



Virtual 3rd Annual  
RESEARCH SYMPOSIUM

# POSTER SESSION

Friday, November 13, 2020

4:00 - 5:15 p.m.

# Schedule of Presentations

7M Overview	Student Presenter	Presentation Title	Faculty Advisor	Dept.
4:01-4:08	Savannah Benjamin	Synthetic Metaschoepite Transformations: Effects of High Relative Humidity and Radiation	Peter Burns	Chemistry
4:09-4:16	Jeffrey DuBose	TiO <sub>2</sub> -Assisted Halide Ion Segregation in Mixed Halide Perovskite Films	Prashant Kamat	Chemistry
4:17-4:24	Eva Gulotty	Ionic Liquid Structure Function Relationships in LCST and UCST Solutions	Brandon Ashfeld	Chemistry
4:25-4:32	Ashley Hastings	Advancements in Actinide MOF Chemistry via Synthesis of Pu-UiO-66	Amy Hixon	CEEES
4:33-4:40	Tsuyoshi Kohlgruber	Synthesis of Actinide Polyoxometalates Using Ionic Liquid Media	Peter Burns	CEEES
4:41-4:48	Preethi Susan Mathew	Photoinduced Iodide Expulsion from Mixed Halide Perovskites	Prashant Kamat	Chemistry
4:49-4:56	Neha Mehra	Computational Interrogation of Single-Site, Oxide-Supported Group 4 Metal Hydrides for Ethylene Oligomerization	William Schneider	CBE
4:57-5:04	Bumjun Park	Magnesium ion conduction in dual cation exchanged poly(ionic liquid)s electrolytes	Jennifer Schaefer	CBE
5:05-5:12	Zachary Tucker	Thermodynamic and Molecular Descriptors of Sensible Heat Driven Liquid-Liquid Phase Separation	Brandon Ashfeld	Chemistry

## Department Key

CBE – Chemical and Biomolecular Engineering

CEEES – Civil and Environmental Engineering and Earth Sciences

Chemistry – Chemistry and Biochemistry

# **Synthetic Metaschoepite Transformations: Effects of High Relative Humidity and Radiation**

Savannah Benjamin, Ph.D. Candidate  
Department of Chemistry and Biochemistry  
College of Science

Advisor: Peter Burns, Henry Massman Professor, Department of Civil and Environmental Engineering and Earth Sciences; Concurrent Professor, Chemistry and Biochemistry; Director, Center for Sustainable Energy at Notre Dame (ND Energy); Director, NNSA Actinide Center of Excellence (ACE)

## **Abstract**

Characterizing nuclear materials under controlled storage conditions promotes a better understanding of their long-term stability. The uranyl oxy-hydroxide hydrate, metaschoepite  $[(\text{UO}_2)_8\text{O}_2(\text{OH})_{12}](\text{H}_2\text{O})_{10}$ , has garnered substantial interest in the study of used nuclear fuel as a prominent corrosion product. Like many uranium-bearing phases, transformations of metaschoepite rely heavily on its sub-bulk chemical properties. In this work, the surface build-up of peroxide via alpha radiolysis and subsequent formation of the uranyl peroxide phase studtite  $[(\text{UO}_2)_2\text{O}_2(\text{H}_2\text{O})_2](\text{H}_2\text{O})_2$  is studied. Humidity and ionizing radiation conditions were introduced to probe the interfacial properties of this system and elucidate a formation mechanism. Raman spectroscopy and powder X-ray diffraction were employed to characterize altered samples. Preliminary results suggest distinct alteration pathways for humidity and irradiation experiments, though both produce phases consistent with studtite. Experiments probing the relationship between particle size and alteration rate indicate the importance of surface area as a mechanistic driver.

# **TiO<sub>2</sub>-Assisted Halide Ion Segregation in Mixed Halide Perovskite Films**

Jeffrey DuBose, Ph.D. Candidate  
Department of Chemistry and Biochemistry  
College of Science

Advisor: Prashant Kamat, Rev. John A. Zahm Professor of Science, Department of Chemistry and Biochemistry and Radiation Laboratory  
Concurrent Professor, Department of Chemical and Biomolecular Engineering

## **Abstract**

Metal halide perovskites (MHPs) are the most promising new material for photovoltaic applications due to their low cost and high efficiency. Additionally, the perovskite structure allows for facile tunability of the light absorption properties by simply mixing different ratios of halide atoms (e.g. bromide, iodide) into the structure. In MHP solar cells, electron-selective contacts such as TiO<sub>2</sub> dictate the overall photovoltaic performance by effectively funneling charges. However, the same electron capture property of TiO<sub>2</sub> indirectly impacts device stability. The mobile halide ions (bromide, iodide) phase segregate upon pulsed laser excitation. Phase segregation is only observed when the MHP is deposited on electron-accepting TiO<sub>2</sub> but not on an insulating ZrO<sub>2</sub> substrate. Injection of electrons from the perovskite into TiO<sub>2</sub> followed by scavenging of electrons by O<sub>2</sub> causes accumulation of photo-generated holes. Localization of holes on the iodide site in the MHP induces instability, inducing movement of the iodide ions. Segregation is suppressed when photo-generated holes are extracted by a hole transport layer (spiro-OMeTAD) deposited on the MHP, thus avoiding hole build-up. These results provide further insight into the critical role of photo-generated holes in inducing phase segregation of metal halide perovskites.

# **Ionic Liquid Structure Function Relationships in LCST and UCST Solutions**

Eva Gulotty, Ph.D. Candidate

Department of Chemistry and Biochemistry

College of Science

Advisor: Brandon Ashfeld, Associate Professor, Department of Chemistry and Biochemistry

## **Abstract**

Ionic liquids (ILs) are exploited for their unique properties as room temperature salts for applications in extractions, cooling systems, energy storage, and as solvents. IL solvents exhibit attractive environmental properties such as low vapor pressure, flammability, and stability to heat, pressure, and radiation. Changes in charge distribution across ILs through drastically alter bulk solution properties and interfacial bonding. The ability to predict new IL frameworks and their material properties will allow for design of task specific IL fluids. Current explanations for IL separation behavior are based on temperature-controlled hydrogen bonding and hydrophobicity, and do not fully predict the complexity of these solvents or what structural features contribute to the solution properties. Refrigeration is linked with energy challenges as temperature control is required for physics, chemistry, biology and engineering applications, and represents 15% of current global electricity consumption. Technological improvements in absorption and adsorption technologies must meet the growing need for more efficient refrigeration. ILs as absorption and adsorption materials for cooling applications require less energetic input and are more environmentally friendly than current refrigerants. Some ILs form LCST solutions, with a minimum temperature below which the mixture is miscible in all proportions and above which separation occurs spontaneously, while others form UCST solutions that absorb water at high temperatures and separate at low temperatures. LCST/UCST ILs can form membrane free Directional Solvent Extraction (DSE) systems that use less energy input from heat and electricity. Cost effective ILs in DSE systems have yet to be realized due to the lack of systematic understanding of which structural and electronic factors govern this separation behavior. Designer solvent systems are also sought for nuclear waste remediation applications Actinides are useful materials in technology and industry; however, the mining and processing of Actinides have large environmental impacts. Over 90,000 metric tons of nuclear waste are stored in the United States of America at a cost of \$800 million annually. The recovery of Actinides from nuclear waste is an attractive alternative source for these materials, and solvent extraction is currently the most efficient method for Actinide recovery. Knowledge of the structural factors that govern IL interfacial behavior will allow development of new IL solvents that selectively extract actinides from waste materials. The elements that govern IL solution separation behavior have not been studied methodically from the organic chemist's perspective. The Ashfeld group has designed and constructed new ionic liquids to probe the contribution of sterics, charge density, hydrogen bonding strength, pKa, coordination site availability, and functional group involvement in the control of LCST and UCST separation in IL-solvent systems. We have targeted task specific ILs in collaboration with the Luo Group (ND) to investigate DSE applications, with the Burns Group (ND) to study actinide separation applications, and with the Moghaddam Group (UF) to develop models to predict separation behavior. The systematically modulated ILs we design, synthesize, and study via variable temperature NMR and Mass Spectroscopy to elucidate the bonding contributions of the IL cation and anion to phase separation in LCST and UCST solutions.

# **Advancements in Actinide MOF Chemistry via Synthesis of Pu-UiO-66**

Ashley Hastings, Ph.D. Candidate

Department of Civil and Environmental Engineering and Earth Sciences

College of Engineering

Advisor: Amy Hixon, Associate Professor, Department of Civil and Environmental Engineering and Earth Sciences

## **Abstract**

We report the synthesis and characterization of the first plutonium metal-organic framework (MOF). Pu-UiO-66 expands the established UiO-66 series, which includes transition-metal, lanthanide, and early actinide elements in the hexanuclear nodes. The thermal stability and porosity of Pu-UiO-66 were experimentally determined and multi-faceted computational methods were used to corroborate experimental values, examine inherent defects in the framework, and decipher spectroscopic signatures. The crystallization of a plutonium chain side product provides direct evidence of the competition that occurs between modulator and linker in MOF syntheses. The existence of a plutonium-based MOF is of interest to the many facets of the nuclear fuel cycle. Such a structure could provide opportunities for the simultaneous sequestration of plutonium and fission product or other actinides into a stable form. Incorporating an alpha emitter as the metal node could satisfy more fundamental curiosities regarding the radiation stability of MOFs. Actualization of a plutonium MOF provides a platform for nanoscale control of a high-profile nuclear material and has been executed for the first time in this work. Ultimately, the synthesis of Pu-UiO-66 demonstrates adept control of Pu(IV) coordination under hydrolysis-prone conditions, provides an opportunity to extend trends across isostructural UiO-66 frameworks, and serves as the foundation for future plutonium MOF chemistry.

# **Synthesis of Actinide Polyoxometalates Using Ionic Liquid Media**

Tsuyoshi Kohlgruber, Ph.D. Candidate

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College of Engineering

Advisor: Peter Burns, Henry Massman Professor, Department of Civil and Environmental Engineering and Earth Sciences; Concurrent Professor, Chemistry and Biochemistry; Director, Center for Sustainable Energy at Notre Dame (ND Energy); Director, NNSA Actinide Center of Excellence (ACE)

## **Abstract**

Nuclear power provides approximately 20% of the total electricity for the United States and over 50% of its clean energy. Uranium, the element that fuels nuclear power plants, was identified over two hundred years ago, yet its fundamental chemistry lags behind much of the other metals on the periodic table. Polyoxometalates (POMs) or metal oxide clusters represent a unique class of materials useful for studying fundamental structure-function properties given their varying shapes and sizes. While transition metal POM chemistry has enjoyed several decades of research and development, it was only 15 years ago that the first major family of actinide POMs was discovered. This family of actinide POMs requires the incorporation of the peroxide ligand, which is essential in providing the needed curvature in the formation of the distinct hollow caged nanocluster structure. While the chemistry of actinide peroxide POMs has developed significantly since their inception, there are very few actinide POMs lacking peroxide. The design and synthesis of peroxide-deficient actinide POMs remains a challenge, but two characteristics shared among the few examples in the literature include the presence of organics and/or transition metals. In this study we use organic-based salts, termed ionic liquids, in the synthesis of two novel hybrid actinide-transition metal POMs with unprecedented cluster architectures. These hybrid clusters can further coordinate with one another to form larger dimeric moieties and even extended structures. The solution speciation was probed to understand the formation mechanism and crystallization of these novel materials, which add to the rich and continually evolving chemistry of uranium.

## **Photoinduced Iodide Expulsion from Mixed Halide Perovskites**

Preethi Susan Mathew, Ph.D. Candidate  
Department of Chemistry and Biochemistry  
College of Science

Advisor: Prashant Kamat, Rev. John A. Zahm Professor of Science, Department of  
Chemistry and Biochemistry and Radiation Laboratory  
Concurrent Professor, Department of Chemical and Biomolecular Engineering

### **Abstract**

Light irradiation on a Mixed Halide Perovskite (MAPbBr<sub>1.5</sub>I<sub>1.5</sub>) film in contact with a solvent, in our case dichloromethane (DCM), results in selective expulsion of iodide from the film. We have explored the effect of A-site cation (Methyl ammonium, MA and Cesium, Cs) on the mobility of iodide ions in perovskite films. We have seen that with increasing Cs content in the A-site, the rate of photoinduced segregation decreases. The rate of iodide expulsion strongly depends on the rate of segregation. The role of A-site cation in iodide mobility in perovskite films is discussed in this poster.

# Computational Interrogation of Single-Site, Oxide-Supported Group 4 Metal Hydrides for Ethylene Oligomerization

Neha Mehra, Ph.D. Candidate

Department of Chemical and Biomolecular Engineering  
College of Engineering

Advisor: William Schneider, Dorini Family Chair of Energy Studies and Department Chair, Department of Chemical and Biomolecular Engineering  
Concurrent Professor, Chemistry and Biochemistry

## Abstract

Molecular complexes of group-IV metals (M= Ti, Zr, Hf) are well known Ziegler-Natta catalysts for ethylene polymerization. As heterogeneous catalyst, they are synthesized as single site, M(IV)hydrides on oxide supports. The support plays the role of a ligand that can tune their ability of C-C coupling and C-C cleavage. This is seen for zirconium hydride anchored on silica-alumina as it dimerizes 2-butene with remarkable selectivity. Today, increase in shale production has made oligomerization of inert ethylene to more valuable oligomers (C<sub>4</sub>-C<sub>12</sub>) an avenue of immense importance. Our goal is to provide molecular level insights on the catalytic performance of group-4 metal hydrides supported on silica and silica alumina for ethylene oligomerization using periodic Density Functional Theory (DFT). In this work, representative site models of monohydride (SiO)<sub>3</sub>MH and dihydride (SiO)<sub>2</sub>MH<sub>2</sub> sites are built on (111) and (001) surface of  $\beta$ -cristobalite, a silica polymorph. Metal hydrides anchor onto the surface oxygen atoms by replacing the protons. We follow the Cossee-Arman mechanism for ethylene dimerization to 1-butene. The kinetics and energetics of the three key steps, (1) C<sub>2</sub>H<sub>4</sub> insertion into M-H bond, (2) C-C coupling by insertion into M-C bond and (3) release of 1-butene by  $\beta$ -H transfer to M are compared. Further, to investigate the role of Lewis acidic Al as in silica-alumina we systematically substitute a Si(+4) with Al(+3)/H(+1) in the silica model to form (SiO)<sub>2</sub>(AlOH<sup>+</sup>)MH site. The oligomerization behavior of Ti, Zr and Hf hydride sites on silica (no Al) and Zr-monohydride on 1Al/silica is compared based on rates and average degree of polymerization (DOP) obtained from DFT computed kinetic parameters. Amongst the metals, Ti has the highest C-C coupling barrier compared to Zr and Hf, irrespective of the hydride. The DOP analysis shows that Zr and Hf hydrides on silica make longer chains, while Ti has the potential of more controlled chain growth. The trend in DOPs is also reflected in turn over frequencies (TOF) as Zr  $\geq$  Hf > Ti making Zr-hydrides most active for ethylene chain growth. Presence of Al in the vicinity of Zr-monohydride (1Al/silica) does not significantly change the TOF of the site having no Al but the chain length of the oligomers is reduced by more than an order of magnitude. These predictions are in agreement with experimental observations where reaction of ethylene over Zr-hydrides on silica alumina produces higher fraction of C<sub>4</sub>s, followed by C<sub>6</sub>+ range hydrocarbons. The microscopic details and reactivity comparisons in this work aid in catalyst development under different reaction conditions. This approach can be used to expand the material space by screening other 4+ metals for oligomerization.

# **Magnesium ion conduction in dual cation exchanged poly(ionic liquid)s electrolytes**

Bumjun Park, Ph.D. Candidate

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College of Engineering

Advisor: Jennifer Schaefer, Assistant Professor, Department of Chemical and Biomolecular Engineering

## **Abstract**

Demand on large scale electrochemical energy storage has increased with advances in electric vehicles and energy storage systems for renewable energy. Magnesium is one of the desired metal anode materials for such energy storage devices due to its abundance and high theoretical volumetric capacity. Due to the highly reductive nature of magnesium metal, however, common liquid electrolytes can be decomposed to form passivate layers. Poly(ionic liquid)s can avoid this challenge with the high electrochemical stability of the polymer matrix and tethered anions on the polymer backbone, which can reduce anion decomposition on the electrode surface. Here we introduce poly(ionic liquid)s-based magnesium conducting electrolytes with magnesium and organic cations. Ion transport, thermal and structural characterization will be discussed in various molar ratio of magnesium/organic cations. Magnesium deposition is investigated via electrode polarization experiments and scanning electron microscopy (SEM)-energy dispersion X-ray spectroscopy (EDS). Sporadic magnesium deposition was observed on a copper electrode after electrode polarization for 20 hours at 80 °C, indicating successful magnesium transport in the poly(ionic liquid)s electrolyte.

# **Thermodynamic and Molecular Descriptors of Sensible Heat Driven Liquid-Liquid Phase Separation**

Zachary Tucker, Ph.D. Candidate  
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College of Science

Advisor: Brandon Ashfeld, Associate Professor, Department of Chemistry and Biochemistry

## **Abstract**

The process of separating chemical mixtures into pure materials through phase-change is utilized for a broad spectrum of multicomponent combinations. Industrial methods of purification including distillation, evaporation, and drying are responsible for an estimated 15% of global energy consumption, and are responsible for generating roughly 100 million metric tons of carbon dioxide in the United States annually. The principle factor which dictates the thermodynamic efficiency of phase-change separation processes, is latent heat of vaporization, which varies depending on the chemical substance and leads impediments on phase-change based separation. Although, gradual advancements in equipment and methodology have led to more efficient purification processes, fundamental changes in the mechanism of separation itself are underutilized, and represent the greatest opportunity to radically improve the efficiency of separation processes. The exploitation of upper critical solution temperature (UCST) and lower critical solution temperature (LCST), constitutes a conceptual alternative to existing approaches for the design of considerably more energy efficient separation processes. By definition, mixtures which exhibit UCST remain miscible above the critical temperature, while LCST exhibiting solutions are miscible under the critical temperature. Thus, allowing one to perturb the miscibility of a mixture through either heating or cooling. Furthermore, the temperatures at which UCST/LCST behavior is observed, often only require sensible heat for operation and are frequently an order of magnitude less than the latent heat of vaporization. Ionic liquids (ILs) have demonstrated exceptional promise as a molecular framework for the development of task-specific fluids due to their design flexibility and inherently low volatility. Notably, ILs are comprised of organic or inorganic ions and reside in a liquid state between room temperature and 100 °C. A multitude of ILs have shown promise as working fluids across a variety of applications including: separation of organic compounds, sequestration of transition metals, carbon dioxide capture, purification of aqueous media, as well as UCST/LCST behavior. However, the primary challenge in implementing UCST/LCST for phase separation remains the delineation of the molecular structural parameters responsible for the temperature and concentration dependent critical behavior, as well as the elucidation of the thermodynamics of the solution. In collaboration with the Moghaddam group of the University of Florida, we have enlisted a joint approach including experimental and computational methods to study the fundamental molecular interactions which dictate LCST/UCST phase separation of binary IL-mixtures. Experimentally, our efforts have verified and discovered several LCST/UCST exhibiting fluids which have been studied via variable temperature (VT) mass spectroscopy (MS) and VT nuclear magnetic resonance (NMR) spectroscopy. While computationally ab-initio simulations, statistical mechanics, and classical thermodynamic were utilized to model the binary IL-mixtures. Our joint efforts have resulted in the successful prediction of the critical physical properties of phase separation temperatures and concentrations for 50 solute-solvent pairs exhibiting LCST/UCST behavior. Additionally, this approach allowed for the identification of those molecular structural features that influence the temperature and concentration dependent miscibility of multicomponent solutions.



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