

Chemistry Seminar Abstracts for Spring 2018

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Rhenium Silicides: Tailoring the Structures and Properties

Fei Wang, Dept. of Chem., Missouri State University

Abstract: Rhenium silicide, $\text{ReSi}_{1.75}$, is of interest due to its complex crystal structure and potential application as a thermoelectric material. Its crystal structure is closely related to molybdenum silicide, MoSi_2 . The off-stoichiometry, i.e. 1.75 instead of 2 for Si, is due to Si vacancies. These vacancies are orderly distributed in the crystal structure. By doping $\text{ReSi}_{1.75}$ with a third element, e.g. Al, we can tune the amount and also the arrangement of the vacancies, giving rise to an *incommensurate* crystal structure, which has to be expressed in a 4-dimensional superspace. Meanwhile, physical property measurements reveal that the doping also tunes the thermoelectric properties of $\text{ReSi}_{1.75}$, improving its isotropic ZT value. In this talk, I will present the crystal structures of $\text{ReSi}_{1.75}$ and its doped variants, rationalize the adjustability of the crystal structure with first-principle calculations, and discuss the relationship between structure and improved thermoelectric properties.

Water-Rock Interactions in Alluvial Aquifer Systems

David Borrok, Dept. of Geosciences & Geological & Petroleum Engineering , MS&T

Abstract: Shallow, geologically-young (alluvial) aquifer systems are critical sources of freshwater for irrigation, drinking, and industry in the U.S. and globally. Many of these aquifers are under pressure from increasing demand and from natural and anthropogenic sources of contaminants such as arsenic (As). The inorganic chemistry of groundwater can be used as a powerful tool to help elucidate reaction pathways, areas of surface water recharge, mixing of fluids, and the cycling of contaminants. This talk will examine case studies of the use of inorganic geochemistry to characterize two alluvial aquifers in Louisiana; (1) The coastal Chicot aquifer system, and (2) The Lower Mississippi River Alluvial aquifer system. In both studies we collected data on pH, T, salinity and bulk geochemical parameters (concentrations of major and some trace cations and anions) from 20 to 25 wells in each aquifer system. These data were supplemented with the analysis of O and H isotopes. Using the geochemical data we were able to identify zones of recharge, including rainfall and infiltration from rivers. Relationships between Na and Cl concentrations were key to identifying areas in the aquifers influenced by salt water intrusion or mixing with brines. We also identified important water-rock reaction pathways resulting in “excess Na” or water in which the Na cation is in excess of the Cl anion and is counterbalanced by bicarbonate. In the Lower Mississippi River Alluvial Aquifer this reaction pathway appears to be driven by dissimilatory Fe reduction, which is further linked to the cycling of arsenic in the aquifer. The results from this work demonstrate the utility of geochemical analyses to better understand the dynamics of alluvial aquifer systems and how, why, and where we are likely to have problems with arsenic contamination.

Soft Chemical Route to Polyanion-based Cathode Materials for Alkali-ion Batteries

Prashanth Sandineni, Dept. of Chem., MS&T

Abstract: Efforts are underway to synthesize low-cost, efficient and environmentally benign cathode materials for Li- and Na-ion batteries. Polyanion-based compounds of transition metals have been actively investigated as cathode materials for Li-ion batteries since the discovery of electrochemical activity in LiFePO_4 . The polyanions, especially phosphates, sulfates, silicates and borates are capable of forming a wide variety of 2-dimensional (2D) and 3-dimensional (3D) structures with transition metals, which are stable and amenable for facile electrochemical Li-ion insertion. There are several other advantages of polyanion based materials over simple oxides. The electronegativity of the central atom of the polyanion due to its inductive effect increases the potential of the transition metal redox couple $\text{M}^{n+} / \text{M}^{(n-1)+}$ with respect to Li^+ / Li compared to pure oxides. Secondly, the polyanion-based cathodes are inherently safer due to the strong covalent bond between the central atom (P, Si, S, and B) and the oxygen, which prevents them from dissociation when the cell is fully charged or fully delithiated.

The presentation will include the syntheses, structure determination and the electrochemical properties of Jarosite and new iron phosphate phases. Jarosite is the mineral name of the compounds with general formula $A\text{Fe}_3(\text{SO}_4)_2(\text{OH})_6$ ($A = \text{NH}_4, \text{Na}, \text{K}, \text{H}_3\text{O}$). Sodium and ammonium Jarosites were synthesized employing hydrothermal routes and partial fluorine substitution has been achieved through a solution mediated route. New iron phosphate phases include synthesis of $\text{NaFe}(\text{HPO}_4)_2$ and its subsequent conversion to $\text{Li}_3\text{Fe}(\text{PO}_4)_2$ through an intermediate phase, $\text{Li}_2\text{Fe}(\text{HPO}_4)(\text{PO}_4)$. Both solution and mild condition solid-state ion-exchange routes have been employed to obtain the lithiated phases and their structures have been solved from high-resolution synchrotron powder X-ray diffraction data. Detailed electrochemical investigation of these phases will be discussed with respect to Li- and Na-ion insertions.

Are there Martians in Australia? How Acid Saline Lakes Can Serve as a Mars Analog

Melanie Mormile, Dept. of Biological Sciences, MS&T

Abstract: For as long as there have been telescopes, people have long wondered if there is life on Mars. With the confirmation of the presence of water on Mars, this question can be seriously considered. The acidic saline lakes of Australia can serve as analogs for previous bodies of water on Mars due to similar geochemical features. The microbial communities in these extreme sites can provide targets for the investigation of the possible presence of life on Mars.

Surface-functionalized Mesoporous Carbons for Electrochemical and Hydrogen Storage Applications

Eric Majzoub, Dept. of Physics, UMSL

Abstract: Energy storage materials for transportation applications and consumer electronic devices require (1) high energy density, (2) fast kinetics, and (3) reversibility. It is also desirable that they be environmentally friendly and inherently safe. For electrochemical applications, high surface area materials with both an electric double layer and a faradaic response are currently receiving attention for pseudo- and super-capacitors. For hydrogen storage applications, confinement of "complex hydrides" into nanoporous scaffolds is a powerful method to control the chemistry of the decomposition and rehydriding reactions; even thermodynamics may be modified by through the hydride/surface interactions. Our group synthesizes and investigates high surface area carbon materials with highly ordered nanoscale morphologies for these energy-related applications. Amorphous hard carbons with nanoscale morphology are easily prepared using a variety of self assembly methods or nanocasting. These carbon scaffolds may be functionalized through the addition of heteroatoms during the synthesis or with the introduction of functional groups afterwards. We will present results for two different projects in our group. The first focusing on carbon scaffolds for lithium-ion applications and the second for hydrogen storage applications. Nanoporous amorphous carbons have a Li-ion capacity in excess of 800 mAh/g, far in excess of the capacity of the LiC_6 formed in graphite anodes, suggesting that it may be possible to plate metallic Li directly into the pore structure of the carbons and mitigate the dendrite problem that precludes the use of metallic lithium itself. Finally, for hydrogen storage applications we will show results for the infiltration of alane (AlH_3) in the form of dimethylethylamine (DMEAA) into a functionalized scaffold where Lewis-acid/base interactions with the surface stabilize the alane. Time permitting we will discuss the effects of nanoconfinement on other complex hydrides.

Combinatorial Synthesis of High-efficiency Transition Metal Selenides as Oxygen Evolution Electrocatalysts

Xi Cao, Dept. of Chem., MS&T

Abstract: Water electrolysis has become a crucial part of sustainable, clean energy generation and it has become very imperative to discover highly active electrocatalysts composed of earth-abundant materials for the oxygen evolution reaction (OER), the most challenging half-cell reaction for water electrolysis. Combinatorial method has been reported to provide an efficient way to screen and discover material composition for promising OER electrocatalysis. Here, we have investigated a series of binary and ternary mixed metal selenides containing varying compositions of nickel, iron/copper, and cobalt as potential OER electrocatalysts. Specifically, ternary phase diagrams of Ni-Co-Fe and Ni-Co-Cu systems were explored through combinatorial electrodeposition and their OER electrocatalytic activity was measured in order to systematically

investigate the trend of catalytic activity as a function of catalyst composition. In our investigation, we have synthesized series of transition metal selenide films containing mixed metal compositions such as $(\text{Ni}_x\text{Fe}_y\text{Co}_z)_3\text{Se}_4$ and $(\text{Ni}_x\text{Cu}_y\text{Co}_z)_3\text{Se}_2$ utilizing electrodeposition technique on different conducting substrates including Au-coated glass and glassy carbon (GC). Accordingly, the quaternary composition(s) exhibiting the best catalytic efficiency for the quaternary Fe-Co-Ni selenide was identified. It was observed that the quaternary selenide outperformed the binary as well the ternary metal selenides in this phase space. The structure, morphology, and composition of these new electrocatalysts were characterized by power X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM) and Energy dispersive analysis (EDS). The catalytic activities were studied through electrochemical measurements in alkaline media using the linear sweep voltammetry (LSV) and cyclic voltammetry (CV), while the stability of the catalyst was probed by chronoamperometric studies at a constant potential.

Photoelectrochemistry of Nanostructure/Ultrathin Electrodeposited Metals on n-Silicon

Qingzhi Chen, Dept. of Chem., MS&T

Abstract: The photoelectrochemical conversion of solar energy into fuels or electricity requires a semiconductor to absorb light and generate electron-hole pairs, and a catalyst to enhance the kinetics of electron transfer between the semiconductor and solution. In photoelectrochemical cells containing reactive semiconductors such as Si, the catalyst can also serve to protect the semiconductor from passivation caused by the formation of a thick SiO_x interfacial layer. Herein, we explore the use of electrochemically deposited Co nanowire(NW)s and ultrathin Au on n-Si to serve as the protection layer and the catalyst for aqueous photoelectrochemical reactions. In the case of Co NWs, the oxygen evolution reaction (OER) was studied. And the Au deposited on Si was used as a catalyst for $\text{Fe}^{2+/3+}$ redox reaction in a regenerative photoelectrochemical cell. The band-bending, in other words, the barrier heights were measured and found to be determined by the Si-metal junction. Furthermore, the coverage of Au on Si was also found to have an effect on the photovoltage of the cell: There was a decrease in the barrier height from 0.81 to 0.73 eV as the gold coverage was increased from island growth with 10% coverage to a dense Au film with a thickness of 11 nm. We also proved that there is a trade-off between the cell efficiency and the stability, which happens commonly among photoanode materials.

From Food Pathogen to Cancer Immunotherapy: An Update on Research Advances in *Listeria Monocytogenes*

Chen Chen, Dept. of Plant & Microbial Biology, University of California- Berkeley

Abstract: *Listeria monocytogenes* is a Gram-positive food-borne facultative intracellular bacterial pathogen that can cause serious foodborne infections in immunocompromised individuals and pregnant women. *L. monocytogenes* has been extensively studied as a model intracellular pathogen, which led to several important fundamental discoveries in pathogenesis, and has been developed as a vaccine vector for the delivery of therapeutic cancer vaccines. Using bacterial genetic, synthetic chemical probe, and basic cell biological tools, my previous studies had advanced the understanding of the superior immunogenicity of *L. monocytogenes* and proposed a new strategy for the future *L. monocytogenes*-based cancer immunotherapy.

Prebiotic Astrochemistry in the THz Gap

Susanna Widicus-Weaver, Dept. of Chem., Emory University

Abstract: Small reactive organic molecules are key intermediates in interstellar chemistry, leading to the formation of biologically-relevant species as stars and planets form. These molecules are identified in space via their pure rotational spectral fingerprints in the far-IR or terahertz (THz) regime. Despite their fundamental roles in the formation of life, many of these molecules have not been spectroscopically characterized in the laboratory, and therefore cannot be studied via observational astronomy. The reason for this lack of fundamental laboratory information is the challenge of spectroscopy in the THz regime combined with the challenge of studying unstable molecules. Ions, radicals, and small reactive organics tend to be produced in trace quantities, often at high energies, and therefore have weak laboratory spectra. In addition, THz spectrometers have historically lagged behind those in other wavelength regimes because of a lack of sources and detectors that provide the power and sensitivity needed for such studies. The laboratory astrochemistry portion of my research program combines innovative spectroscopic approaches that seek to increase spectral sensitivity in the THz regime with novel chemical production mechanisms for species of astrochemical interest. Our laboratory work involves characterization of astrophysically-relevant unstable species, including small radicals that are the products of photolysis reactions, organic ions formed via plasma discharges, and small reactive organics that form via O(1D) insertion reactions. In this seminar, I will present recent results from our laboratory studies, and discuss these results in the broader context of my integrative research program that encompasses laboratory spectroscopy, observational astronomy, and astrochemical modeling.