-excitation-driven chemistry present in nonthermal plasmas. Using a model verified by base-case experimental measurements has allowed us to probe conditions that are often difficult to isolate in an experimental setting. The results of this modeling investigation reveal a landscape of parameter space that expands our understanding of the chemical opportunities of ethane reforming in a nonthermal plasma. We track the product yield and ethane conversion as major outputs of our model, and explore the impact of two inputs: time in plasma and reduced electric field. Within the multi-dimensional results of our modeling, we find opportunities to optimize ethylene and acetylene yields, minimize methane or other less-valuable products yields, and maximize ethane conversion. For example, limiting the time in plasma to a few micro seconds and increasing the reduced electric field to over 200 Td provides a maximum ethylene yield while keeping methane yield relatively low.

Exploring Chain Length and OH-Spacing Effects of Choline-Chloride Based Alkanediol Deep Eutectic Solvents Via Classical Molecular Dynamics

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Abstract

Deep eutectic solvents have become increasingly popular due to their environmentally friendly nature and tunability. In this work, the extensively studied DES ethaline (a 1:2 mixture of choline chloride with ethylene glycol) is compared to other alkanediol-based DESs with ChCl as the hydrogen bond acceptor molecule for a wide range of compositions. Classical molecular dynamics simulations have been validated against experimental data and used to investigate the local liquid structure and dynamics that result from the hydrogen bonding network of the solvent. It has been found that vicinal diol hydroxyl (OH) groups cause stronger intermolecular interactions than terminal OH groups. The viscosity of the solvent has also been found to correspond to the strength of the key interactions, or hydrogen bonds, of the system with the most significant being the Cl-OH and OH-OH self-interactions. Both alkyl chain length and OH spacing are important factors in DES design.

Stochastic Modeling of Electron Scattering in Liquid Water

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Abstract

The scattering and transport processes of electrons with incident energies between 0.2 eV and 10 keV in liquid-phase water are simulated using a Monte Carlo (MC) method. The effects of electron capture processes such as trapping and dissociate electron attachment (DEA) at resonance peaks, the entry spectrum of secondary electrons in the subexcitation range, and isotropic elastic cross-sections on electron penetration are investigated. We show that the use of unscaled amorphous solid water (ASW) cross sections combined with dipole oscillator strength distribution (DOSD) data, solely employed for representing electron energy loss, can eliminate the historically recognized discrepancy in results between pulse radiolysis data representing spur recombination and MC track calculation results. This work also indicates that track termination events, such as electron capture, are necessary to reproduce the mean thermalization distance from both direct photoinjection measurements obtained in the very low-energy range below 2.5 eV and the continuously slowing down approximation (CSDA) reported in the high-energy range up to 10 keV.

A Custom 3D Printed Permeate Probe Device for High-throughput Membrane Characterization

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Abstract

Sustainable energy solutions and electrification are driving the demand for critical mineral and metal resources. While membranes present an opportunity to sustainably fractionate and purify critical minerals, fundamental questions regarding transport phenomena in multicomponent feed streams hinder their integration into processes. Enhancing the rate of material and process development requires systems and techniques that can reduce the time, energy, and resources needed to characterize the transport properties of polymer membranes. For instance, systematic studies on complex multi-component feed streams are needed to elucidate the effect of ion-ion and ion-membrane interactions on the performance of membranes.

Within this study, we create a stirred filtration cell that uses two conductivity probes to continuously monitor the upstream (i.e., retentate) and downstream (i.e., permeate) solutions. By continuously monitoring the bulk solutions, the measurements can be used to determine the concentration of ions at the membrane-solution interfaces; information that is critical to regressing membrane transport parameters. Here, we begin by focusing on the design and constraints of the permeate conductivity probe reservoir. Notably, a stir bar is necessary to ensure the solution in the reservoir is well mixed. Albeit, the stir bar needs to be positioned at an appropriate distance from the sensor to ensure that its magnetic field does not influence the accuracy of the conductivity measurements. Subsequently, the device is used in conjunction with high-throughput experimental techniques to characterize commercial polyamide nanofiltration membranes. Diafiltration experiments systematically change the retentate solution above a membrane and enable the characterization of membrane transport parameters over a broad range of concentrations. For NF90 and NF270 membranes, we use the permeate probe device to obtain a complete evolution of the membrane performance. These results support data generated from previous studies where aliquots of permeate solution were collected and analyzed. We subsequently extend our study to feeds containing lanthanum and sodium. Preliminary results demonstrate that the inline permeate and retentate probes enable high-throughput evaluation of membrane performance in mixed feed solutions that are critical to recycling fluorescent lamps and treating acid mine drainage.

An Analysis of the Potential of Solar Panel Recycling as a Sustainable Regional Redevelopment Tool in Fukushima, Japan

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Abstract

In recognition of the interconnectedness of green energy initiatives and socioeconomic impacts on communities around the world, this paper uses estimated employment factors and population trends to analyze the potential impact of solar panel recycling on local populations using a case study of Namie, Japan, considering the research question “To what extent would population in Namie, Japan, be impacted by jobs created from a 1500-ton solar recycling and refurbishment facility with varying scenarios for potential expansion?” It further analyzes the potential changes in Namie’s gender ratio if female employment increased by considering “To what extent would the gender ratio in Namie, Japan, change due to employment at the recycling facility if a 70% female worker quota was established?” We model the potential job creation associated with a hypothetical new photovoltaic (PV) panel recycling facility in Namie, Japan, under three scenarios: the facility has a yearly capacity of 1500 tons of PV panel waste, the facility expands from 1500 tons to 5000 tons, and the facility expands from 1500 tons to 20000 tons. The model also considers a change from 30% female employment to an incentivized 70% female employment. The calculations showed that jobs created would account for 7%, 23%, and 92% of the projected 2035 population in Namie for the 1500-, 5000-, and 20000-ton scenarios, respectively. An incentivized 70% female employment at the facility would increase the percentage of women in Namie’s projected 2035 population by 2%, 5%, and 14%, respectively. The results showed that PV panel recycling could be used as a long-term regional redevelopment strategy, but due to associated socioeconomic considerations, accompanying policy needs to be implemented to improve worker work-life balance and remove systemic barriers to women in the workplace.

Oxygen Atom Transfer in Layered Hybrid Materials: A Molecular Approach to Solid-State Synthesis

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Abstract

Solid-state materials are desirable for their chemical and thermal stability. However, the energy required for their syntheses and their lack of post-synthetic tunability leave room for improvement. We target the synthesis of new or difficult-to-access metal oxyhalides and pseudohalides that are promising materials for applications in energy-storage and catalysis by using hybrid material intermediates that contain pyridine-N-oxide based ligands. The synthesis of these materials requires milder conditions than their solid-state analogs, and through eventual atom transfer and breaking of the N-oxide N–O bond, they will form a metal oxyhalide or oxypseudohalide. N-oxides are versatile oxygen atom transfer reagents since their N–O bond strength is tunable depending on their aromatic substituents. Further, these ligands allow for multiple binding modes—either a terminal or a bridging metal-oxygen bond. In this work, focus has been placed on the synthesis of these hybrid materials using pyridine-N-oxide and its derivatives in various metal halide and metal pseudohalide structures. We aim to synthesize a range of hybrid intermediates where the effects of N–O bond strength on atom transfer can be studied.

Tailoring Light Olefin Oligomerization through the Design of Polyoxometalate-Based Catalysts

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Advisor:

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Abstract

Oligomerization of light alkenes is a strategic reaction that allows the exploitation of largely available domestic feedstocks, contributing to secure the energy safety of the US. Low molecular weight olefins, derived from shale gas resources or from biomass processes, can indeed be transformed into liquid fuels and value-added chemicals by means of catalysts that promote C-C coupling. Currently adopted homogeneous catalysts based on nickel complexes, however, despite their good performance in terms of activity and selectivity, require the use of toxic co-catalysts and solvents and are difficult to recover. Numerous efforts have been made to tailor Ni(II)-based solid catalysts for this reaction. A primary example are metal organic frameworks (MOFs) that host isolated nickel sites, designed to emulate homogeneous systems. However, these materials tend to have low thermal resistance and often require the use of toxic methyl-aluminoxane for activation. Another great example are nickel-exchanged zeolites that take advantage of inherent microporosity and high active site density to provide strong catalyst performance. Nevertheless, they show rapid deactivation due to multiple mechanisms that involve the heavier hydrocarbons produced in the reaction. Furthermore, the Brønsted acidity of the zeolite promotes cracking and skeletal isomerization, leading to unselective product mixtures.

To overcome these challenges we have isolated Ni²⁺ cations by substituting them onto various types of polyoxometalates. These materials not only allow the precise synthesis of single sites catalysts but also proved to be stable and regenerable during the oligomerization of both ethylene and propylene. Additionally, their high selectivity towards linear alkenes, along with their resistance to impurities, make them interesting catalysts worth to further exploration. Current work is being devoted to structural and compositional modifications of polyoxometalate platforms, with the final objective to tune the reactive performance of nickel sites up to target applications.

Assessing the Radiation Stability of Key Ligands in Nuclear Waste Separation

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Abstract

Radical intermediates derived from di-n-Butyl N,N-Diethylcarbamoylphosphonate (DBDECP), N,N-Bis(2-ethylhexyl)butyramide (DEHBA), dioctyl phosphate (DOP), tributyl phosphate (TBP), N,N,N,N-tetraoctyl diglycolamide (TODGA), and octyl(phenyl)-N,N-diisobutylcarbamoylmetliylphosphine oxide (CMPO), were examined by EPR spectroscopy at 77 K. In all cases, carbon-centered radicals originating from alkyl or amide compounds were consistently identified in the experimental spectra (Figure 1). The spectral assignment was based on the advanced quantum chemical calculation at the DFT(B3LYP)/L1a_3 level of theory allowing determination the approximate conformations of the radicals involved. The measured kinetics exhibit a linear accumulation of radicals up to an irradiation dose of 1 kGy. The relative yield of stabilized radicals in organic phosphates (TBP, DOP) is approximately three times higher than in amide (DEHBA) or carbamoyl phosphonate (DBDECP) samples. The proposed approach for estimating radiation stability can be expanded to other compounds or mixtures relevant to nuclear waste separation, as well as other substances of particular interest.

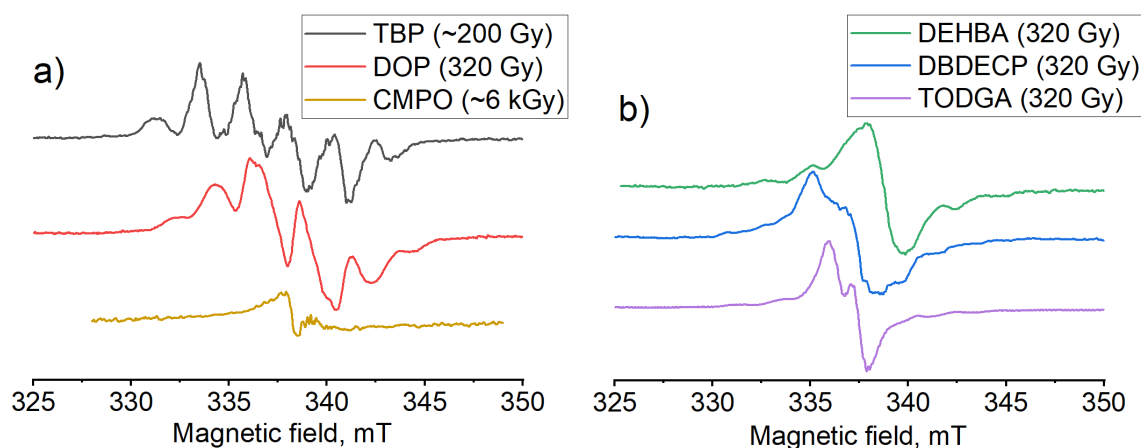


Figure 1. EPR spectra of irradiated TBP, DOP, CMPO (a) and DEHBA, DBDECP, TODGA (b) at 77K.

Computing Noble Gas Solubility in Alkali Halide Molten Salts

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Abstract

In this study, we addressed the solubility of noble gases in molten alkali halide salts, crucial for the management of the fuel salt cycle in molten salt reactors (MSRs). Understanding the interactions of fission products, especially xenon and krypton, with spent fuel salts is vital for MSR efficiency and safety. We combined molecular dynamics simulations, conducted with LAMMPS and CP2K, and Monte Carlo simulations, using Cassandra, to predict Henry's law constants for the interactions between molten salts (NaCl and KCl) and noble gases (Ar and Xe) through the application of the Widom insertion method.

Our application of the Widom insertion method to systems of molten NaCl and KCl with Ar and Xe successfully yielded Henry's law constants and enthalpy of solvation values. These findings align with indirect experimental data, underscoring the potential of the Rigid Ion Model (RIM) for accurately predicting gas solubility in molten salts. A notable advancement of our research is the enhancement of RIM parameter accuracy through ab initio simulations, offering an improvement over traditional methods reliant on the Lennard-Jones potential.

Our study navigated through challenges, particularly the limited direct experimental comparisons, to advance our grasp of noble gas solubility in molten salts. This study represents a crucial development in understanding the interactions of noble gases within alkali halide molten salts, contributing fundamentally to the solute-solvent interaction science important for MSR operation and safety.

Iptycene-based Polybenzoxazole Membranes for High-temperature Hydrogen Separations

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Abstract

The efficient separation of hydrogen from hydrocarbon mixtures at high temperatures is crucial for numerous industrial applications, including refining and petrochemical processes. Polymer membranes are energy-efficient candidates for separating industrial gases because they are cheaper, more robust, easier to fabricate, and scalable. They have been chiefly deployed to separate and purify hydrogen. However, current commercial polymer membranes can't meet this industrial need due to poor thermal stability resulting from their low glass transition temperatures (T_g). While high T_g polymers, such as polybenzimidazole, often have low permeabilities because of their strong hydrogen bonding and pi - pi electron stacking. Additionally, polymer membranes characteristically lose their selectivity for hydrogen during separation at high temperatures because the gas permeation is an activated process, and higher temperature expands the polymer's free volume, enabling gases larger than hydrogen to also pass more quickly at higher temperatures. This study focuses on a novel class of Polybenzoxazoles (PBO) incorporating iptycene motifs engineered to enhance gas separation performance under extreme thermal conditions. The configuration free volume afforded by the bulky and rigid iptycene motifs is hypothesized to be less sensitive to free volume expansion at higher temperatures than the regular polymer's conformational free volume, thus improving selectivity at higher temperatures.

Here, we investigate the separation performance of triptycene and pentyptycene PBOs for hydrogen at temperatures up to 200 °C. The gas permeation tests were conducted using hydrogen and methane to evaluate the selectivity and permeability of the membranes in single and binary gas conditions. These polymers' pure gas separation was also performed for nitrogen and carbon dioxide up to 200 °C. The solid-state morphology characterization of these Iptycene-based PBOs was compared with conventional PBO. The increased hydrogen permeabilities and selectivity of 16 achieved at 200°C demonstrate that the Iptycene-based PBOs exhibit excellent performance at extreme temperatures, which is untypical for gas separation polymers. The study further explores the relationship between membrane structure at high temperatures, specifically the impact of incorporating iptycenes in PBO on separation performance. Molecular simulations of the polymer microstructure at high temperatures are being done to provide additional insights into the observed high-temperature performance. This study underscores the potential of iptycene polybenzoxazoles in high-temperature applications and provides insights for designing advanced materials for gas separation. The promising findings from this study are envisaged to improve the heat integration of industrial processes and separation conditions by eliminating or reducing the need for interstage cooling and trimming down the capital and operating costs incurred on heat exchangers.

Iodine Expulsion at Photoirradiated Perovskite/hole Transport Layer Interface

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Abstract

Lead halide perovskite solar cells have emerged as one of the most exciting candidates in solar energy conversion devices. The progress made regarding the cell architecture to achieve power conversion efficiency compatible with Si photovoltaics has drawn attention toward commercialization. However, in recent years, the increase in efficiency has only been incremental, mostly achieved by decreasing cell area. Increasing the cell area without significant losses and with improved stability remains a challenge. To overcome this challenge, it is crucial to understand the processes that prevent achieving the desired long-term stability. In the past, it has been demonstrated that under continuous photoirradiation, iodine gets expelled from lead iodide perovskites when in contact with non-polar solvents, such as dichloromethane or toluene. The expulsion can be explained by the accumulation of photogenerated holes and the subsequent oxidation of iodide ions to elemental iodine. Recent reports in the literature showed that iodine may get expelled to organic hole transport layers (HTLs) as well. Therefore, it is most crucial to understand how iodine is expelled from lead halide perovskites to the most commonly used organic HTLs, such as spiro-MeOTAD (2,2',7,7'-Tetrakis[N,N-di(4-methoxyphenyl)amino]-9,9'-spirobifluorene). After establishing the oxidation states and the corresponding spectral features of spiro-MeOTAD by combining electrochemistry and UV-Vis absorption spectroscopy, we found that spiro-MeOTAD has multiple oxidation states, and iodine oxidizes the HTL in multiple steps. Lead halide perovskites relevant for solar cell applications (methylammonium lead iodide, MAPbI₃ in this case) have absorption in the same range where the features of oxidized spiro-MeOTAD appear. To facilitate the study of the expulsion, we employed an approach where MAPbI₃ and spiro-MeOTAD are deposited on different substrates and physically paired together during photoirradiation. Our findings reveal that this process might have a significant contribution to the efficiency losses in devices; therefore, it needs to be fully understood to develop efficient and stable perovskite solar cells.

Hybrid Tungsten Bronzes: A Tunable Organic-inorganic Platform

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Abstract

Tungsten oxide (WO_3) has been investigated for applications including electrochromic devices, catalysis, and energy storage as well as for intriguing solid-state physical phenomena such as metal-insulator transitions and superconductivity. WO_3 can be reduced to form a non-stoichiometric compound known as a bronze with the formula A_xWO_3 (A^+ = charge-balancing cation). Reduction populates the conduction band, yielding free electrons with high carrier mobilities that dramatically alter the chemical and electronic properties of the system. However, some tungsten bronzes require high-temperature synthesis, and their post-synthetic tuning is challenging. To address these challenges, enhance the properties of the inorganic parent compound, and engender emergent properties, we are developing hybrid organic-inorganic tungsten bronzes. This new material platform consists of two-dimensional mixed-valence tungsten oxide layers in proximity to organic molecules that can incorporate added functionality, such as catalytic, redox-, or photo-activity. Our work (1) explores the synthetic control of layered hybrid tungsten bronzes, and (2) studies the structure-property relationships within this new material system, thereby leading to design principles for tuning their optical and electronic properties toward energy-related applications.

Adaptive Experimental Design: Data-driven Optimization of Additive Manufacturing for Thermoelectric Materials and Devices

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Abstract

Solid-state thermoelectric (TE) generators (TEGs) are promising for powering distributed sensor networks, biomedical devices, wearable electronics, and beyond. However, the efficiency of TEGs is limited by TE materials and their manufacturing methods. The Edisonian search, widely adopted by experimentalists to improve TE materials performance, remains expensive, slow, and unsuitable to handle large search space, e.g., $O(10^6)$. In recent years, artificial intelligence and machine learning have offered new approaches to leverage data to overcome these challenges.

This poster will focus on the data-driven optimization framework, integrating first-principle, machine learning, and BO to reduce the order of magnitude of fewer experiments than the Edisonian search. The application of the proposed framework for the optimization of TE materials and corresponding manufacturing methods, including material composition, 3D printing, and sintering, will be highlighted.

Sustainable Aviation Fuels (SAF) from Ethanol: An Integrated Systems Modeling Approach

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Advisor:
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Abstract

Brazil was one of the first countries to use biofuels for transportation due to government incentives since the 1970s. Biofuels, especially those produced at large scales, have gained increasing interest, specifically from the aviation industry. Bioethanol from Brazilian sugarcane mills can be upgraded to sustainable aviation fuel (SAF) via the ASTM certified pathway alcohol-to-jet (ATJ); however, challenges exist for commercial implementation including high technology costs, market uncertainty, and policy dependence. In this work we address complex, interdependent, multi-scale optimization problems at the intersection of SAF and the sugarcane industry. We conclude by showing the role of optimization and analysis in guiding technology development, and highlight opportunities to integrate techno-economic analysis, life cycle analysis, and policy design.

Future Reading: Watson, M. J., Machado, P. G., da Silva, A. v., Saltar, Y., Ribeiro, C. O., Nascimento, C. A. O., & Dowling, A. W. (2024). Sustainable aviation fuel technologies, costs, emissions, policies, and markets: A critical review. *Journal of Cleaner Production*, 449. <https://doi.org/10.1016/j.jclepro.2024.141472>

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