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STEM Degrees: **STEM Participants:**

Major Goals: Each year in Austin, Texas, the CEC Annual Workshop on Electrochemistry brings together experts in fields of engineering, materials, and electrochemistry to focus on a topic in an important area of research. Participants address specific challenges in the field, exchange ideas and information, and catch up with colleagues from around the world. These exclusive workshops feature scientists and researchers from top universities, national laboratories, and electrochemical industries discussing cutting-edge electrochemical science, and addressing issues with respect to the mechanisms of electron transfer. Each workshop features technical presentations and posters from several different perspectives covering areas ranging from electrocatalysis, electrochemical sensors, and electroanalysis.

Accomplishments: See Attachment.

Training Opportunities: Nothing to Report

Results Dissemination: Nothing to Report

Honors and Awards: Nothing to Report

Protocol Activity Status:

Technology Transfer: Nothing to Report

RPPR Final Report

as of 02-Jan-2020

2019 CEC Annual Workshop on Electrochemistry
February 09–10, 2019

Each year in Austin, Texas, the CEC Annual Workshop on Electrochemistry brings together experts in fields of engineering, materials, and electrochemistry to focus on a topic in an important area of research. Participants address specific challenges in the field, exchange ideas and information, and catch up with colleagues from around the world. These exclusive workshops feature scientists and researchers from top universities, national laboratories, and electrochemical industries discussing cutting-edge electrochemical science, and addressing issues with respect to the mechanisms of electron transfer. Each workshop features technical presentations and posters from several different perspectives covering areas ranging from electrocatalysis, electrochemical sensors, and electroanalysis.

The Center for Electrochemistry (CEC) at the University of Texas at Austin held its eleventh annual electrochemistry workshop February 09–10, 2019 in Welch Hall on the campus of The University of Texas at Austin. There were 104 registered attendees for this conference, including experts from academia, industry, and national laboratories, brought together with the goal of improving understanding in electrochemistry. Four sessions were held sequentially, covering the following topics: Biological Applications in Electrochemistry, Single Atom and Cluster Size Effects on Electrocatalysis, Photoelectrochemistry and Optical Imaging of Electrodes, and Electrical Energy Storage. CEC faculty members moderated the sessions and promoted discussion.

CEC Associate Director Cynthia Zoski opened the workshop with a discussion of the CEC mission and the request that all participants actively engage in the lectures and poster session. The workshop format encouraged interactive exchange with each of the eleven speakers having a full 50 minutes to present their research and engage in discussions with the attendees. In addition to these presentations, the meeting featured a poster session and reception. Students and postdocs from UT-Austin and other schools, as well as some industry representatives presented about 24 posters and answered questions from attendees in an informal evening session. Students and postdocs also met in small groups with individual invited speakers and individual industrial associates in attendance for discussions over lunch.

The CEC would like to acknowledge and thank the meeting's sponsors who made it possible: The U.S. Army Research Office (Contract No. 76593-CH-CF), the Cockrell School of Engineering at The University of Texas at Austin, and the Robert A. Welch Foundation (Grant H-F-0037). The views, opinions, and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy, or decision, unless so designated by other documentation.

CEC intends to continue a tradition of excellence and host an electrochemistry workshop annually with new topics in important areas of research to be addressed each year. The 2020 meeting will again focus on a variety of current topics in a session format.

AGENDA

Sunday, February 9, 2019
Welch Hall – Room 2.122

7:30-8:25a Check-in and continental breakfast

8:30-8:40 Introductory remarks

Biological Applications in Electrochemistry – Richard Crooks, Moderator

8:45-9:35 *Kevin Plaxco, UC Santa Barbara*
Counting Molecules, Dodging Blood Cells: Continuous, Real-time Molecular Measurements Directly in the Living Body

9:40-10:30 *Shelley Minteer, University of Utah*
Tailoring Enzyme/Electrode Interfaces for Energy Conversion and Electrosynthesis

10:35-10:50 Break

10:55-11:45 *Jill Venton, University of Virginia*
Tunable Carbon Electrodes for Neurotransmitter Detection

11:50-1:15p Lunch break

Single Atom and Cluster Size Effects on Electrocatalysis – Allen Bard, Moderator

1:20-2:10p *Radoslav Adzic*, *Brookhaven National Laboratory*
Enhancing Electrocatalysis of Platinum Monolayer and Single Atom Electrocatalysts by Core-Shell Interaction

2:15-3:05 *Xueliang Sun*, *University of Western Ontario*
Single Atom Electrocatalysts for Fuel Cells

3:10-3:25 Break

3:30-4:20 *Allen Bard, Graeme Henkelman*, *University of Texas at Austin*
The HER on Isolated Single Platinum Atoms, Clusters, and Nanoparticles: Experiment and Theory

4:25-5:00 Discussion: Single Atom, Cluster Size Effects in Electrocatalysis

Poster Session, Reception, and Exhibition – TX Union, Santa Rita Room (3.502)

5:30-8:00p Posters and reception

Sunday, February 10, 2019
Welch Hall – Room 2.122

7:30-8:25a	Continental breakfast

Photoelectrochemistry and Optical Imaging of Electrodes – Zak Page, Moderator

8:30-9:20	*Shirley Meng, UC San Diego* Electrochemical and Chemical Quantification of SEI on Lithium Metal Anodes
9:25-10:15	*John Reynolds, Georgia Institute of Technology* Conjugated Polymers for Organic Photovoltaics: The Minimal Structural Change Approach in Active Material Design and Optimization
10:20-10:35	Break
10:40-11:30	*Frédéric Kanoufi, Université Paris Diderot* Optical Imaging of Single Nanoparticle Electrochemistry
11:35-12:55p	Lunch break

Electrical Energy Storage – Arumugam Manthiram, Moderator

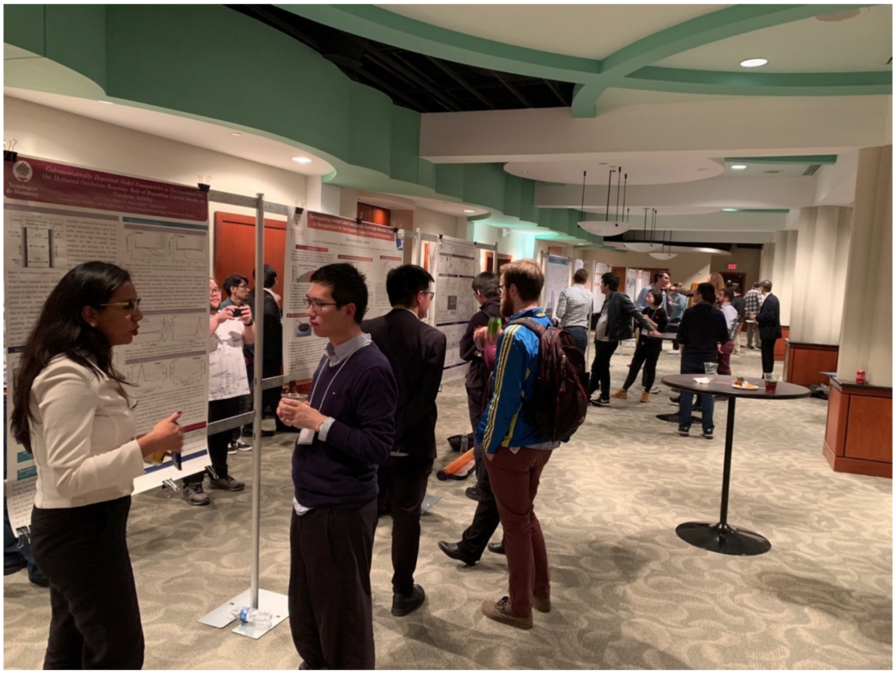
1:00-1:50	*Michael J. Aziz, Harvard University* Organic-Based Aqueous Flow Batteries for Stationary Electrical Energy Storage
1:55- 2:45	*Jeff Sakamoto, University of Michigan* Solid-state Batteries
2:50-3:00	Closing Remarks

2019 CEC Workshop speakers (from top left): Radoslav Adzic, John Reynolds, Frederic Kanoufi, Allen Bard, Jeff Sakamoto, Michael Aziz, Kevin Plaxco, Xueliang Sun, Shirley Meng, Jill Venton, and Shelley Minteer.

Poster Session

Attendee Name	Poster Title
Jeremy Meyers	Molecular Rebar discrete carbon nanotubes for battery applications
Nicole Pollok	Paper-Based Electrochemical Device for the Monitoring of Heart Failure at Home
Juliette Strasser	Gold Dendrimer-Encapsulated Nanoparticles for Size-Dependent Catalysis
Jonathan Thompson	Relating voltammetry at a closed bipolar electrode to a two-electrode cell
Jamie Trindell	Activity and Stability of Highly-Faceted PdxIr(100-x) Nanoparticles for the Oxygen Reduction Reaction
Collin Davies	Chloride Oxidation at an Embedded Microelectrode for Faradaic Ion Concentration Polarization
Olja Simoska	Real-Time Electrochemical Detection of Pseudomonas aeruginosa Phenazine Metabolites
Melissa Meyerson	The Effect of Lithium Surface Chemistry and Topography on Solid Electrolyte Interphase Composition and Dendrite Nucleation
Kenta Kawashima	Highly Porous LaW(O,N)3 Crystal Structures from La4W3O15 for Photoelectrochemical Water Oxidation
Jason Weeks	Improved Cycling of Tin Dioxide-Carbon Composite Anode Materials
Bryan Wygant	Probing the Degrada-on Chemistry and Enhanced Stability of 2D Organolead Halide Perovskites
Caleb Alexander	Anion-Based Pseudocapacitance of the Perovskite Library La1-xSrxBO3-δ (B = Fe, Mn, Co)
Cesar Ortiz	Role of Surface Roughness on Attachment of Nanoparticles on Carbon Fiber Surfaces: From a Collection to Single Nanoparticle
Thom Hersbach	Of Shapes and Surfaces: Cathodically Corroding Polygons into Platinum, Rhodium and Gold
Won Tae Choi	Irreversible doping of polymer semiconductor for organic photocathodes
Dylan Jantz	In-situ and Operando Detection of CO2 Reduction and HER Products via SECM
Raúl Márquez-Montes	Sulfur dioxide exploitation by electrochemical oxidation of sulfite in near-neutral pH electrolytes: Kinetics and Reaction Mechanism
Nicolas Holubowitch	Conductive molecularly imprinted polymers for the electrochemical sensing of explosive compounds
Birane Fall	Thermal and Electrochemical Properties of Adiponitrile/LiPF6 Co-crystalline electrolyte
Jan Borchers	Visual Voltammogram Generated at an Array of Closed Bipolar Electrodes
Zhaoyu Jin	Electroplating Isolated Cobalt Oxide Deposits from Single Molecular Clusters to Nanoparticles for Size-Dependent Oxygen-Evolving Electrocatalysis
Jianan Xu	High Capacity Li/Ni Rich Ni-Ti-Mo Oxide Cathode for Li-ion Batteries
Babu Ganguli	High Capacity Li/Ni rich Ni-Ti-Mo oxide cathode for Li-ion batteries
Jordan Aguirre	Novel Silane-Based Matrices for Silica-Mediated Electrolyte-Binder Coatings in All-Solid-State Hybrid Ceramic Electrolytes for Lithium Metal Batteries

Pictures from Saturday night poster session



Summaries of Speaker Lectures Written by Graduate Students and Postdocs:

***Kevin Plaxco**, University of California, Santa Barbara*

Counting Molecules, Dodging Blood Cells: Real Time Molecular Measurements Directly in the Living Body

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Modern medicine is dependent on the appropriate usage of prescription drugs for rapid and successful treatment of many health conditions and diseases. One of the primary shortcomings of drug based treatments can be elucidated by simply reading the label on a bottle of Ibuprofen, a common over-the-counter anti-inflammatory drug. In an era of highly personalized technology and medical treatment, drug dosage remains, at best, a universal approach dependent on the weight or surface area of the patient and, at worst, dependent on two age categories (child, < 12 years old; adult > 12 years old).

To enable appropriate and personalized drug administration, researchers at the University of California, Santa Barbara set out to develop an analytical technique that would allow the continuous real-time measurement of any molecule in the body. Initial criteria required that the technique allow continuous monitoring on a solvent-free, selective, and stable platform. To realize these goals, an electrochemical detection strategy based on measuring the rate of electron transport (current) from a methylene blue redox reporter to a gold electrode was conceived. Aptamers modified with methylene blue were designed to undergo a conformational change following a binding event with the detection molecule of interest. Compared to the unfolded aptamer, the methylene blue attached to the aptamer is oriented closer to the electrode surface upon folding and an increase in measured current is observed. Using this strategy, the Plaxco group have detected a wide range of molecules including drugs, metabolites, toxins, and biomarkers.

These aptamer-based electrochemical sensors operate in serum and have been used for the real-time monitoring of molecules during *in vivo* rat studies. Transitioning from studies in serum to *in vivo* animal studies has required optimization of the operation of the electrochemical sensor. The operating voltage window is limited by oxygen reduction and the self-assembled monolayer of aptamers can degrade within extreme environments or at extreme potentials. *In vivo* studies introduced a significant amount of signal drift that is not well understood. Using square wave voltammetry, a frequency-dependent electrochemical technique, the signal drift was eliminated by subtracting the current measured during a high frequency measurement from that observed during a low frequency measurement. *In vivo* experiments have become more sophisticated allowing for improved quality of life for the animal subjects, thus improving the relevance of the measurements.

Real-time molecular measurements directly in the living body can transform medical treatment and pharmaceutical studies. The Plaxco group has developed a high resolution analytical method which has enabled temporally resolved measurement of pharmacokinetics within live animals. These measurements have clarified that even in seemingly identical test subjects, there can be large variation in drug delivery and metabolism. The generality of present drug dosage is not adequate to account for these observed differences. While entire pharmacokinetic plots have been previously derived from one or a few data points, Plaxco's research enables real-time measurement of pharmacokinetics within the subject of interest. A feedback loop controlling drug delivery has been integrated with the electrochemical sensor to allow targeted dosages for up to 6 hours at a time.

Though there are still unanswered questions regarding the operation of the aptamer-based electrochemical sensor, this technology has the potential to change the landscape of drug-based treatments. The present challenge is in identifying the optimal application to tackle. Fundamental studies will seek to understand how the gold electrode maintains electrochemical activity within whole blood and this technology will be used to understand drug addiction. The Plaxco group have their sights set on a bottom-up approach to transforming the modern pharmaceutical industry.

Shelley Minteer*, The University of Utah*

Tailoring Enzyme/Electrode Interfaces for Energy Conversion and Electrosynthesis

Prof. Minteer was introduced as “bioelectrochemistry incarnate, a major theme of her talk. In bioelectrocatalysis, proteins are used as catalysts instead of inorganic materials like nanoparticles. When performing bioelectrocatalysis, it is important to properly orient the protein on the electrode, to efficiently mediate electron transfer, and to synthesize or obtain the protein.

Research in the Minteer group is focused on replacing or mimicking the Haber-Bosch process, where nitrogen is reduced to ammonia. Minteer uses nitrogenase, the only enzyme known to reduce nitrogen to ammonia at room temperature and pressure. Nitrogenase consists of an iron protein and a molybdenum protein, and both are required to perform the nitrogen reduction reaction. The initial iteration of this catalyst was found to be inefficient because it required ATP to function. It was also sensitive to air, which was later reduced by introducing a protective protein to perform the oxygen reduction reaction. These strategies enabled the nitrogen reduction reaction to be performed under ambient conditions and are mechanisms used by organisms protect their own enzymes from oxygen. Minteer discussed strategies to enhance enzyme production in bacteria for use in whole-cell biocatalysis in order to increase the stability of nitrogenase where it remains in a cell environment, and improving efficiency because the cell would produce its own ATP.

Several specific and specialized procedures were discussed that could be performed using this system. Since the Haber-Bosch process will not be replaced at an industrial scale, Minteer looked to make chiral amines from ammonia. These chiral amines are typically expensive pharmaceutical precursors that use expensive reactants. Using electrochemistry allows regeneration of these reactants, an indication that catalytic activity was seen in this case. Minteer discussed the advantage of using square wave voltammetry instead of cyclic voltammetry to determine the cofactor potentials of these systems. The cofactors have different potentials from different metals, but biologists haven’t previously been able to study them. This detection technique allows deeper understanding of the enzyme/cofactor system and could make it possible to engineer cofactors to get different potentials for different processes.

Many of the questions from the audience involved the logistics of these experiments, and her answers considered the difficulties of engineering experiments using biological materials. For example, the purchased enzymes have an activity variability of 30% that must be normalized between experiments. It is also difficult to use labeled nitrogen as a feedstock to trace contamination because the labeled nitrogen is made from ammonia, which adds an inherent contamination. A question was asked whether the cofactors had ligand effects in addition to the effects from the different metal centers. However, it is difficult to remove these cofactors intact, purify them, and perform experiments in a relevant amount of time. Minteer suggested that synthetic groups making mimics of these enzymes will help provide more information on their electrochemical activity and effects.

***Jill Venton**, University of Virginia*

Tailoring Enzyme/Electrode Interfaces for Energy Conversion and Electrosynthesis

The Venton group performs in-vivo detection of adenosine, a neurotransmitter that plays many different biological functions throughout the body. A major limitation in performing this study is the need to follow very fast kinetics in order to record real-time information. Venton's group has pioneered the use of live fruit fly brains as models for this study. Because fruit fly brains are so small, extremely small electrodes are necessary. Prof. Venton described her work on traditional carbon micro- and nanoelectrodes where the surface of these electrodes was analyzed electrochemically using dopamine as a redox probe in fast-scan cyclic voltammetry. A disadvantage of dopamine as a redox probe is that its oxidation is an inner-sphere reaction where the redox rate is limited by adsorption-controlled kinetics.

Prof. Venton described studies on carbon nanotube (CNT) yarns as electrodes to improve on the shortcomings of traditional carbon microelectrodes. The diameter of the CNT yarns is around 20 μm and surface roughness of the CNT yarn electrodes is on the order of approximately double the roughness of traditional carbon fiber microelectrodes. Venton showed that the redox behavior of dopamine on CNT yarns is not dependent on scan rate in contrast to smoother carbon electrodes. They observed no decrease in current at sampling frequencies from 10 to 500 Hz, an indication that CNT yarn electrodes are capable of monitoring extremely fast kinetic events. The Venton group concluded that due to the extreme roughness of the CNT yarns, dopamine molecules are essentially 'trapped' on the electrode surface during an electrochemical measurement so that the electrode behaves as if covered by a thin-film.

To further enhance the surface sensitivity of the CNT yarns, Venton described three different types of surface treatments: O_2-plasma, anti-static gun, and laser. The surface of the CNT yarns were characterized after each treatment using SEM and XPS. They found that both the oxygen-content and the physical arrangement of the CNT yarns could be altered by these surface treatments and correlated surface modifications to changes in the redox activity of dopamine.

Venton discussed their current examination of various other carbon-based electrodes such as carbon nanopipettes as well as carbon electrodes of various shapes and sizes fabricated using a 3D-printer.

***Radoslav Adzic**, Brookhaven National Laboratory*

Enhancing Electrocatalysis of Platinum Monolayer and Single Atom Electrocatalysts by Core-Shell Interaction

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Fuel cells offer the promise of potentially efficient and clean energy systems. However, technical and economic barriers still exist in the development of electrocatalysts thus preventing their widespread application in vehicle traction and on-site power generation. Rational design of highly efficient durable and cost-effective electrocatalysts for the hydrogen oxidation reaction (HOR), oxygen reduction reaction (ORR) and alcohol (methanol or ethanol) oxidation reaction (AOR) remain considerable challenges in fuel cell implementation.

Platinum (Pt) is the most active and preferred electrocatalyst for the both anodic HOR and cathodic ORR. However, high cost and low utilization efficiency of state-of-the-art Pt electrocatalysts are key obstacles for broad application in fuel cells. Prof. Adzic's group have developed new approaches to design and synthesis of Pt electrocatalysts, including Pt monolayers, core-shell nanostructures, and single atoms. The effect of the physical structure of Pt in prepared catalysts was discussed and significant differences with commercial Pt/C catalysts were identified. The interaction between substrate and Pt or core and shell via in-situ x-ray absorption spectroscopy, electronic microscopy etc., was discussed. These characterization methods enable further optimization of the electrocatalytic performance of platinum.

Electrochemical measurements were used to evaluate the kinetics, stability, mechanism and overall performance for the HOR, ORR and AOR. Coupled with in-situ physical characterization, these results provided fundamental understanding between catalyst structure and activity. Pt-based catalysts were used to prepare membrane electrode assembly (MEA) based fuel cells which were shown to outperform commercially available Pt/C based fuel cells.

Questions and discussion focused on practical applications of fuel cells, especially for automotive power. The expenditure and power density of a prototypical fuel cell using catalysts prepared by the Adzic group were compared to commercial proton-exchange membrane fuel cells.

Xueliang Sun, *University of Western Ontario*

Single Atom Electrocatalysts for Fuel Cells

Discovery of efficient and cost-effective electrocatalysts is crucial for the development of high performance electrochemical energy devices. Investigations continue to be conducted in the fields of fuel cells and batteries for either changing the properties of active materials (e.g. Pt) and/or improving catalyst interaction with supporting materials.

Prof. Sun discussed a novel approach to enhancing the catalytic activity of proton reduction by single atom catalyst (SAC) deposition using atomic layer deposition (ALD). The presence of single atoms was confirmed locally using HR-TEM or globally by X-ray absorption near edge structure (XANES). During the ALD process, the Pt precursor ($MeCpPtMe_3$) was absorbed onto a carbon support (i.e., graphene and CNTs) through the interaction with hydroxyl terminal groups of the substrate followed by reduction to platinum metal (Pt^0). The Pt deposit size and number of ALD cycles were investigated. The highest quantity of single atom Pt (i.e., ~ 70 % SAC on graphene and 100 % SAC on N-doped CNTs) was obtained at 50 ALD cycles. A single atom supported on graphene exhibited a significant enhancement in current density (~ 40 times) over conventional Pt/C nanoparticles. However, Pt/C nanoparticles were found to be highly stable with negligible change after thousands of cycles.

Synthesis, characterization and performance of single bimetallic dimers were also discussed. An additional step of 50 ALD cycles using a ruthenium complex was performed following the deposition of single platinum atoms, resulting in the formation of Pt-Ru dimers with a coordination number of 1. The Pt – Ru dimers displayed strong enhancement in catalytic activity and stability. Using a computational approach, the active site of a dimer was predicted to be located at the ruthenium atom. Extending from this work, Zn – Co dimers were prepared and studied. Related studies from the literature (i.e. the preparation of a single iron hydroxide onto a single platinum nanoparticle) were also discussed.

Improvement in stability of SAC supported on graphene and on CNTs was discussed. It was found that a single atom could be stabilized after being trapped in between an organic network (i.e., aniline stacked graphene) or surrounded by a metal oxide wall. A trapped SAC was found to be highly stable with negligible decay after 2000 catalytic cycles with a strong current density (~ 50 times higher than commercial Pt/C).

Concluding remarks emphasized that single atoms and single bimetallic dimers were deposited onto different carbon supports (graphene and CNTs) using ALD technique. A SAC exhibits outstanding catalytic activity towards the hydrogen evolution, oxygen reduction and methanol oxidation reactions. Trapped and anchored single atoms were developed to improve stability.

A majority of questions from the audience focused on determination of the real surface area of the platinum catalysts and on possible substrate effects due to the interaction/affinity between a single atom and the supporting material. Diffusion of redox molecules to a trapped single atom center is not well understood. For example, steric hindrance induced by a metal oxide, organic polymer or aniline ring do not appear to affect the electrocatalytic performance of the atomic platinum center that resulted in enhanced kinetics observed in the proton reduction reaction.

***Allen J. Bard and Graeme Henkelman**, The University of Texas at Austin*

The HER on Isolated Single Platinum Atoms, Clusters and Nanoparticles: Experiment and Theory

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Prof. Bard established the principles of single atom electrochemistry for the HER (hydrogen evolution reaction). Prof. Henkelman followed with a description of a DFT (density functional theory) approach to understanding the response of a single atom on a particular surface towards the HER. A major theme of the presentation was on expanding electrochemical boundaries to consider the smallest surface on which one can measure a current-potential signal using current electroanalytical techniques.

Prof. Bard explained the fundamentals of the single atom experiment on the blackboard. He explained that when an electrode surface is small enough (i.e., a few hundreds of nm), the flux of a single redox species **A** towards the electrode surface depends on the concentration and diffusion coefficient of that species. When the concentration of **A** reaches fM levels, one can consider time-dependent arrival of single molecules at the electrode surface. At a given potential, a single $[PtCl_6]^{-2}$ ion is reduced to Pt^0 at the electrode surface, which then can be characterized by cyclic voltammetry (CV). For example, surprisingly, a CV for a single Pt atom for the HER was observed, indicating that electrochemistry is sensitive enough to characterize single atoms to large atomic clusters. Prof. Bard explained that with this experiment, HER kinetics from a single atom, atomic cluster, and nanoparticle can be addressed roughly using the Butler-Volmer model assuming the first electron transfer is the rate determining step. After extracting the rate constant from each CV for different sizes of atomic clusters and nanoparticles, the rate constant was found to decrease as Pt approached the size of a single atom. Bulk Pt behavior was found at nanoparticles of radius > 5 nm.

Prof. Henkelman explained how DFT calculations are used to estimate the activity of single atoms, atomic clusters and nanoparticles as a function of size. His approach to these DFT calculations was based on DFT methodology published earlier by Jens Norskov for estimating activity of different materials using similar reactions. Prof. Henkelman discussed the difficulties in estimating a rate constant for each atomic cluster size. His strategy was to select a current density and estimate the onset potential based on an energy landscape for each nanoparticle size which he then correlated with experimental data from Prof. Bard's group. Prof. Henkelman showed preliminary DFT results that illustrated the *d*-band center on a Pt single atom moving towards that in bulk Pt as the atom increased in size.

Profs. Bard and Henkelman both concluded that more experiments and calculations are necessary to fully understand how the activity of Pt single atoms and clusters changes, what causes the change, and what model to use in understanding kinetic activity of single atoms and clusters, and if there are substrate effects to consider.

Three of the workshop speakers asked fundamental questions during the question session. Radoslav Adzic asked about impurities in solution and if these impurities obscure observation of H *upd* on a single atom. Shirley Meng praised the overall research and asked how the *d*-band center is changing and how DFT helps in understanding the *d*-band effect. Prof. Sun was concerned about the stability of the atoms on the electrode surface.

Shirley Meng, *University of California San Diego*

Electrochemical and Chemical Quantification of SEI on Lithium Metal Anodes

Dr. Meng discussed her research on lithium metal anodes for lithium ion batteries (LIB). Lithium metal is viewed as the ultimate battery anode because of its high theoretical capacity and low electrode potential. Determining the fundamental properties dictating lithium metal plating−stripping behavior is challenging because characterization techniques are limited by the sensitivity of lithium metal to damage (i.e., altered morphology and chemistry) by external probes. Motivated by a recent application of cryogenic transmission electron microscopy (cryo-TEM) to characterize lithium metal at the atomic scale, Dr. Meng described the use of a cryogenic focused ion beam (cryo-FIB) method as a quantitative tool for characterizing the bulk morphology of electrochemically deposited lithium and as a technique that enables TEM observation of Li-metal/solid-state electrolyte interfaces.

Dr. Meng described how these advanced technologies (i.e., XPS, cryo-TEM and cryo-FIB) are used to investigate electrochemical performance and mechanistic effects of incorporating two salts in an ether electrolyte in Li–metal cells. She explained that the solid electrolyte interphase (SEI) formed from the electrolyte primarily consists of larger anion fragments, suggesting that the anion chemistry strongly influences the extent of reduction and resulting surface chemistry. Dr. Meng also described a method to quantify the amount of inactive lithium in lithium metal batteries using a combination of H_2O titration and gas chromatography.

There was lengthy discussion to clarify how to accurately determine the quantity of inactive lithium in lithium metal batteries.

John Reynolds, *Georgia Institute of Technology*

Conjugated Polymers for Organic Photovoltaics: The Minimal Structural Change Approach in Active Material Design and Optimization

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Tunability of chemical structures of semiconducting polymers has led to significant improvement in performance of organic photovoltaics by reaching a power conversion efficiency of 15%. An effective strategy has been to utilize conjugated co-polymers composed of fused aromatic rings. Considerable effort has gone into developing fused aromatic rings that have electron-rich or electron-deficient moieties and into co-polymerizing both types of aromatic rings to have donor-acceptor alternating arrays of conjugated co-polymers that can tailor electronic properties (e.g., band gap and Fermi energy). Chemical structure affects electronic properties and also impacts polymer conformation and crystal packing morphology in films. Thus it is important to understand chemical structure-morphology-optoelectronic property relationships of these co-polymers to further enhance performance of organic photovoltaics.

Dr. Reynolds used a “one atom change” approach to study the impact of chemical structure of the co-polymer on morphology, optoelectronic properties, and device performance. A donor-acceptor conjugated co-polymer composed of bithiophene fused ring and thienopyrrolodione was used as a model system. Three different co-polymers were prepared by one atom variation with group 14 atoms (e.g. C, Si, Ge) at the center of a bithiophene unit: poly(dithienosilole-thienopyrrolodione) P(DTS-TPD), poly(dithienogermole-thienopyrrolodione) P(DTG-TPD), and poly(cyclopentadithiophene-thienopyrrolodion) P(DTC-TPD). The C-centered co-polymer, P(DTC-TPD), showed a different rotational conformation compared to Si- and Ge-centered co-polymers, P(DTS-TPD) and P(DTG-TPD), confirmed by ^{1}H-NMR. The difference in chain conformation affected crystalline structures. Grazing incident wide angle X-ray scattering (GI-WAXS) was used to investigate inter-chain packing in co-polymer thin films. P(DTC-TPD) films displayed edge-on backbone orientation in contrast to ace-on orientation found to be dominant in P(DTS-TPD) and P(DTG-TPD) films. Transient absorption spectroscopy was used to examine charge dynamics under illumination, where a P(DTC-TPD):fullerene blend film showed triplet formation resulting in higher bimolecular recombination. Performance of organic photovoltaics was compared and lower power conversion efficiency was observed for those with P(DTC-TPD) due to unfavorable morphology for charge separation and transport. Variation in chemical structure of the semiconducting polymers was found to have dramatic impact on conformation, morphology, charge dynamics, and device performance.

There was lengthy discussion on cost and stability of organic solar cells. One of the bottle necks of the high cost of organic solar cells is the fullerene and many studies are ongoing to develop organic solar cells without it. In terms of stability, semiconducting polymers can degrade under ambient conditions so that encapsulation is required to address this issue.

Frédéric Kanoufi, *Universite Paris Diderot*

Optical Imaging of Single Nanoparticle Electrochemistry

Dr. Kanoufi discussed novel in situ optical imaging of single nanoparticles (NPs) and real-time monitoring of their electrochemical behavior. He introduced Ag NP collision experiments on microelectrodes and how to image NPs in situ optically. Because the imaging resolution was limited by diffraction ($\lambda \sim 500$ nm), super-resolution imaging techniques were necessary in obtaining images of NPs below 300 nm. Utilization of dark-field microscopy for studies of electrodissolution of Ag NPs and electrosynthesis of Ag NPs was described. By correlating the optical and electrochemical signals, Kanoufi's group obtained the dissolution rate of Ag NPs at microelectrodes during electrochemical oxidation. They also studied the size effects on the Ag NP electrochemical reactions and transport pathways.

Kanoufi's group also investigated another interesting electrocatalyst, Co oxide. Using dark field microscopy, they monitored electrodeposition of Co-based NPs on nanoelectrodes with nanoelectrodes of 5 nm radius. They proposed a reaction mechanism for Co ion anodic electrodeposition at different pH values.

The basic principle of backside absorbing layer microscopy (BALM) was also discussed. An antireflective Au coating was used on the substrate to decrease optical signal noise. This optical microscope provides a much higher spatial resolution compared to the dark field microscope. Real-time monitoring of the electrodeposition and electrodissolution of smaller Ag NPs was achieved. Optical voltammograms on single Ag NPs were obtained. AgCl NP reduction was monitored in a pippet-based microelectrochemical cell.

During the discussion, a question was raised regarding the stability of the Ag NP attachment on the substrate during electrochemical oxidation. For example, how does one determine whether NPs are oxidized or are detached from the substrate? Kanoufi emphasized that the 3D imaging capability of his optical microscope permits observation of NP detachment.

***Michael J Aziz**, Harvard University*

Organic-Based Aqueous Flow Batteries for Stationary Electrical Energy Storage

Prof. Aziz emphasized that the national electric grid of the US and those of countries across the world is slowly shifting to renewable sources of energy such as wind and solar. However, the intermittent nature of these sources warrants the need for energy storage systems such as redox flow batteries (RFBs). He showed the importance of energy density and power density in RFBs. He also emphasized that implementation of such systems is highly sensitive to cost. Although vanadium RFBs have been successfully implemented, the volatile nature of the cost of vanadium is a major deterrent for fully embracing this technology. This motivates his group to study a class of organic molecules called quinones. Quinones are easily available from “green” sources such as broccoli and can be synthesized in the lab with myriad of favorable properties making them an attractive candidate for RFBs.

Quinones undergo a highly-reversible, two-electron redox reaction in a flow battery. The seminal work from his group, published in *Nature* (2014), consisted of sulfonated anthraquinones that are water soluble and also possess excellent kinetics, to enable high energy and power densities comparable to vanadium-based RFBs. This compound however operates in acidic media and thus requires the use of the corrosive and toxic HBr/Br_2 couple as the cathode.

To overcome this limitation, 2,6-dihydroxyanthraquinone was used in basic media to enable the use of much safer potassium ferricyanide as the active cathode species. This type of battery showed promising performance and was reported in *Science* (2015). They expanded on this discovery by attaching carboxylate groups to anthraquinone, which resulted in a class of compounds they coined as “Methuselah” quinones. These compounds exhibited increased cycling stability and low self-discharge, which were new firsts for organic flow battery materials. Despite several advantages, this material fell short in terms of calendar-life which is critical for RFBs. They identified the potential degradation mechanism through DFT calculations. Knowing this, they designed a phosphonate-functionalized “Lazarus” quinone in which the performance of the battery could be resurrected through a simple aeration technique.

Recently, the group developed an ambidextrous material that can work as both the anode and the cathode, depending on the number of quinone groups that are oxidized. A 1 V difference between these two states makes it attractive for RFBs and greatly minimize the drawback of the cross-over of active species across the membrane separating the two halves of a flow cell. This represents an important advantage over vanadium RFBs, and opens up an avenue for further exploration that could be promising in the future.

Questions from the audience focused on the active-material cross-over occurring with quinones and the effect that membrane selection had on it. This was followed by a noteworthy observation by Prof. Bard on the pumping losses occurring in a flow cell. Prof. Aziz acknowledged this as an issue and said they could correct for such losses. He also emphasized the need for further development of compounds that could facilitate the use of thinner, porous and inexpensive membranes which would not only reduce the pumping costs but also the system cost.