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Agenda

Thursday, September 6

12:00 - 2:00 pm	Arrival and registration
2:00 - 3:00 pm	MEM-C/CEU Entrepreneurship Workshop
3:00 - 4:00 pm	Concurrent Sessions IP Patent Briefing PowerPoint animation Resume/mock interview Science Communication
5:00 - 6:00 pm	Dan Schwartz, Clean Energy Institute *The Clean Energy Institute and Energy Research at the University of Washington*
6:00 - 7:30 pm	Dinner
7:30 - 9:00 pm	Poster session 1

Friday, September 7

7:45 – 8:15 am	Breakfast

Session 1: Batteries and Electrochemical Processes

8:30 - 9:05 am	Steve Reece, Lockheed Energy *Coordination Chemistry Flow Battery*
9:05 - 9:40 am	Fikile Brushett, Massachusetts Institute of Technology *Materials design criteria for next-generation redox flow batteries*
9:40 - 10:15 am	Curtis Berlinguette, University of British Columbia *Converting CO2 into something useful*
10:15 - 10:35 am	Break
10:35 - 11:10 am	Gerald Meyer, University of North Carolina *The Influence of Electronic Coupling on Electron Transfer and Electrochemical Energy Storage*
11:10 - 11:45 am	Joaquin Rodriguez Lopez, University of Illinois *Redox-Active Polymer Electrolytes: New Solutions for Size-Exclusion Flow Batteries*

11:50 am - 12:00 pm	Group picture
12:15 - 12:45 pm	Lunch
1:00 - 3:30 pm	Free time

Session 2: PV and Solar Photochemistry

3:40 - 4:15 pm	Matt Law, University of California, Irvine *Charge Transport in Mesoscale Assemblies of Quantum Dots for Solar Energy Conversion*
4:15 - 4:50 pm	Daniel Kroupa, University of Washington *Lanthanide-Doped Quantum-Cutting Metal Halide Perovskites for Solar Energy Conversion*
4:50 - 5:25 pm	Giles Eperon, National Renewable Energy Lab *Halide perovskites - a game-changer for photovoltaics?*
5:25 - 6:00 pm	Cody Schlenker, University of Washington *Tales from the Darkside: ‘Forbidden’ transitions and non-covalent interactions in light-harvesting materials*

6:00 - 7:30 pm	Dinner

Session 3: Keynote Lecture

7:30 - 8:30 pm	Harry Atwater, California Institute of Technology *Fueling Human Progress with Sunlight*
8:30 - 10:00 pm	Poster Session 2

Saturday, September 8

7:45 - 8:15 am	Breakfast

Session 4: Power Systems and Energy Markets

9:00 - 9:35 am	Goran Strbac, Imperial College London
9:35 - 10:10 am	Chongqing Kang, Tsinghua University *Cloud Energy Storage in Low-carbon Energy System*
10:10 - 10:30 am	Break
10:30 - 11:05 am	Qixin Chen, Tsinghua University *The path towards spot power market in China*
11:05 - 11:40 am	Christine Chen, University of British Columbia

Dynamic Contingency Analysis in Electric Power Systems

12:00 - 1:00 pm Lunch and group departure

Speaker Abstracts

The Clean Energy Institute and Energy Research at the University of Washington

Dan Schwartz
University of Washington

Batteries and Electrochemical Processes:

Coordination Chemistry Flow Battery

Steve Reece
Lockheed Energy

The Lockheed Martin Coordination Chemistry Flow Battery (CCFB) enables affordable, durable, and safe long-duration energy storage for utility-scale projects. Built upon metal ligand coordination complexes, CCFB electrolytes enable a simple and reliable system design, providing stable performance and long service life. Taken together, the CCFB system is a large step forward in flow battery technology evolution. Significant improvements in performance and cost reduction have been enabled through a system-level optimization effort with design resolution down to the molecular level of the battery chemistry. As such, the technology is well positioned to add significant commercial value in long-duration grid energy storage applications.

Materials design criteria for next-generation redox flow batteries

Fikile Brushett
Massachusetts Institute of Technology

Electrochemical energy storage has emerged as a critical technology to enable sustainable electricity generation by alleviating intermittency from renewable sources, reducing transmission congestion, enhancing grid resiliency, and decoupling generation from demand. Redox flow batteries (RFBs) are rechargeable electrochemical devices that store energy via the reduction and oxidation of soluble active species, which are housed in external tanks and pumped to a power-generating reactor. As compared to enclosed batteries (e.g., lithium ion), RFBs offer an attractive alternative due to decoupled power and energy, long service life, and simple manufacturing, but have not yet achieved widespread adoption because of high prices.

Recent research has focused on the discovery and development of new chemistries. Of particular interest are low cost organic molecules and nonaqueous electrolytes with wide electrochemical windows, since decreasing materials cost and increasing cell potential offer credible pathways to lowering battery prices. Though exciting, most of these emerging concepts only consider new materials in isolation rather than as part of a battery system. Understanding the critical relationships between material properties and overall battery price is key to enabling systematic improvements in RFBs. In this presentation, I will discuss chemistry-agnostic design principles for economically-viable RFBs realized through the combination of techno-economic modeling, reactor optimization, and materials analysis. This approach emphasizes the fundamental differences in cost reduction strategies for aqueous and nonaqueous RFBs, specifies design criteria for future materials, and highlights new research avenues for the energy storage community.

Converting CO2 into something useful

Curtis Berlinguette
University of British Columbia

The electrochemical conversion of CO2 provides a platform for utilizing inexpensive renewable electricity to convert waste greenhouse gasses into products of value. CO2 electrolyzer technologies are, however, in their infancy compared to water electrolyzers. This presentation will outline our development of gas and liquid phase flow cells (i.e, lab scale pilot cells) that show how CO2 can be converted into products at the high current densities needed for commercialization.

The Influence of Electronic Coupling on Electron Transfer and Electrochemical Energy Storage

Gerald Meyer
University of North Carolina

Electron transfer theories predict that an increase in the quantum mechanical mixing of electron donor and acceptor wavefunctions (HDA) at the instance of electron transfer will lower the absolute value of the Gibbs free energy change. Kinetic and equilibrium studies of acceptor-bridge-donor (A-B-D) compounds anchored to TiO2 thin films provide experimental validation of this prediction. Optical studies revealed that even when the bridge identity was fixed, the pathway for electron transfer was dependent on the direction of electron flow. In unpublished work, the free energy barriers for electron transfer were found to be nearly insensitive to the magnitude of HDA. The implications of these results for vectoral electron transfer and energy storage will be discussed.

Redox-Active Polymer Electrolytes: New Solutions for Size-Exclusion Flow Batteries

Joaquin Rodriguez Lopez
University of Illinois

I will present on the intriguing electrochemical dynamics of highly-soluble Redox-Active Polymers (RAPs) and their colloidal forms, Redox-Active Colloids (RACs). These are a new class of materials with applications in energy storage in the form of fluid dispersions that support a new concept in size-exclusion flow batteries that was introduced in our laboratory. Despite RAPs displaying excellent charge storage properties, their complex electrochemical reactive pathways are just becoming elucidated. RAPs and RACs rely on intra-particle electron transfer to yield quantitative charge accessibility and high rate in order to achieve full electrolysis. Charge mobility via inter-pendant electron hopping combines with their polyelectrolyte nature to exhibit a rich electrochemical behavior that is strongly modulated by specific and non-specific interactions with the electrolyte, by the packing of the polymer chains, and by the structure of the polymeric backbone. In this talk, I will highlight the impact of several variables on the electrochemical signatures created by RAPs and RACs and how we have elucidated them using a combination of spectroscopic, viscometric, and nano-electrochemical approaches.

The mechanistic characterization of RAPs and RACs requires a spectrum of powerful electrochemical techniques, ranging from bulk methods to single-particle analysis. I will describe how the application of nano-resolved electrochemical microscopy techniques and Raman spectroscopy has helped us understand the mechanisms of individual electrochemical entities. These experiments provide us with unprecedented versatility to identify kinetic bottlenecks, such as charge trapping, and to determine the maximum current densities attainable in flow devices. Altogether, the combination of novel structural motifs, the identification of structure-reactivity relationships, and the use of advanced electrochemical techniques, results in new directions to make better polymers that exploit the versatility of this new type of reacting fluids for energy storage and conversion.

PV and Solar Photochemistry:

Charge Transport in Mesoscale Assemblies of Quantum Dots for Solar Energy Conversion

Matt Law
University of California - Irvine

Colloidal semiconductor quantum dots (QDs) are attractive building blocks for next-generation solar cells, photodetectors, and other optoelectronic devices. In this talk, I will highlight our recent progress in understanding, improving, and controlling charge transport within mesoscale assemblies of PbSe QDs, with the aim of creating a new class of materials that combine the size-tunable photophysics of QDs with the excellent electronic properties of bulk semiconductors. I will begin by reviewing QD film fabrication, charge transport processes, and evidence that the carrier diffusion length is short and limited by electronic states in the QD band gap. The use of atomic layer deposition (ALD) infilling to functionalize the internal surfaces and interfaces of QD films will be introduced as a powerful “matrix engineering” approach to optimize coupling, remove surface states, eliminate hysteretic charge trapping and ion motion, and achieve long-term environmental stability for high-performance, robust QD films. This approach has been applied to achieve record-performance XSWIR photodetectors based on big PbSe QDs. I will highlight our use of infrared transmission spectroscopy to understand state filling and ligand electronic effects to tune the band edge energies and doping of QD films. A central challenge in this field is to achieve the delocalization of electronic wavefunctions and formation of bulk-like electronic bands (“mini-bands”) in highly-ordered, highly-coupled QD superlattices (i.e., crystals of QDs). I will present recent results and prospects for single-crystalline epitaxially-fused QD superlattices that are self-assembled on liquid substrates.

Lanthanide-Doped Quantum-Cutting Metal Halide Perovskites for Solar Energy Conversion

Daniel Kroupa
University of Washington

Recent advances in lanthanide doping of CsPbX3 (X = Cl, Br, I) perovskites have opened exciting new opportunities for their application as spectral downconverters in solar energy conversion technologies. Here, we describe the preparation of lanthanide-doped CsPbX3 materials and, through a combination of variable-temperature and time-resolved spectroscopy, we detail the energy transfer mechanism between the semiconductor host and dopant center. We highlight ytterbium-doped materials, which show near-infrared PLQYs as high as 190% with near-zero excitonic luminescence. In this case, we show that the formation of shallow ytterbium-induced defects plays a critical role in facilitating a picosecond nonradiative energy-transfer process that de-excites the photoexcited semiconductor while simultaneously exciting two ytterbium dopant ions through the photophysical process of quantum-cutting. The application of these materials as solar downconverters for next-generation photovoltaics will be discussed.

Halide perovskites - a game-changer for photovoltaics?

Giles Eperon
National Renewable Energy Lab

The cost of generating electricity from silicon solar panels has continued to drop in recent years, in some locations already being the cheapest way of generating power. The cost of installing solar panels is now limited by non-module costs which cannot easily be reduced, such as frames, transportation, power handling and installation. Thus, the best way to reduce the cost of generating power is to make each module more efficient. However, silicon modules are approaching their practical maximum efficiencies, so to move beyond this will require new technologies.

Perovskite halides have emerged in the last five years as an extremely promising material for solar energy conversion, with efficiencies rising from 4% to over 23% in that time frame. These are low-cost solution-processable semiconductors with bandgap tuneable between 1.2 and 3eV by the choice of specific components of the crystal lattice. A typical perovskite solar cell consists of a thin film of the perovskite material sandwiched between p-type and n-type selective contacts.

Here I will introduce the perovskite technology, briefly discuss how it has evolved over the last few years and explain why perovskites have generated so much interest in the scientific community. I will focus on the recent progress we have made in demonstrating all-perovskite tandems, which leverage the wide range of bandgaps for perovskites to stack two perovskite layers absorbing different parts of the solar spectrum, thus minimizing energy losses. These offer the potential for realistic efficiencies of almost 30% while retaining the benefits of low-cost material and processing of the perovskite. We have already reached efficiencies of over 19%, and importantly have demonstrated robust thermal and operational stability of the tin-containing low bandgap perovskite.

Tales from the Darkside:
'Forbidden' transitions and non-covalent interactions in light-harvesting materials

Cody Schlenker
University of Washington

From charge trapping in semiconductors to exciton fission/annihilation to photocatalytic water splitting, optically dark states and non-covalent interactions can dramatically influence the behavior of light-harvesting materials. One specific example that I will discuss from our laboratory involves photon-initiated homolytic cleavage of hydrogen/oxygen bonds of water in an inter-molecular heptazine:H2O complex.

Heptazine-based materials, including graphitic carbon nitride and poly(heptazine imides), are garnering increasing attention due, in part, to their improving photocatalytic hydrogen evolution activities (approaching 0.04 mol h-1 g-1, with apparent quantum yields above 34%). As such, there has been a recent focus on understanding the photochemistry of these materials. One major roadblock that has impeded those mechanistic studies is the chemically-ambiguous nature of the bulk carbon nitride active material. We have combined time-resolved photoluminescence (TR-PL) spectroscopy and computational chemistry to reveal upper excited-state dynamics that engender inter-molecular proton-coupled electron transfer (PCET) from water to a structurally-distinct small-molecule heptazine photocatalyst. To the best of our knowledge, this is the first direct spectroscopic evidence that the heptazine unit drives H-atom abstraction from water by PCET. This result yields rare spectroscopic evidence of an upper-excited state reaction pathway in a heptazine:H2O complex. This photoreaction exhibits a significant kinetic isotope effect (KIE) of 2.9, indicating homolytic O-H bond scission of water, and it liberates detectable hydroxyl radicals. Our results lay the groundwork for molecular design rules aimed at controlling organic photochemical reactivity by manipulating early-time photophysical dynamics. Photophysical and photochemical insight from our results can be leveraged in solar fuels research, photovoltaics, and LEDs.

Keynote Lecture:

Fueling Human Progress with Sunlight

Harry Atwater
California Institute of Technology

Research in nanophotonic materials and design is yielding advances that are opening conceptually new paths to address "grand challenges" that have not previously been achievable. One of these is the challenge of bringing next-generation solar energy technology to fruition. The recent rapid, global growth of solar photovoltaics has moved scientific research frontiers for solar energy conversion towards new opportunities such as i) high efficiency (η = 30% and beyond) photovoltaics and ii) direct synthesis of energy-dense chemical fuels from solar energy, including hydrogen and products from reduction of carbon dioxide. I will illustrate several examples of how photonic design combined with material synthesis advances can enable progress in each of these areas. Photonic design with highly luminescent semiconductors has opened new directions for ultrahigh efficiency photovoltaics. Semiconductors coupled to water oxidation and reduction catalysts have enabled approaches to >19% efficiency solar-to-hydrogen generation using artificial photosynthetic structures. Present work and future directions in electrocatalytic and photocatalytic materials for artificial photosynthesis aimed at catalytic reduction of carbon dioxide will also be discussed.

Power Systems and Energy Markets:

Goran Strbac
Imperial College London

Cloud Energy Storage in Low-carbon Energy System

Chongqing Kang
Tsinghua University

Energy storage is extensively recognized as a significant potential resource to facilitate low carbon power systems. Although small residential and commercial consumers of electrical energy can now purchase energy storage to store their rooftop PV and shift their electric load, many factors, such as cost, policy and control efficiency, limit the spread of distributed energy storage (DES). This talk will propose a new type of energy storage business model—cloud energy storage (CES). It is a grid-based storage service that enables ubiquitous and on-demand access to a shared pool of grid-scale energy storage resources. The talk will introduce the business model of CES and its economic analysis, as well as the control and communication technologies that are required for its implementation and its operating mechanism.

The path towards spot power market in China

Qixin Chen
Tsinghua University

This presentation will firstly discuss the background of market perform in China, focus on the motivations and the current progress. Secondly, I will conclude the major problems confronted, and discuss the necessities to establish spot market mechanism. Thirdly, I will introduce the aim and path for China's spot market reform, including the structure, mechanism, participants, coordination and sequences. Finally, I will briefly introduce the research incomes the contributions of our group.

Dynamic Contingency Analysis in Electric Power Systems

Christine Chen
Tsinghua University

Gradual displacement of turbine-based generators with inverter-interfaced renewable resources reduces total rotational inertia in the power system, leading to larger transients following a disturbance, such as the sudden loss of solar photovoltaic generation. This calls for the development of dynamic contingency analysis tools to predict whether or not the system will meet operational reliability requirements in case of outage in any one particular asset, a condition known as N-1 security. Leveraging a reduced-order power system dynamical model, we derive analytical closed-form expressions for time-domain functions that uncover the mapping from a generation-load

imbalance to (i) system frequency, (ii) synchronous-generator outputs, and (iii) transmission-line flows. These variables must remain within acceptable ranges to satisfy the N-1 security criterion. We demonstrate the accuracy of the closed-form solutions via simulations of standard IEEE test systems.

Poster Abstracts

Strain-Engineering of Luminescent Inorganic Nanostructures for Imaging Applications

Brittany Bishop

Quantum-confined semiconductor nanostructures that emit in the near-infrared (NIR) are desirable materials for both biological imaging and clean energy applications that require photon management in the NIR. Currently, there are several options for NIR emitters, ranging from dyes to quantum dots, but quantum yields remain limited in the NIR spectral range, with 30% only being achieved very recently. In addition, virtually all of the most efficient NIR nanomaterials contain toxic elements, such as cadmium and lead, making them unfavorable for biological or clean energy applications. Several alternative, less toxic materials are being investigated as new NIR emitters; however, these materials still exhibit abysmally low quantum yields. Here, we discuss strain-engineering strategies used to suppress the formation of interfacial defects, which can be detrimental toward the formation of efficient NIR-emitting colloidal nanostructures, with an overall aim of improving the quantum yields of non-toxic, colloidal NIR emitters.

Printed Optoelectronic Nanomaterials for Use in Antireflective Coatings and 2D Photonic Devices

Holly Brunner

Scalable nanomanufacturing of optical surfaces or “metasurfaces,” by a hierarchical print-based process could lead to new classes of low cost, ultrathin, photonics for applications in energy, information processing, and communication. The initial goal for this project was to develop silica nanostructured coatings to improve the durability and lifetime of photovoltaic (PV) cells; however the project scope has expanded to include printed 2D photonic devices as similar fabrication techniques can be used for both applications. A variety of materials have been investigated in an attempt to develop printed, ordered arrays of inorganic nanostructures in a range of sizes. Nanoimprinted silica sol-gels and slot-die printed self-assembled silica nanoparticles show promise as metasurfaces for the desired applications. Nanoimprinted sol-gels can be printed in structures that are specifically tailored to each application but challenges persist with imprint time and long-term durability. A monolayer of silica nanospheres functionalized with quartz-binding peptides only allows a specific geometry but the printing processes established in this project are highly compatible with existing manufacturing processes. Both methods result in coatings that drastically reduce the amount of reflected light, specifically at off-normal incident angles. Post printing surface modification of the nanostructures with a high resolution 3D printer is under active investigation. This will enable the shape of the printed nanostructures to be modified locally, allowing for a wider range of device applications. Optimizing these processes will significantly impact the field of printed anti-reflective coatings and optoelectronic devices while paving the way for fully printed 2D optical sensors.

Interfacial Electric Fields in Electrochemical Energy Storage

Emma Cave

Monitoring and manipulating interfacial electrostatics are critical challenges in electrochemistry that may have potential benefits for certain battery technologies. The presented work aims to better understand how local electric fields influence the charge transfer kinetics and electrolyte stability at such interfaces. We hypothesize that altering the interfacial electrostatic environment, either through changes in the electrolyte or electrode surface dipoles, could improve charge/discharge kinetics in rechargeable batteries. One model system that we will discuss is a titanium dioxide (TiO_2) electrode immersed in an electrolyte of perchlorate salt dissolved in acetonitrile. Additional work will focus on extrinsic TiO_2 modification to better understand the effect of surface dipoles on charge transfer kinetics in a real system. By changing the electrolyte concentration and composition, the interfacial electric field can be enhanced or diminished (screened) to varying degrees. Concentration dependence of lithium perchlorate ($LiClO_4$) was measured using cyclic voltammetry. As expected, improved coulombic efficiencies (ratio of charge extracted to charge injected) were observed with lowering concentrations. Bulk electronic spectroelectrochemistry measurements were used to monitor the trap state population as a function of applied potential. Binary perchlorate salt mixtures were studied to gain insight on the effects of charge screening and trap states. Increased screening by the introduction of a larger cation (tetratbutylammonium) into the $LiClO_4$ electrolyte resulted in lower trap state populations, possibly implying more efficient charge transfer kinetics. The current work will inform future studies using the vibrational Stark effect to quantify interfacial electric fields during device operation.

Controlled Oxidation of Phosphorene Using Molecular Oxidants

Christine Chang

Phosphorene, a 2-D layered material derived from the exfoliation of black phosphorus, presents promising applications in optoelectronics due to its high carrier mobility (400-4000 cm2V-1s-1; comparable to supported graphene) and direct, tunable band gap (0.3 – 2.1 eV, depending on layer thickness). However, phosphorene readily oxidizes under ambient conditions, preventing immediate practical use. Our work pursues the chemical modification of phosphorene with precursors using the chemistry of molecular phosphines as a guide, both protecting the surface against ambient degradation and creating an avenue for tuning their structural, chemical, and optoelectronic properties in a specific and controlled manner. The successful functionalization of phosphorene with a variety of organic precursors was characterized spectroscopically using vibrational spectroscopy, and surface characterization techniques (XPS, XES) were used to analyze surface coverage of the organic groups on phosphorene. By controlling the level of surface functionalization, we aim to use these results to produce materials which carefully balance stability against favorable optoelectronic properties.

Efficient Solutions of Poisson–Nernst–Planck (PNP) and Electroneutrality–Nernst–Planck (EN-NP) models for Lithium Symmetric Cells

Jerry Chen

One-dimensional Poisson–Nernst–Planck (PNP) model is used in the simulation of lithium symmetric cells. [Wood, 2016] However, the nature of the PNP equations entails a substantial computational effort to achieve acceptable accuracy. In this study, we proposed two approaches to solve the ion transport system efficiently but with a coarse grid. One is to solve the PNP model in the electroneutral limit (EN-NP), which yields an elegant analytical solution for concentration in a binary electrolyte formulation. The other is to use dimensionless groups and implement mass-conservative finite volume method to discretize the PNP system. Those proposed methods enable greatly simplify and speed up long cycle simulations and parameter estimation for electrochemical systems.

Novel design and use of redox-active inorganic cluster ligands for small molecule activation

Andrei Chirila

Inspired by solid-state heterogeneous catalysts and natural biological systems, cluster-based multi-metallic systems were developed as a novel class of complexes that target to activate small molecules and convert them to value-added chemicals by tuning the reactivity of the metal-ligand multiple bonded intermediates. The redox active clusters of choice feature the Co_6Se_8 core stabilized by L-type ligands (carbonyl, phosphines) coordinated at the cobalt sites. The use of aminophosphanes as ligands allowed us to introduce a secondary binding site for transition metals (Co, Fe) that are in close contact with the cluster (Co_6Se_8). The system can be regarded as a base metal coordination complex bearing a redox active inorganic ligand in the form of the Co_6Se_8 cluster. Similarly to an organic non-innocent ligand, the cluster acts as an electron reservoir capable of low energy barrier on-demand electron shuttling to the active site, due to the flexible interaction of the metal active site with the cluster. Moreover, the main advantage of the inorganic cluster compared to an organic backbone is that it can undergo up to four reversible redox events at minimum entropic cost allowing facile electronic tuning of the metal center in order to bind and activate small molecules.

Authors: Jerry Chen, Akshay Subramaniam, Tae-Jin Jang, and Venkat R. Subramanian

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Tandem-Like Luminescent Solar Concentrators with Quantum-Cutting Ytterbium-Doped $CsPbCl_{3(1-x)}Br_{3x}$ Nanocrystals

Theodore Cohen

Luminescent solar concentrators (LSCs) can concentrate diffuse solar radiation and reduce the overall area of silicon solar panels required to meet current energy demands. This technology requires emitters that absorb a large fraction of the solar spectrum, emit with high photoluminescent quantum yield (PLQY), and have an emission spectrum that does no overlap with the emitter’s absorption spectrum. Luminescent nanocrystals (NCs)with high effective Stokes shifts and near or above unity PLQY are well-suited to meet these needs. In this work, we describe a LSC based on quantum-cutting $Yb^{3+}:CsPbCl_{3(1-x)}Br_{3x}$ NCs with a NIR PLQY of 170%. We use a combination of solution-phase 1D LSC measurements and modeling to show that there are no reabsorption losses associated with $Yb^{3+}:CsPbCl_{3(1-x)}Br_{3x}$ NC based LSCs. We then extend this model to predict the flux gain of a new and unique tandem-like LSC that contains a $Yb^{3+}:CsPbCl_{3(1-x)}Br_{3x}$ NC based top layer and a CuInS/ZnS core-shell NC-based bottom layer, both within the same waveguide and interfaced with the same Si PV. Due to the exceptionally high PLQY of the $Yb^{3+}:CsPbCl_{3(1-x)}Br_{3x}$ NCs, this device has a projected flux gain of 82 for a 120 x 120 cm^2 device, which represents a 36% enhancement in performance over the optimized CuInS/ZnS LSC.

Ultrafast electron transfer cascade between carbon nitride photocatalysts found to improve hydrogen evolution

Katie Corp

Graphitic carbon nitride, a photocatalyst for hydrogen evolution, can be prepared via pyrolysis of inexpensive, metal-free precursors. Although the synthesis is straightforward, the structure is ambiguous and therefore the underlying photophysical and photochemical processes are not well understood. Here, we use visible and near-infrared femtosecond transient absorption spectroscopy to reveal an electron transfer cascade that correlates with a near doubling in photocatalytic activity when we infuse a suspension of bulk graphitic carbon nitride with chemically exfoliated carbon nitride. We provide unique insight based on global target analysis of the transient absorption spectra showing that exfoliated carbon nitride quenches photogenerated electrons on graphitic carbon nitride at rates approaching the molecular diffusion limit. This correlation between electron transfer and photocatalytic activity of oligomeric species suggests molecular heptazine-based photocatalysts could provide insight into the structure-function relationship for controlling charge separation dynamics and activity.

Incorporating GIS Data into a Predictive Maintenance Model for Hybrid-Electric Buses

Erica E. Eggleton, Daniel T. Schwartz

Maintenance protocols for most hybrid-electric bus fleets are currently ineffective due to unpredictable battery service requirements. We are developing a predictive maintenance algorithm that combines physics-based and data science approaches that are parameterized by variables such as road grade, stop-start frequency, velocity, acceleration, age, and weather conditions during operation. A battery and vehicle model is proposed that utilizes geographic information system (GIS) data to predict the state of health of lithium-ion battery packs in vehicles based on the real-time GIS data available through the open source OneBusAway API. This poster focuses on the protocol for extracting and filtering road elevation data to determine road grade. Ten-meter resolution LiDAR elevation data is processed for multiple bus routes in the Seattle area. The data is filtered and fitted to create a more accurate representation of the road surface. With this data, bus routes are compared and ranked in order of strain on the battery. Incorporating this model into a fleet management system can help transportation companies better predict when batteries need to be replaced and help create more efficient routes.

Frequency-Resolved Evaluation of Electrode Oxidation State of La0.6Sr0.4CoO3 Thin Films with operando XAS

Brian Gerwe

Commercial adoption and implementation of renewable, but intermittent, energy sources relies on a new generation of high performance energy conversion and storage devices, such as solid oxide fuel cells (SOFC) and solid oxide electrolysis cells (SOEC). Performance of the oxygen electrode in SOFC is a limiting factor; however, improvements are hindered by inadequate understanding of reaction mechanisms, and transport pathways. Conventional techniques rely on model interpretation of voltage and current response, but generally lack chemical speciation measurements that are required to uniquely understand reaction mechanisms.

In recent years, workers have developed in operando X-ray absorption spectroscopy (XAS) to study oxygen chemical potentials in SOFC cathodes under operating temperatures and Po2. In this material, oxygen vacancies, which are tied to oxygen chemical potential, are compensated by the valence state of transition metal which is detected as shifts in the X-ray absorption edge. So far, operando XAS has only been measured under DC polarization, and thus lacked the ability to probe processes of different timescales [1]. In this work, we extend operando XAS to AC impedance measurements and confirm that oxygen vacancy kinetics are directly related to the impedance of dense La0.6Sr0.4CoO3 thin films. Furthermore, we apply this technique to patterned thin films to measure frequency-resolved oxygen vacancy profiles extending from an electrode/electrolyte interface. Ultimately, we intend to apply this approach to nonlinear harmonic responses in pursuit of unambiguously determining reaction mechanisms and oxygen vacancy transport pathways in La0.6Sr0.4CoO3 electrodes.

Modeling photothermal imaging of metal nanoparticle aggregates

Harrison Goldwyn

There has been recent interest in the ability of plasmonic metal nanoparticles to capture and convert solar energy into electrical power. The utility lies in the strongly localized near fields surrounding the plasmon resonance with frequency response tunable with nanoparticle geometry. But attempts to integrate plasmonic nanoparticles into photovoltaic devices have suffered from efficiency losses as the plasmon resonance decays into incoherent electronic excitations and heat. Resolving this issue, new schemes have been proposed to convert thermal energy in absorbing metal nanoparticles into electrical current. But this nanoscale heat engine is limited by the Carnot efficiency and requires extreme temperature differentials between neighboring nanoparticles.

Fortunately, hybridized plasmon resonances provide both sharp spectral features and localized nanoscale heating. Hybrid modes can absorb more light then the sum of each component alone, while localizing the electronic excitation and subsequent heat dissipation to one particle in the aggregate. This localization of heat generates a steady state temperature distribution with hot spots confined to sub-diffraction limited regions. Photothermal imaging allows direct observation of the temperature distribution around nanoparticle aggregates, but at present quantitative extraction of temperature is complicated by a lack of understanding the role of interference effects. To understand the mapping of local temperature to photothermal signal, I present a simple analytical model to relate trends in the photothermal observable to basic physical properties of a nanoparticle aggregate supporting hybridized plasmon modes.

Electricity Market Equilibrium Analysis Integrating Risk-Averse: A Modified Refinement Approach

Hongye Guo

Since many electricity markets in the world are in the process of institutional change, the importance of the power market equilibrium analysis tools become more prominent. This paper fully considers the various risk averse characteristics of different kind of market participants and proposes a bilevel Nash equilibrium model to practically simulate market behaviors. The mathematical model is essentially a modified equilibrium problem with equilibrium constraints (EPEC). The upper level problem of the model maximizes the profits of each Genco with the consideration of bidding risks, while the lower level problem represents the market clearing processes of day-ahead markets. The bidding risk is mainly caused by the uncertainty of load, which is expressed by multiple scenarios. The conditional value at risk method is introduced into the model for managing the risk due to uncertainties. Based on the supply utilities with consideration of bidding risks, a modified market equilibrium refinement objective function is proposed to determine the more real and appropriate market equilibrium solution among all. The proposed bi-level model is transformed as a quasi-mix-integer linear problem model and solved by a novel iterative framework. Case studies and comparison with conventional equilibrium refinement approaches are performed to show the effectiveness, advancements and adaptabilities of the proposed model.

Nonlinear electrochemical impedance for lithium-ion batteries

Victor Hu

Nonlinear electrochemical impedance spectroscopy (NLEIS) can be used as a natural extension to traditional EIS by applying moderate-amplitude perturbations that excite weakly nonlinear responses. While EIS can provide whole-cell diagnostics for many kinetic, transport, and thermodynamic phenomena, it is inherently limited because it restricts any system to behave in the linear regime. However, increasing the amplitude of the input perturbation generates second-harmonic responses that, when completed over a full frequency sweep, can be used to construct a second harmonic NLEIS spectra. In this work, the first full frequency NLEIS spectra for lithium-ion batteries are shown through commercially-available, high-power Samsung LiNMC|C 1.5 Ah cells. By using a nonlinear extension of the pseudo-two-dimensional impedance model for lithium-ion batteries with our experimental data, we are able to gain more insight about the effects of states-of-charge and states-of-health than traditional EIS. At low frequencies, it is evident that NLEIS spectra show a much more distinct response to potential-dependent thermodynamics and diffusion processes. In addition, NLEIS is highly sensitive to symmetry, giving it the capabilities to supplement the charge-transfer kinetics information of linear EIS by allowing access to charge-transfer symmetry coefficients. Fresh-cell experiments elicit no responses at kinetically sensitive frequencies as a result of symmetric charge-transfer on both electrodes, whereas aged cells have distinct kinetic features, indicating that there has been a shift away from perfectly symmetric charge-transfer. Initial results of this combined analysis of EIS and NLEIS show promise for improved parameter estimation and electrode characterization.

Accelerating Battery Research with Lab-Based XAFS and XES

Evan Jahrman

Advanced x-ray spectroscopies are traditionally applied to the characterization of a material's molecular and electronic properties. In particular, XAFS and XES permit the element-specific interrogation of a material's oxidation state, molecular symmetry, and atomic geometry. For that reason, synchrotron-based XAFS analyses have met with ample recent success in the ex- and in-situ characterization of a battery material's state-of-charge (SOC) and state-of-health (SOH), two properties which can be difficult to assess by other analytical means. Unfortunately, advanced x-ray spectroscopies have been largely unable to provide rapid feedback for battery chemistry prototyping applications as they have been almost exclusively within the domain of synchrotron x-ray facilities.

Over the last four years, the Seidler group at the University of Washington developed several new families of lab-based instruments to expand the accessibility of advanced x-ray spectroscopies, XAFS and XES, to projects requiring more routine analytical characterization. Here, I outline the utility of these instruments for rapid analysis of energy storage materials. From the standpoint of materials inquiry, I will present a wide range of results, including XAFS and valence-to-core XES measurements of NMC and VOPO4 cathode materials, a study of ion pairing in electrolyte materials of interest for the next generation of battery research, and a brief survey of one such instruments recently achieved extended-XAFS (EXAFS) capabilities.

CO2 Reduction as a Strategy for Hydrogen Storage in C1 Products

Cecilia Johnson

Pairing the reduction of CO_2 with H_2 storage in C1 products simultaneously addresses the needs for clean burning fuel and a sustainable clean carbon source. These products, such as formate and methanol, offer a storage medium that is easily transported and that can be reversibly dehydrogenated for hydrogen to be used as fuel or they can be used as commercial products in their own right. A tripodal and facially coordinating bis-(N-heterocyclic carbene)phosphine ligand has been developed, with two protic N-heterocyclic carbene (PNHC) wing-tips. When coordinated to a ruthenium(II) metal center, these PNHC sites can be deprotonated and have displayed metal-ligand cooperation in CO_2 activation and reduction with H_2. Initial catalytic studies under high pressure and temperature conditions have shown the production of formate (TON = 130) and methanol (TON = 7). Condition optimizations and mechanistic investigations along with an extended library of catalysts will be presented.

Synthesis and Characterization of a Tri-Iron Propeller-Shaped Cluster

Jonathan Kephart

Herein, we present the synthesis and characterization of a novel class of ligand-stabilized transition metal chalcogenide clusters. Two homoleptic cobalt selenide clusters of the formula Co6Se8(Ph2PNHR)6 (R = iPr or 4-tolyl) were prepared through the treatment of dicobalt octacarbonyl with selenium powder and PPh2(NHR) at 110 °C in toluene. Similar attempts at the preparation of a diisopropyl variant, Co6Se8(iPr2PNHiPr)6, were not successful, and instead yielded a cobalt paddlewheel dimer, Co2(CO)6(Ph2PNHiPr)2. A [4,2] cluster, Co4Se2(Ph2PNHiPr)4(CO)6, was isolated as an intermediate, and was converted to Co6Se8(Ph2PNHiPr)6 upon treatment with SePPh2(NHiPr). A novel [3,1] cluster, Co3Se(μ2-PPh2)(Ph2PNHiPr)3(CO)4, tentatively produced through the cleavage of the aminophosphine P-N bond, was isolated as a reaction byproduct and could not be converted to [6,8] cluster. Treatment of Co6Se8(Ph2PNHR)6 with nBuLi in a mixture of toluene and pyridine promoted the deprotonation of the distal N-H substituents to afford a lithium-amide salt, Co6Se8(Ph2PNR)6Li6, a transformation which is corroborated by a 10 ppm upfield shift in the phosphorous NMR. Upon addition of FeCl2, transmetalation proceeded via a salt metathesis mechanism to yield a three blade propeller-shaped heterometallic cluster, Co6Se8(Ph2PNR)6Fe3. These compounds were characterized by single-crystal X-ray diffractometry, and feature a novel Co6Se8Fe3 core with D3d symmetry. The solid-state structure exhibits Fe-Se bond lengths averaging 2.52 Å, which is within the range expected for a dative Fe-Se bond. In this regard, the Co6Se8 core effectively acts as a metalloligand coordinating to three 14-electron ferrous ions. Additionally, an average Co-Fe distance of 2.87 Å is observed, which is shorter than the average Co-Co distance (2.95 Å), suggesting that the iron atoms have effectively expanded the metal chalcogenide core. Isostructural zinc metalated analogues, Co6Se8(Ph2PNR)6Zn3, were synthesized as diamagnetic model complexes. The tri-metallated clusters were studied by UV-visible absorption spectroscopy and cyclic voltammetry. While Co6Se8(Ph2PNiPr)6Fe3 appears to be relatively inert, Co6Se8(Ph2PNTol)6Fe3 exhibits reactivity with carbon monoxide, organic azides, and isocyanides.

Lanthanide-Doped Metal Halide Perovskites for Solar Energy Conversion

Daniel Kroupa

Recent advances in lanthanide doping of CsPbX3 (X = Cl, Br, I) perovskites have opened exciting new opportunities for their application as downconverters in solar energy conversion technologies. Here, we describe the preparation of lanthanide-doped CsPbX3 materials and, through a combination of variable-temperature and time-resolved spectroscopy, we detail the energy transfer mechanism between the semiconductor host and dopant center. We highlight ytterbium-doped materials, which show near-infrared PLQYs as high as 170% with near-zero excitonic luminescence. In this case, we show that the formation of shallow ytterbium-induced defects play a critical role in facilitating a picosecond nonradiative energy-transfer process that de-excites the photoexcited semiconductor while simultaneously exciting two ytterbium dopant ions through the photophysical process of quantum-cutting. The application of these materials as solar downconverters for next-generation photovoltaics is discussed.

Printed Flexible Thermocouple Arrays for Improved Aerospace Safety Monitoring and Manufacturing

Joey Law

Novel particle-less molecular electronic ink for printing ultra thin, flexible, highly tunable alloys at temperatures <300˚C was developed. Application demonstration of printing T-Type (Cu/Constantan) thermocouples for in-situ temperature monitoring to improve aerospace propulsion system safety and composite manufacturing & repairs.

Defect Engineering in Copper Chalcogenide Nanostructures with Tunable Optical Resonances

Soohyung Lee

Careful control over composition and morphology are critical in virtually every materials system, and plasmonic semiconductor nanostructures have emerged as a powerful class of materials since they exhibit localized surface plasmon resonances that can be tuned over a wide spectral range through compositional engineering of the free charge carrier density. This contrasts with metallic nanostructures where the tuning of plasmonic resonances is typically achieved by changing the polarizability of the nanostructure through shape control. In particular, the copper chalcogenides have been studied widely in recent years due to their intrinsic plasmon band in the near-infrared spectral range, generated via resonant excitation of free hole carriers. Herein, we discuss our recent efforts to control optical resonances and photothermal transduction in ternary metal chalcogenide nanocrystals through morphological and compositional tuning. We investigate changes in the plasmon response via control over shape and polarizability and demonstrate compositional tuning of the localized surface plasmon resonance frequency and photothermal transduction efficiency via careful control over chalcogen composition, defect density, and oxidation, as well as the introduction of additional optical resonances through the gradual incorporation of metallic impurities.

Detailed Modeling on Luminescent Solar Concentrators

Yilin Li

Luminescent solar concentrators have attracted a lot of attention in recent years for their potential application to zero-energy buildings. This study will present a new insight into the modeling of luminescent solar concentrators, in which the type of incidence, non-perfect total internal reflection, and attenuation of matrix are included.

Efficient photo-induced hole transfer occurs in polymer/non-fullerene acceptor organic photovoltaic blend over times from 10 ps to 1 ns

Yun Liu

We study photo-induced charge generation in a model polymer/non-fullerene acceptor organic photovoltaic (OPV) blend with a seemingly minimal driving force for hole transfer. Specifically, we focus on hole transfer kinetics from the photoexcited electron acceptor thiophene-thieno[3,2-b]thiophene-thiophene-3-(dicyanomethylidene)indan-1-one (4TIC) to the conjugated polymer poly[(4,4′-bis(2-butyloctoxycarbonyl-[2,2′-bithiophene]-5,5-diyl)-alt-(2,2′-bithiophene-5,5′-diyl)] (PDCBT) using ultrafast transient absorption and time-resolved photoluminescence spectroscopy. We measure the hole transfer dynamics by selectively exciting the 4TIC electron acceptor and monitoring the bleach of the PDCBT ground-state population. We find that, in the blend, the 4TIC excitons decay within 7 ps of photoexcitation, accompanied by a concomitant rise in the ground state bleach of the polymer that has mostly completed within the first 8 ps, indicating that hole transfer from 4TIC to PDCBT occurring roughly an order of magnitude slower than in previously reported polymer/NFA blends. Notably, the ground state bleach of the polymer, continues to grow, not reaching its maximum until ~1 ns. We propose that some 4TIC polaron-pairs are generated, which undergo hole-transfer to the polymer on hundred ps time-scale. Our findings provide new insight into the kinetics of hole-transfer in non-fullerene OPV blends in the regime of small driving force, while also supports the proposal that non-fullerene acceptors may generate long-lived charge species upon direct photoexcitation.

Decentralized Control for 100% Power-electronics-based Microgrids

Minghui Lu

This poster will outline recent advances that enable modular and resilient microgrids. Special emphasis is placed on novel power electronics control strategies that enable plug-and-play architectures and bypass the need for communication channels. In essence, these advances enable self-organizing ac systems that provide reliable power.

Synthesis of benzodipyrrole for direct arylation polymerization

Amy Mayhugh

Indoles are a biologically important class of molecules that have been synthesized using many known pathways. Pyrroloindoles like benzodipyrrole (BDP) have been studied for use in conjugated polymers, as they form electronically active and environmentally stable materials. BDP type compounds have the potential to directly cross-couple with haloarenes, where C-H activation may occur at C-2 on BDP. This allows for the synthesis of more complex conjugated materials without the need for organometallic functionalization. Known synthetic pathways for pyrroloindoles include routes common for substituted indole synthesis. Herein, the Batcho-Leimgruber and Larock methods of indole synthesis have been adapted for synthesizing BDP. C-H functionalization of BDP will be studied for creating novel methods for direct arylation polymerization of organic electronic materials.

Optimally Designed Subsidies for Achieving Carbon Emissions Targets in Electric Power Systems

Ahmad Milyani

One of the major contributors to global warming is the amount of carbon dioxide (CO_2) released from burning fossil fuel (primarily coal) as a by-product of the production of electric energy. Imposing carbon taxes to mitigate the emissions from the electricity sector is a well-established method to counteract the detrimental effects of CO_2 on the environment. This added tax, however, has a negative impact on the economy and wholesale electricity prices. A fact that is more evident when regulating authorities set higher reduction targets which require a higher tax rate. This paper proposes a framework in which regulating authorities can use the revenue from the levied taxes to subsidize more expensive producers that have lower CO_2 emissions, allowing them to be more competitive in the day-ahead energy market. The problem is formulated as a bilevel optimization in which the upper level represents the regulating authority whose objective function is to minimize the total cost of subsidies given to producers and the lower level represents the day-ahead market clearing process. This nonlinear bilevel model is then transformed into a mixed-integer linear programming problem that can be solved using commercial tools. Numerical studies demonstrate that implementing the proposed approach would make it possible to achieve any feasible emissions target at a much lower tax rate.

Aminophosphines as Versatile Precursors for the Synthesis of Metal Phosphide Nanocrystals

Beth Mundy

We have broadened the scope of the aminophosphine precursor chemistry that has been developed for InP quantum dots to the synthesis of cadmium, zinc, cobalt, and nickel phosphide nanocrystals. The generalized synthetic conditions involve thermolysis of the appropriate MX2 salt with tris-diethylaminophosphine in a long chain primary amine. The resulting Cd3P2 nanocrystals exhibit size tuning effects based on the metal halide reactivity. 31P NMR studies show that the II-V materials form via the previously described mechanism observed for InP, demonstrating the invariance of this chemistry to the metal valence. We also demonstrate that electrocatalytically active transition metal phosphides, specifically Co2P, CoP, and Ni2P, can be produced using this synthetic method at relatively mild temperatures and in high yields.

Mixed-Ionic Electronic Conductors for Organic Electronics

Jonathan Onorato

A new class of materials called mixed ionic/electronic conductors (MIECs) has the potential to be highly useful for many applications, ranging from biological sensors to battery electrode materials. The majority of current organic MIECs are created through the blending of two materials, where one component provides ionic conductivity, and the other electronic. This leads to a complex phase behavior that is still not fully understood. This difficulty is exacerbated by the difficulty of synthesis for most MIEC materials. In order to design effective MIECs that can open avenues to these new applications, this morphology/conduction relationship must be understood. Our attempt to answer this question is centered on synthesizing a new MIEC which should have less complex morphologies, enabling analysis of the MIEC morphology.

The Synthesis, Surface Modification, Electrochemical Application, and Assembly of Semiconductor Nanowires

Elena Pandres

Semiconductor nanowires (NWs) have garnered great interest due to their impressive optical, mechanical, and electronic characteristics, with applications in sensing, energy conversion, and energy storage. In particular, silicon and germanium NWs have demonstrated high capacity and long cycle life as negative electrodes for lithium ion batteries. Nonetheless, the reductive decomposition products that result from the consumption of intentionally incorporated electrolyte additives, such as fluoroethylene carbonate (FEC), are still deemed necessary to mitigate the recurrence of irreversible reactions that form the solid-electrolyte interphase (SEI) layer between the electrode and the electrolyte. This highlights the critical importance of interfacial chemistry for robust electrochemical systems. Yet, the surface chemistry of the active material is often neglected prior to electrode formulation, which results in uncontrolled—likely oxidized—surfaces, influencing the critical reactions that take place at the interface. Here, we investigate the electrochemical cycling of germanium nanowire composite conversion electrodes with controlled surface chemistry, formulated with an array of polymeric binders, both in the presence and in the absence of fluorinated electrolyte additives. We see that controlled electrode surface modification, when paired with certain binders, significantly improved germanium nanowire-based electrode cycling retention and longevity in the absence of fluorinated reductive decomposition products. In addition, work related to an exciting new strategy for the production of colloidal semiconductor nanowires will also be discussed.

The Role of Oxidation in Controlling the Interfacial Structure and Luminescence Properties of InP Quantum Dots

Nayon Park

Synthetic efforts to prepare indium phosphide quantum dots have historically generated emissive materials with lower than unity quantum yields. This property has been attributed to structural and electronic defects associated with the InP core as well as the chemistry of the shell materials used to overcoat and passivate the InP surface. Consequently, the uniformity of the core-shell interface plays a critical role. Using X-ray emission spectroscopy (XES) performed with a recently developed benchtop spectrometer, we studied the evolution of oxidized phosphorus species arising across a series of common, but chemically distinct, synthetic methods for InP QD particle growth and subsequent ZnE (E=S, Se) shell deposition. XES afforded us the ability to measure the speciation of phosphorus reliably, quantitatively, and more efficiently (with respect to both quantity of material required and speed of the measurement) than traditional techniques, i.e. X-ray photoelectron spectroscopy and magic angle spinning solid-state NMR spectroscopy. Our findings indicate that even with deliberate care to prevent phosphorus oxidation during InP core synthesis, typical shelling approaches unintentionally introduce oxidative defects at the core-shell interface, limiting the attainable photoluminescence quantum yields. Moving on from this initial set of studies we are examining the systematic effect of post-synthetic oxidation of InP QD cores on the quantum yield of shelled particles in order to probe the role of oxides in impacting particle composition and interfacial strain, and in turn quantum yield and luminescence linewidths.

Electrochemical Engineering Models for Lithium Sulfur Batteries

Caitlin Parke

As lithium ion batteries are approaching their performance limits, research on alternative chemistries that can meet the energy demands for electric vehicles and grid applications has increased. Lithium sulfur is one chemistry with a high theoretical specific capacity of 2500 Wh/kg and practical values of 500-600 Wh/kg1. Physics-based battery models can provide control and insight into better battery performance and design by modeling the internal states of a battery. The challenging aspects of modeling lithium sulfur batteries are due to the complicated reaction network, the number of species involved, and the multiple phase changes, from solid sulfur dissolution to Li2S precipitation. Because of this, lithium sulfur battery models result in complex equations and require a stiff solver. In this work we present results from a modified Kumaresan lithium sulfur continuum model for applications in aerospace systems. The study includes an attempt to reduce the simulation time to enable real-time control and integration into Battery Management Systems (BMS).

Electron-driven proton transfer from water to a model heptazine-based molecular photocatalyst

Emily Rabe

Coordinated electron and proton motion is important for various energy storage and conversion targets, from fuel cells to solar fuel production. However, harnessing these processes requires deeper fundamental insight. Based on time-resolved multichannel photo-luminescence (PL) spectroscopy, we kinetically reveal a new emis-sion feature that emerges in aqueous dispersions of 2,5,8-tris(4-methoxyphenyl)-1,3,4,6,7,9,9b-heptaazaphenalene (TAHz), a mod-el molecular photocatalyst that is chemically related to graphitic carbon nitride ($g\text{-}C_3N_4$). We attribute this new PL peak to a delocal-ized excited state with partial charge-transfer (pCT) character that forms when photoexcited $n \to \pi^*$ state is delocalized over the hydro-gen-bonded H_2O, transferring in part, electron density away from water. Using global analysis, we observe a prompt pCT PL decay component exhibiting a kinetic isotope effect (KIE) of 2.9. We at-tribute this KIE to CT quenching by electron-driven proton transfer from water in the TAHz:H_2O complex. Radical dosimetry with terephthalic acid confirm hydroxyl radicals form when TAHz is illuminated in water. Our findings are consistent with recent theo-retical predictions that g-C_3N_4-based photocatalysts can participate in electron-driven proton transfer with H_2O, forming neutral hy-drogenated heptazinyl and hydroxyl radicals.

Investigating the Intercalation Properties of Colloidally Synthesized WSe2 for Improved Hydrogen Evolution

Tyler Robison

Transition metal dichalcogenides (TMDCs) are layered 2-D materials that have been the focus of an immense amount of research due to their potential applications as electrocatalysts for the hydrogen evolution reaction (HER). These materials exhibit two primary crystal phases: the thermodynamic 2H phase (semiconducting) and the kinetic 1T phase (metallic). The 1T phase is a more suitable electrocatalyst due to its conductive nature, however materials in the 1T phase will revert to the more stable 2H phase under common treatments, including annealing temperatures. Sheets of TMDC are held together by weak van der waals interactions, however these sheets can be intercalated by various guest species that can change the material’s phase from 2H to 1T. For example, it has been shown that the 1T phase of prototypical TMDCs such as MoS2 and WSe2 can be stabilized upon intercalation by alkali metals such as lithium. Intercalation by neutral species is less commonly encountered for group VI TMDCs. In my work, approaches to large-batch colloidal syntheses of nanoscale WSe2 are investigated. We found in ligand studies that the degree of ligand amine substitution has no effect on the interlayer spacing of intercalated WSe2. Overpotentials for HER were able to be reduced by up to 14 % by using amines with varying substitution.

Selective Interdigitated Electrodes for Perovskite Photovoltaic Devices

Brandon Rotondo

Selective interdigitated electrodes (IDEs) were fabricated using both printing and electrodeposition for the purpose of rapid perovskite photovoltaic device fabrication and optimization. Through a combination of inherent long carrier diffusion lengths and photon recycling perovskite photovoltaic devices have the ability to be fabricated in a lateral geometry utilizing interdigitated electrodes with finger spacing within printed resolutions. Previous work has utilized patterned ITO with electrodeposited TiO2 and PEDOT:PSS to achieve selective contacts; however these methods require high temperatures to sinter the deposited TiO2 as well as subtractive manufacturing leading to a waste of valuable Indium. To allow for large scale processing through both reduced cost and lower processing temperatures we have replaced the electrode with inkjet printed silver with low temperature electrodeposited and post treated SnO2 and NiOx transport layers. IDE dimensions, electrodeposition conditions, and process flow were explored and optimized to ensure replicable device performance and final conditions were utilized to fabricate printed perovskite photovoltaic devices. While initial work has been done utilizing inkjet printing and small bath electrodeposition, the processes are directly compatible and transferable to roll to roll applications through flexographic/gravure printing and on web electrodeposition allowing a platform for rapid fabrication of perovskite devices on large scales enabling further rapid large scale perovskite device research.

Exploring copper/ copper oxide catalyst for supercritical fluid-based silicon nanowire synthesis

Saibihai Rousidan

Technology is driving the development of electrode materials for batteries with higher lithium(Li) storage capabilities. Silicon (Si) exhibits the highest known lithium alloying capacity, is one of the most promising anode materials. However, alloying process is accompanied by a large volume expansion which induces cracking and rapid pulverization of Si-based anodes. Significant improvements have been made over the past decades by employing Si nanostructures, particularly nanowires. However, Si nanowire-based structures still exhibit limited cycling stability for faster charge and discharge. In my research, I have been focusing on improving transport characteristics in Si nanowires, mitigating sources of defects induced in nanowire synthesis, to make the selection and self-assembly of high-quality Si nanowires easily tunable. As well as to improve the electrical performance of Silicon-based anodes by incorporating dopants, which do not directly participate in the electrochemical process, into the Si nanowire matrix.

Staudinger-like Reaction for Phosphorene: Wafer-scale Investigations

Yuka Sakazaki

Phosphorene, or exfoliated black phosphorus, is a 2D material with a tunable bandgap and favorable electron transport properties for optoelectronic applications. However, its instability under ambient conditions presents challenges for successful integration into devices.

Here we investigate the controlled oxidation of phosphorene using molecular reagents as a passivation strategy. In particular, we treat the phosphorene flakes with azides under photolyzing conditions to test if a Staudinger-like reaction occurs at the surface to form -P=N-R groups.

To support promising results obtained through solution-phase reactions, we performed wafer-scale reactions by depositing single phosphorene flakes on a silicon substrate. Atomic force microscopy (AFM) shows a height increase of 1.0 nm after treatment, which is consistent with the expected height of the =N-R group. Subsequent treatment of the substrate with deoxygenated water in the absence of light results in significant degradation of the phosphorene flakes, suggesting that the P=N bonds have been formed and converted to P=O bonds, giving way to further oxidation. For future studies, we will investigate milder methods to convert the P=N-R groups to form a stable phosphorene oxide.

Reducing Power Ramp Rates for Residential Houses with On-Site Photovoltaics Using Deep Reinforcement Learning

Lane Smith

The mass integration of solar photovoltaics (PVs) has created many challenges for the electric power grid. States with large penetrations of solar energy face stability issues when PV generation creates sudden changes in the grid’s net demand. Such changes create steep ramp rates that greatly tax the system’s generation units. Ramp rates can have a reduced impact when demand and renewable generation are better balanced throughout the day. This study introduces a solution using deep reinforcement learning (DRL) where a single-family (SF) home is dynamically controlled to take advantage of solar generation and the house’s thermodynamics, helping to decrease the ramp rate for the grid while maintaining energy consumption and comfort levels. A deep Q-network (DQN) was developed to learn the optimal policy in a simulation environment, which consisted of a comprehensive PV model and an EnergyPlus SF home model that was selected from the DOE Residential Prototype Models. The DQN, once trained, effectively reduced the ramp rate while maintaining a comfortable in-home temperature.
Additional Author: Yunzhi Huang

Total Differential Capacity Plot Analysis Using Data Science Methods

Nicole Thompson

While total differential capacity plots are valuable tools for examining electrode performance, much of the analyses reported in literature are largely qualitative, with general statements of peak shifting, flattening, or broadening over cycles. We present software with a database backend capable of quantitatively analyzing cycling data by extracting peak characteristics from every cycle. A machine learning model has been applied using peak descriptors, and initial results indicate the ability to distinguish between two different battery chemistries. We hope this software will eventually lead to an open source database of experimental cycling data for researchers to reference.

Other authors: N.L. Thompson, S. Alamdari, T.A. Cohen, R.C. Masse, G.Z. Cao, V.C. Holmberg, J. Pfaendtner, and D.A. Beck

Benchmarking the Effects of Surface Ligands on CoP for the Hydrogen Evolution Reaction

David Ung

Surface ligands are a ubiquitous trait of all colloidally synthesized nanoparticles. They are needed to stabilize the surface of the nanoparticles and prevent agglomeration. While the identity of surface ligands can be varied over a wide range, they are generally thought to inhibit the activity of nanoparticle electrocatalysts because they occupy active sites and impede charge flow. However, there is no known direct correlation between type of surface ligand and its affect on electrocatalysis. In this study, we are interested in exploring how the identity of surface ligands affect the catalytic properties of cobalt phosphide nanoparticles for the hydrogen evolution reaction.

Operational modeling of a high PV system

Nina Vincent

The U.S. Department of Energy has set goals to significantly reduce the cost of solar energy by 2030. To understand the impact of reaching these cost targets, we modeled three scenarios: a reference-case solar photovoltaic (PV) cost scenario, a low-cost PV scenario that achieves the PV targets in 2030, and a low-cost PV scenario that also assumes that low-cost storage is available. Capacity and transmission expansion projections were made using NREL’s Regional Energy Deployment System (ReEDS) model. To better understand the hourly operations of these high PV scenarios, we further explored the results using a detailed operational model. To analyze operation at an hourly scale, ReEDS scenario outputs from 2050 were converted and modeled in PLEXOS, a commercial production cost simulation model. The scenario with low-cost storage and PV resulted in load shedding, indicating that the current ReEDS model formulation was insufficient for properly modeling high levels of PV and storage. Based on the hourly production cost model results, adjustments were made to ReEDS’s storage capacity value to ensure grid reliability. Using the now reliable system, we further examined the impact on generation, prices, and curtailment modeled in PLEXOS. We found that with increasing PV capacity, there were more zero price hours, prices were generally lower, excess PV generation was put into storage and used overnight, and curtailment projections from ReEDS were lower than from PLEXOS.

Active spatial control of nanoscale temperature gradients through plasmon hybridization on metallic nanoparticle aggregates

Claire West

Manipulating temperature gradients on metallic nanoparticle aggregates opens a new class of promising materials capable of improving the functionality of nanotechnology, however presents fundamental challenges due to ubiquitous heat diffusion. Previous work has demonstrated the ability to locally heat nanoparticle assemblies placed in insulating backgrounds, yet the active switch-ability or invertibility of such heat and temperature distributions remains unexplored until now. In this work, invertible nanoscale temperature gradients are realized by means of coupling and hybridizing two plasmon-supporting nanoparticles and separately driving the new pair of hybridized plasmon resonances by incident optical light at each wavelength. This method not only allows for the nanoparticles to locally spike in temperature, but also the ability to selectively turn up and down the temperature on each particle. Models of plasmon hybridization and computations of heat diffusion are used to guide experimental fabrication of three gold nanorod heterodimers of varying gap size all capable of achieving such tunabilty. Subsequently, simulated temperature maps of the system showing this active control encourage experimental confirmation. But while nanoscale temperature maps are straight-forward to simulate, quantitative experimental measurements are quite difficult to do due to the small length scales involved. Instead, photothermal heterodyne imaging is used to create images of hot areas on the nanoparticle assemblies by collecting the scattered light off of the heated system. Computations and analytical models confirm that these images do in fact indicate regions of hot temperature when temperature gradients are appreciable. For the first time, actively invertible temperature gradients are demonstrated not only by simulating temperature maps, but also by experimentally and theoretically taking photothermal images at each plasmonic mode on heterodimers of three varying gap size.

Electrochemical Alloying and Supercritical Fluid-Based Synthesis of Antimony Conversion Electrodes with Controlled Anisotropy

Grant Williamson

Antimony is one of the most promising high-rate-capability Na- and Li-ion conversion electrode materials, demonstrating extraordinarily high rates of lithiation and sodiation. For example, small isotropic antimony nanocrystals have exhibited stable, reversible, long-term cycling at charge/discharge rates as fast as 20C without significant capacity loss. Herein, we investigate the effect of structural anisotropy on the sodiation of high-capacity, high-power density antimony electrodes fabricated from an engineered set of highly anisotropic, nanostructured antimony electrode materials produced via a supercritical fluid-based synthesis. By controlling reaction conditions, precursor concentration, and ligand choice, the synthesis can be tailored to produce an array of nanostructured antimony electrode materials with a variety of morphologies including platelets, truncated octahedra, and dendritic microstructures. In addition to analyzing the growth processes that promote the supercritical fluid-based synthesis of these anisotropic antimony nanostructures, we discuss how this morphological selectivity can be used to evaluate the effects of structural anisotropy on sodiation and desodiation using differential capacity plots, electrochemical impedance spectroscopy and the galvanostatic intermittent titration technique. We also discuss how oxidation and temperature influence the electrochemical alloying process. We hope that a better understanding of the transformations that take place during the high-rate electrochemical alloying of nanostructured antimony will enable the structural optimization of high-rate-capability antimony-based conversion electrodes.

Differential Electrochemical Mass Spectrometry Coupled with Linear and Non-Linear Electrochemical Impedance Spectroscopy of Gadolinia-Doped Ceria: CO2 and H2O Co-Electrolysis

Jonathan Witt

Recent advances in carbon capture create new opportunities for recycling CO_2 into liquid fuels to store intermittent electrical energy (1). One option is to co-electrolyze CO_2 and H_2O at high temperature using solid oxide electrolysis cells (SOECs). Although promising, the factors controlling rates of CO_2 and H_2O reduction in SOECs are not well understood, hampering development (2,3). Traditional electrochemical techniques have difficulty resolving the mechanisms and kinetic parameters of the individual steps governing CO_2 and H_2O reduction. This limitation can potentially be overcome using linear and non-linear electrochemical impedance spectroscopy (EIS and NLEIS) in conjunction with dynamic measurement of gas-phase species using differential electrochemical mass spectrometry (DEMS).

Regarding co-electrolysis, mixed ionic electronic conductors (MIEC) have gained interest as alternatives to nickel-yttria stabilized zirconia (Ni-YSZ) because the active region is not limited to the triple phase boundary and they are more stable in reducing environments (3). The MIEC studied here, gadolinia-doped ceria (GDC), has been well characterized as an electrolyte (3) and is a promising cathode in SOECs. Unlike Ni-YSZ, it does not coke in carbon environments or oxidize completely in a feed of water and CO_2.

We have performed NLEIS and EIS measurements of co-electrolysis on button cells composed of GDC as the working electrode with electrolyte YSZ under various temperatures and gas compositions. Gas atmospheres surrounding the cells contain mixtures of water, CO_2, CO, H_2, and carrier gas such as Ar or N_2, used to manipulate the oxygen partial pressure of the system and thus the oxygen vacancy concentration of the surface and bulk electrode. The data we have collected on co-electrolysis of CO_2 and water on GDC have been compared with model NLEIS spectra developed to include CO-2 reduction, water reduction, and reverse water gas shift reaction mechanisms and rate determining steps. A rough vacuum and low volume reactor was developed to cross-check the proposed mechanisms through measuring a gas phase response in DEMS and a micro-kinetic model was developed to predict product distributions corresponding to the mechanism that most closely matched the results.

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Interface Representation in Electricity-Gas System with An Equivalent Gas Network Model

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Natural gas has become one of the major source of fuels for power systems in many parts of the world due to the increasing deployment of gas-fired generators. However, the availability of natural gas is restricted by the status of the gas network, which is largely influenced by the fast ramping of gas-fired generators in the power system. To better represent the interaction between electricity and gas systems and promote the understanding of gas system for power system operators, a multi-port equivalent model of gas networks and electricity-to-gas sentivity factors are proposed in this paper under both steady and transient state. With the multi-port equivalent model, the gas system operator is able to provide masked information regarding the most important nodes in gas system. Based on this information, the electricity-to-gas sensitivity factors can be calculated by power system operators and thus answer the question of ``Where, When and How much will the the status of gas system change when the power generation varies''. Both the equivalent model and sensitivity factors have explicit analytic formulations and are easy to apply. Several numerical tests prove the accuracy and robustness of the proposed models.

Artificial neural network for the theoretical modeling on luminescent solar concentrators

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A luminescent solar concentrator (LSC) is a stationary photovoltaic (PV) device consisting of a planar optical waveguide embedded with luminophores and PV cells attached to the waveguide edges. The design of LSC allows to integrate PV technologies with the built environment, especially for zero-energy buildings. In this study, a theoretical model on LSCs, considering anisotropic spectroscopic properties of luminophores, and polarization, evanescent and scattering effects of electromagnetic waves, has been developed. Simulation results will be trained by artificial neural networks to obtain simple,fast and reliable predicative model for large-scale LSCs.
