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14. ABSTRACT

The Center for Electrochemistry (CEC) at the University of Texas at Austin held its seventh annual electrochemistry workshop February 7–8, 2015 in Welch Hall on the campus of The University of Texas at Austin. There were 160 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: energy conversion and storage, understanding electrocatalysis through DFT, CO2 reduction, and electrochemical sensors.

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Report Title

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ABSTRACT

The Center for Electrochemistry (CEC) at the University of Texas at Austin held its seventh annual electrochemistry workshop February 7–8, 2015 in Welch Hall on the campus of The University of Texas at Austin. There were 160 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: energy conversion and storage, understanding electrocatalysis through DFT, CO2 reduction, and electrochemical sensors.

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(a) Papers published in peer-reviewed journals (N/A for none)

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Number of Papers published in non peer-reviewed journals:

(c) Presentations

Number of Presentations: 0.00

Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

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TOTAL:

Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received	Paper

TOTAL:

Number of Peer-Reviewed Conference Proceeding publications (other than abstracts):

(d) Manuscripts

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Received	Book

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TOTAL:

Patents Submitted

Patents Awarded

Awards

Graduate Students

NAME	PERCENT_SUPPORTED

FTE Equivalent:
Total Number:

Names of Post Doctorates

NAME	PERCENT_SUPPORTED

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Names of Faculty Supported

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Names of Under Graduate students supported

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FTE Equivalent:	
Total Number:	

Student Metrics

This section only applies to graduating undergraduates supported by this agreement in this reporting period

The number of undergraduates funded by this agreement who graduated during this period:	0.00
The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:......	0.00
The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:......	0.00
Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale):......	0.00
Number of graduating undergraduates funded by a DoD funded Center of Excellence grant for Education, Research and Engineering:......	0.00
The number of undergraduates funded by your agreement who graduated during this period and intend to work for the Department of Defense	0.00
The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields:......	0.00

Names of Personnel receiving masters degrees

NAME
Total Number:

Names of personnel receiving PHDs

NAME
Total Number:

Names of other research staff

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Sub Contractors (DD882)

Inventions (DD882)

Scientific Progress

See Attachment

Technology Transfer

2015 CEC Annual Workshop on Electrochemistry

February 7–8, 2015

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 seventh annual electrochemistry workshop February 7–8, 2015 in Welch Hall on the campus of The University of Texas at Austin. There were 160 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: energy conversion and storage, understanding electrocatalysis through DFT, CO_2 reduction, and electrochemical sensors. CEC faculty members moderated the sessions and promoted discussion. There was additionally a panel discussion on the topic of DFT and electrochemistry by the speakers from that session.

CEC host Allen J. Bard opened the conference with a discussion of the CEC mission and the request that all participants actively engage the topic. The workshop format allowed for interactive exchange with each of the eleven speakers having a full 50 minutes to present their materials 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 40 posters and answered questions from attendees in an informal evening session.

By every account the meeting was a rousing success, and the CEC would like to acknowledge and thank the meeting's sponsors who made it possible: The U.S. Army Research Office (Contract No. W911NF-15-1-0085), The Energy Institute at The University of Texas at Austin, 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 2016 meeting will again focus on a variety of current topics in a session format.

AGENDA

Saturday, February 7, 2015

7:30-8:30a	Check-in and continental breakfast.
8:30-8:40	Introductory remarks.

Energy Conversion and Storage – Arumugam "Ram" Manthiram, Moderator

8:45-9:35	**Sossina Haile**, *California Institute of Technology* Electrochemistry at the Metal-electrolyte-gas Interface of Solid-state Proton-conducting Electrolytes.
9:40-10:30	**Sri Narayan**, *University of Southern California* Advances in Inexpensive and Robust Energy Storage in Aqueous Rechargeable Batteries.
10:30-10:50	Break.
10:50-11:40	**Johna Leddy**, *The University of Iowa* Magnetoelectrocatalysis.
11:40a-1:20p	Lunch break.

Understanding Electrocatalysis through DFT: What's Right and Wrong with this Approach? – Graeme Henkelman, Moderator

1:20-2:10p	**Aleksandra Vojvodic**, *Stanford University* Electrocatalysis of Oxide Surfaces from DFT.
2:15-3:05	**Michael Janik**, *Pennsylvania State University* Electrocatalysis with DFT: Incorporating the Electrode-electrolyte Interface in Mechanistic Analysis.
3:05-3:25	Break.
3:25-4:15	**William A. Goddard, III**, *California Institute of Technology* First Principles-based Simulations of Electrocatalysis including the Role of Solvent and Ions.
4:15-5:15	**Panel discussion** including all speakers from this session.

Poster Session, Reception, and Exhibition

5:15-7:45p Posters and reception

Sunday, February 8, 2015

7:30-8:30a	Continental breakfast.

CO_2 Reduction – Allen J. Bard, Moderator

8:30-9:20	**Jean-Michel Savéant**, *Université Paris Diderot (Paris 7)* Molecular Catalysis of the Electrochemical Reduction of CO2: Recent Advances.
9:25-10:15	**Andrew Bocarsly**, *Princeton University* Electrocatalytic Reduction of Carbon Dioxide.
10:15-10:35	Break.

Electrochemical Sensors – Bob Villwock, Moderator

10:35-11:25	**Adam Heller**, *The University of Texas at Austin* Glucose Monitoring for Diabetes Management.
11:30a-1:10p	Lunch break.
1:10-2:00p	**Rebecca Lai**, *University of Nebraska-Lincoln* Folding- and Dynamics-based Electrochemical Biosensors.
2:05-2:55	**Minshu Du** and **Allen Bard**, *The University of Texas at Austin* Mechano-electrochemistry and Strain Effects.
2:55-3:15	closing remarks.

2015 CEC Workshop speakers (from left): Michael Janik, Sossina Haile, Rebecca Lai, Aleksandra Vojvodic, Bill Goddard, Adam Heller, Jean-Michel Savéant, Sri Narayan, Andrew Bocarsly, Johna Leddy, Allen Bard.

I. Energy Conversion and Storage Session

Sossina Haile, *California Institute of Technology*
"Electrochemistry at the Metal-electrolyte-gas Interface of Solid-state Proton-conducting Electrolytes."

Dr. Haile is part of the materials science and chemical engineering at CalTech. Her research focuses on finding the better materials and understanding the electrocatalysis reactions to increase the efficiency of fuel cells, with particular interest in proton-conducting solid-acid electrolytes. She noted that CsH_2PO_4 is an excellent electrolyte for fuel cells because it is very stable at both oxidized and reduced states, with power density of 415 mW/cm^2. These materials are the focus of a startup company from Caltech. In terms of advancing the fuel-cell technology, what we need to do now is improve electrocatalysis and understanding the system, rather than worrying about making thinner membrane fuel cells. She has particular interest in the anode (Pt, 8 mg/cm^2) preparation and stability.

The general understanding of electrocatalysis in solid acid fuel cells is that the reaction pathway involves a triple-phase boundary (gas phase, electrolyte phase, and electrically conductive solid phase). In these composite electrodes, hydrogen adsorbs, and then diffuses to the triple-phase boundary where the electrochemical reaction occurs. In contrast, Dr. Haile used thin Pt films for electrodes and found that hydrogen oxidation occurs by diffusion of hydrogen through Pt, taking advantage of the entire Pt/CsH_2PO_4 interfacial area rather than being confined to the triple-phase boundary sites. The films were characterized using XRD, SEM, and TGA, and the fuel cell measurements were done by the use of AC-impedance spectroscopy. For flat, planar electrodes of very thin Pt films, she obtained a Pt utilization that is significantly higher than in typical composite electrodes. The activity occurs mainly at the Pt/H_2 interface and not at the Pt/electrolyte interface.

Dr. Haile also showed that Pt-decorated carbon nanotubes electrodes can support ultralow loadings of Pt capable of catalyzing both proton reduction and hydrogen oxidation at low overpotentials. Direct growth of Pt nanoparticles onto carbon nanotubes ensured minimal catalyst particle isolation, whereas electrospray deposition of electrolyte and electrocatalyst-bearing solutions led to composite electrode structures with uniformly distributed and size-matched components. This dramatic improvement in the Pt utilization is likely a result of electrical access to all Pt particles in the structure.

Sri Narayan, *University of Southern California*
"Advances in Inexpensive and Robust Energy Storage in Aqueous Rechargeable Batteries"

Dr. Narayan is a professor at the University of Southern California and has a distinguished record of fundamental and applied research in electrochemical energy storage and conversion. During his previous position at the Jet Propulsion Laboratory, he was involved in the development of direct methanol fuel cells. At USC, he has shifted his focus to large-scale energy storage.

In order for energy storage to enable the widespread adoption of renewable energy and improve electric grid reliability, particularly in developing countries, it must be robust, inexpensive, and sustainable. Most materials used in today's batteries, such as lithium and lead, are not abundant enough to meet these needs. For example, all of the available lead in the world could only make 2 GWh of lead-acid batteries. Therefore, his group is focusing on aqueous batteries using abundant materials such as iron and organic molecules. In particular, they are developing four different battery systems: iron-chloride, iron-nickel, iron-air, and a redox flow battery using quinones. Aside from the quinone battery, none of these battery systems are new; in fact, the iron-nickel battery was first developed over 100 years ago. However, Dr. Narayan believes that with some improvements, one or more of them may be able to meet our needs for large-scale energy storage.

He began by discussing the quinone system, which uses modified forms of dihydrobenzoquinone at the postitive electrode and anthraquinone at the negative electrode. Although many redox reactions of quinones are electrochemically reversible, their stability and solubility in water is limited. Dr. Narayan's group has modified these quinones with sulfonic acid groups to increase their solubility to almost 2 M and has developed a 0.7 V battery that shows almost no capacity loss and 70% energy efficiency. Given the low cost of the quinones and other materials in this battery, this system can potentially be commercialized.

Moving on to the iron-based systems, he noted that the iron electrode has long been hampered by two problems. The most significant problem is the fact that the $Fe(OH)_2/Fe$ redox couple (-0.877 V *vs*. NHE) sits at a more negative potential than the H_2O/H_2 (-0.828 V) redox couple in alkaline solutions. Therefore, H_2 evolution at the Fe electrode results in current efficiencies around 60%. They took three approaches to suppressing H_2 evolution. First, they used high-purity carbonyl iron to make the electrodes, since many metal impurities promote H_2 evolution. Second, they used alkanethiol additives to suppress the transport of H_2 to the electrode surface. Finally, they added Bi_2O_3 to the electrode to increase the overpotential for H_2 evolution. They found that a combination of the first and third approaches reduced H_2 evolution tenfold, resulting in current efficiencies greater than 95%. Also, adding sparingly soluble but conducting FeS prevented passivation of the Fe electrode by $Fe(OH)_2$ during discharge, thereby improving the discharge rate of the battery.

Dr. Narayan's group has spent the most time developing the iron-nickel battery and is in process of scaling up that system. However, despite the high energy density of the battery (>100 Wh/L), the high cost of nickel means that it will be almost impossible to reach the DOE cost target of $100/kWh with that chemistry. Therefore, they have begun to explore the iron-air system, which has the distinct advantage of replacing nickel with free oxygen. Having addressed many of the problems with the iron electrode, they are working on addressing the irreversibility of the oxygen redox couple, which is one of the oldest problems in electrochemistry. Despite extensive work on bifunctional catalysts, they have found greater success using separate electrodes for oxygen reduction and oxygen evolution. Combined with the improved iron electrode, they believe that among the four battery systems they are developing, this system has the most potential to be a low-cost energy storage solution for the future.

Johna Leddy, *The University of Iowa*
"Magnetoelectrocatalysis"

Dr. Leddy is an Associate Professor of Chemistry at The University of Iowa. Her research focuses on magnetic effects in electrochemical systems. These effects are not thermodynamic or equilibrium processes, but rather act upon mass transport and kinetics. The fundamental idea is that when an electron is transferred, both its charge *and spin* must be transferred. Electron spins set magnetic properties of materials, and also interact as small magnets. Electrochemical systems are therefore ideal systems for magnetic modification of reaction kinetics.

Dr. Leddy's main idea is that magnetic fields open new reaction pathways, can alter reaction rates, and modify product distributions. Her studies of magnetic field effects on chemical kinetics run from the fundamentals of theory and modeling through experimental demonstration and evaluation of effects in composite materials to implementation in technologies such as fuel cells and batteries.

Dr. Leddy presented data that indicate a magnetic effect is observed across a wide range of electrochemical systems, especially where there slow mass transfer and high concentrations, such as in solid polymer electrolytes, adsorbates, or near solid matrices. She presented cyclic voltammetry data showing enhanced kinetics in the presence of a magnetic field for $Ru(bpy)_3^{2+}$,

$Ru(NH_3)_6^{3+}$, and $Co(bpy)_3^{2+}$ at ring/disk electrodes with Nafion® films that contained 6 μm magnetic particles (micromagnets). Other systems discussed included: diffusion-limited CO oxidation on Pt enabled by introduction of micromagnets to Pt, enhancement of photogenerated H2 on p-Si with micromagnets, power enhancement from a PEM fuel cell, and improved capacity for alkaline MnO_2 batteries and supercapacitors.

The magnetic effects are dependent upon both the nature of the electrode and the electroactive redox couple. Dr. Leddy presented a Marcusian model that assumes that the standard free energy curves are "split up and down" by the Zeeman energy, $Z'=gSB\beta$, which is proportional to the magnetic field B. The model explains multiple reaction pathways and a shift in $q^{\ddagger}$, but yields an improbably high Z', and is therefore still inadequate to describe our understanding.

II. Understanding Electrocatalysis through DFT: What's Right and Wrong with this Approach?

Aleksandra Vojvodic, *Stanford University*
"Electrocatalysis of Transition-metal Oxide Surfaces from DFT"

Dr. Vojvodic is a Staff Scientist at Stanford University whose work is funded by DOE, SUNCAT and SLAC. Her research focuses on using Density Functional Theory (DFT) to probe the electronic structure of photo- and electro-catalysts used in the Haber-Bosch process and water-splitting reaction. The goal of her work is to design energy- and atom-efficient materials with tailored properties to minimize energy use for these energy intensive processes. Using DFT, Vojvodic simplifies catalysts consisting of N interacting atoms, whose interaction is described by the Hamiltonian operator from quantum mechanics by modeling them as N non-interacting particles, each with an effective potential that can be adjusted to fit experimental data.

The Haber-Bosch process is currently used to produce NH_3 fertilizer to feed a third of the world's population. The reaction itself is slow and needs to be operated at 700-900°C for sufficiently fast kinetics, but to maintain a reasonable conversion the operating pressure must be on the order of 100-150 bar. These harsh conditions combined with the huge industrial scale of the Haber-Bosch process consumes 3-5% of the world's natural gas supply and 1-2% of the energy used. Better catalysts are needed to reduce the energy resource requirements for the process, but for a long time scientists had problems finding an appropriate descriptor for the reaction. It turns out that nitrogen adsorption energy is an excellent descriptor for the reaction and K promoting catalysts make better agreement between theory and experiment. Vojvodic investigated the underlying bonding and anti-bonding states and found the N_2 adsorption energy scales linearly and negatively with d-orbital energy.

The water splitting reaction is limited by the OER's slow kinetics. Each step of the multistep mechanism has a different potential, which is part of the reason for a high overpotential for practical oxygen evolution. She used the adsorption energy of OOH- and OH- to calculate ~0.37 V as the minimum theoretical overpotential. Vojvodic's group screened ~20,000 materials to find one material that could function as a photo-electrocatalyst for H_2O splitting and identified 15 that had the right combination of band gaps and potentials. Unfortunately, all had overpotentials larger than their band gaps and 1 catalyst alone would not suffice. She concluded that co-catalysts would be needed to photo-electrocatalytically split H_2O. She also modeled TiO_2 (a cheap catalyst) doped with metals for OER, but found that its conductivity is too low for practical use. Vojvodic also made a database of ABO_3 perovskite oxides for OER and found that e_g and t_{2g} electron filling is not a proper descriptor as suggested by other scientists. Vojvodic suggested that there appears to be a confinement effect that influences the activation energy needed for OER.

Michael Janik, *Pennsylvania State University*
"Electrocatalysis with DFT: Incorporating the Electrode-electrolyte Interface in Mechanistic Analysis"

Dr. Janik is the Brennan Clean Energy Professor in the Department of Chemical Engineering at Penn State.

Computational methods based on quantum mechanics are an essential tool for relating catalyst activity and selectivity to composition and structure. Quantum mechanical methods may be used to aid in explaining observed catalytic behavior or in some ways to predict the performance of yet untested catalyst formulations.

Dr. Janik's presentation on first-principles electrocatalysis was in two parts. The first part dealt with ion adsorption, approaches to modeling solvation, and potential dependence, with an example of anion and cation adsorption for PEMFC and AEMFCs. The second part dealt with electrochemical activation barriers, that is models of electron transfer at an adsorbed active site. This had examples related to CO2 reduction on CU(111) and also catalyst design for borohydride oxidation.

William A. Goddard, III, *California Institute of Technology*
"First Principles-based Simulations of Electrocatalysis including the Role of Solvent and Ions"

Dr. William Goddard, Director of Materials and Process Simulation Center at CalTech, joined the CEC workshop to share some of his expertise in multiscale and multi-paradigm modeling. Dr. Goddard gave an extensive overview of his computational studies of fundamental mechanisms and potential optimizations for fuel cell reactions. His studies of oxygen reduction reaction (ORR) at several levels of theory will be summarized here to highlight his use of novel computational techniques that address problems in modeling solvation and longer length and time scales.

The first approximation to modeling surface reactions is to assume the reaction occurs in vacuum. Adding one more level of theory, Dr. Goddard implemented continuum Poisson-Boltzmann theory to simulate the effect of solvent on reaction barriers. Implicit solvation models generally describe the volume of solvation with the dielectric constant of the solvent.

Dr. Goddard compared two ORR reaction pathways, O_2 dissociation and OOH association on Pt surface, in vacuum versus implicit solvent. He found both pathways have higher reaction barriers in water, suggesting alternative mechanisms must be considered to describe ORR on platinum (111) surface. A possible reaction pathway, $O_{ad} + H_3O^+ + e^- \rightarrow OH_{ad} + H_2O$, was studied and the optimum voltage which stabilizes the intermediates found to be 0.68 V.

Dr. Goddard presented several examples of how the trade-off between chemical accuracy and increased length and time scales can be addressed using force-field models. Traditionally, the most accurate descriptions of chemical systems are quantum mechanical and parameterized empirical potentials often correctly model only one or two aspects of the system. ReaxFF is a force-field potential, but is parameterized against quantum mechanical systems so does not have as many limitations as empirical potentials.

In one study, several hundred-thousand Pt and Ni atoms were used to simulate alloyed nanoparticles up to several nanometers in diameter using a ReaxFF potential. Experimentally, it was found that Pt_3Ni_7 had the highest activity for ORR reactions but that Ni had been dissolved. Computational models were used to predict the ratio of Pt/Ni, porosity of Pt after Ni is removed, and the critical nanoparticle size for optimum ORR activity. It was found that the experimentally predicted alloy, Pt_3Ni_7, was the most active and this is due to the connectivity of resulting pores in large (>5 nm) Pt nanoparticles.

In a final example, the use of ReaxFF in accelerated molecular dynamics (aARRDyn) was shown for a full model of ORR on a Pt surface with explicit water molecules.

He was able to gain insight into the interfacial structure and determine the free energy barriers of rate determining reactions. The observed ORR pathway was not the expected pathway as it was expected that more H_2O would be involved in mechanism. The ordered first and second shell of H_2O at the interface and the change of the dielectric constant through each shell may have limited the participation of H_2O.

III. CO_2 Reduction

Jean-Michel Savéant, *Université Paris Diderot (Paris 7)*
"Molecular Catalysis of the Electrochemical Reduction of CO_2: Recent Advances"

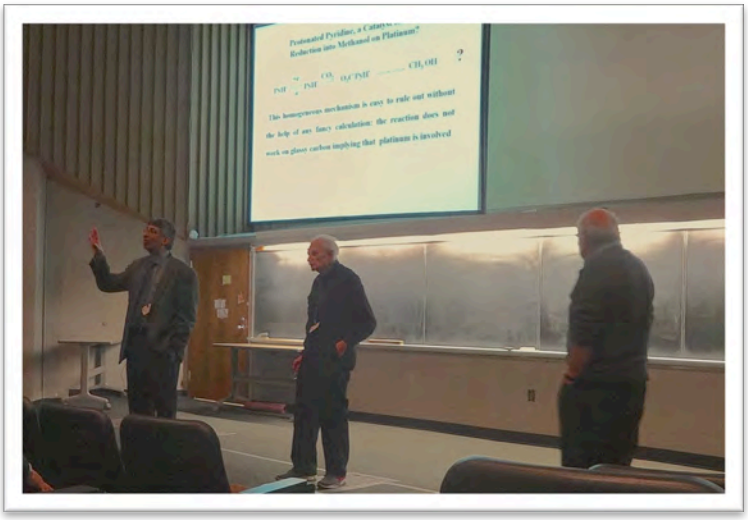
Dr. Savéant is part of the Université Paris Diderot and has had a profound influence on electrochemistry in terms of kinetics. Savéant's talk centered around the electrochemical and electrocatalytic reduction of carbon dioxide, which is work he and his co-workers have been pursuing in the recent years. In the growing industrial climate around the globe, output of carbon dioxide has reached a maximum. Due to this efflux of the greenhouse gas, many scientists have been pursuing methodologies that will convert atmospheric carbon dioxide to useful products, such as methane, methanol, formic acid, etc. Carbon dioxide reduction to carbon monoxide is an essential step in the total reduction of carbon dioxide to methane, and Savéant presented data that indicate iron-porphyrin compounds in an organic solvent (dimethylformamide) can achieve this reduction at an astounding turnover frequency.

Savéant has utilized the cyclic voltammetry technique to show that iron-porphyrin in DMF solution can electrocatalytically reduce carbon dioxide to carbon monoxide with a faradaic yield of 90% at 50 million turnovers over 4 hours. In this system, Savéant and co-workers observed no significant degradation of the catalyst.

Using several molecules of the same nature and changing substituents, Savéant was able to optimize the performance of the carbon dioxide to carbon monoxide turnover. To this end, Savéant showed the efficacy of the method at low overpotentials. Savéant was also interested in the mechanism by which this turnover occurred, and began changing substituents on the molecules to study the turnover frequency as a function of substituent (phenolic position, hydroxyl substituents). He found that the basis for the high activity appears to be the relatively large local concentration of protons associated with his substituent changes, specifically the phenolic-hydroxyl substituents..

Andrew Bocarsly, *Princeton University*
"Electrocatalytic Reduction of Carbon Dioxide"

Dr. Bocarsly's lab group is located in Princeton University's Department of Chemistry and a part of his research focuses on electrochemical and photoelectrochemical CO_2 reduction. Dr. Bocarsly first methanol synthesis by photoelectrochemical CO_2 reduction on a p-GaP semiconductor electrode in the presence of 10 mM pyridine at pH 5.2 in aqueous electrolyte. This process demonstrated 96% faradaic efficiency for methanol formation at a p-GaP electrode at 200 mV of underpotential. He proposed a mechanism for electrochemical reduction of CO_2 catalyzed by pyridinium cation with some known problems such as the formation of a carbamate intermediate resulting from the interaction between pyridinyl radical and CO_2. Dr. Bocarsly presented a study of three derivatives of the pyridinium ion as the *N*-methyl pyridinium cation and two lutidine (dimethyl pyridine) species where he claimed the electro-inactivity of the first one compound and the presence of methanol after CO_2 reduction on p-GaP (100) electrode with lutidine catalysts.



Dr. Bocarsly discussed the mechanism proposed by Batista concerning the crucial role of surface Pt hydride in the electrochemical reduction of CO_2 catalyzed by aqueous pyridinium cation on a Pt electrode, leading to formic acid. On a Pt electrode, proton reduction does not occur by π-system reduction. Presenting cyclic voltammograms, he demonstrated the scan-rate dependence of pyridinium reduction on a Pt electrode in the absence of CO_2, where one can see the presence of an additional reversible system at high scan rates corresponding to proton reduction and hydrogen oxidation, which is evidence of hydrogen adsorption on Pt electrode surface.

Dr. Bocarsly presented the two main controversial points of view through a mechanistic overview of the electrochemical reduction of CO_2 on Pt electrode in the presence of pyridinium cation catalyst where it's showed that in one case hydrogen is produced and in the other case we see methanol production. In particular, Savéant's group has obtained only hydrogen formation upon electrochemical reduction of

CO_2 with pyridinium ion on Pt electrode, while Bocarsly's team has observed between 0 and 25% of methanol in similar conditions. Finally, Bocarsly concluded on these two very different examples by the citation of several important parameters such as the interfacial pH and the surface adsorption, which should be controlling for scaling a real system.

Finally, Bocarsly briefly presented data and a proposed reaction mechanism for the electrochemical reduction of CO_2 to formate in an aqueous electrolyte at an anodized indium electrode surface, showing XPS and also ATR-IR data of the electrode.

IV. Electrochemical Sensors

Adam Heller, *The University of Texas at Austin*
"Glucose Monitoring for Diabetes Management"

Adam Heller is Professor Emeritus in the McKetta Department of Chemical Engineering at UT-Austin and consultant to Abbot Diabetes Care. Generally considered to represent the greatest triumph in the commercialization of an electrochemical biosensor technology, modern electrochemical glucose assays are currently used by about 150 million people to monitor and manage their diabetes. Thanks to electrochemical glucose assays, it is now much easier for patients to keep their glucose levels in check and effectively prevent the severe complications that result from chronic high blood sugar, including but not limited to neuropathy, retinopathy, vascular disease and renal disease.

Professor Heller gave a historical account regarding the evolution of electrochemical glucose sensing from the discovery of glucose oxidase to the advent of state-of-the-art continuous glucose monitoring devices. He stressed the importance of considering the patient's perspective when developing a sensing methodology into a user-friendly technology for patients to monitor, analyze, and effectively treat themselves. Four very important measures of performance in glucose sensors were outlined as the following: simplicity, painlessness, accuracy, and affordability. Heller recognized the interdisciplinary team comprised of scientists, engineers, and medical professionals throughout the years who have dedicated their careers to achieving a wearable subcutaneous continuous glucose sensor of unsurpassed accuracy and convenience to the patient.

Heller's research group is credited for helping to solve a very important fundamental problem in electrochemical glucose sensing, especially for subcutaneous implanted sensors where oxygen concentration is low, the so-called "electrical wiring" of glucose oxidase in order to replace the older methods that relied on charge transport by diffusion of O_2/H_2O_2. This was accomplished by engineering special conductive polymers containing $Os^{2+/3+}$ complex redox centers. The polymers form a conductive hydrogel network whereby electrons hop from one redox center to another and effectively provide direct wiring to the glucose oxidase enzymes. Heller ended the presentation by sharing the latest results of the implanted continuous glucose sensor from Abbot Diabetes Care, which relies on Heller's $Os^{2+/3+}$ polymers to help achieve accurate continuous glucose readings without calibration for up to two weeks! The implanted continuous glucose sensor is an incredible triumph for diabetes care as it provides hundreds of millions of patients the means to effectively monitor glucose levels with ease and comfort.

Rebecca Lai, *University of Nebraska-Lincoln*
"Folding- and Dynamics-based Electrochemical Biosensors"

Dr. Rebecca Lai is currently the Susan J. Rosowski Associate Professor of Chemistry at the University of Nebraska-Lincoln. Dr. Lai shared her most recent advances in biosensors, as well as the path of results and publications that have led up to her most recent findings. She is interested in developing biosensors for the specific detection of DNA, small molecules, metal ions, and proteins. These sensors operate through signal transduction mechanisms where a signal is generated upon specific binding to a synthesized biosensor.

Dr. Lai is in the process of designing various biosensors that could one day be used for widespread application and utilization. Optimal sensors should be reagent-less, reusable, rapid, sensitive, selective, and specific, a combination of features that she referred to as R^3S^3. She has made significant contributions towards advancing the field of electrochemical biosensors, including developing novel E-DNA sensors, which are a promising class of selective biosensors for the detection of specific DNA sequences or mismatches. Specifically, Dr. Lai has utilized copper click chemistry in sensor fabrication to allow for more flexibility in surface modifications, as well as site-specific modifications via electrochemical control.

In addition to E-DNA sensors, Dr. Lai's group at UNL is working on electrochemical-aptamer based (E-AB) sensors. Aptamers are DNA or RNA molecules selected for their ability to fold into three dimensional structures and bind to specific molecular targets with high affinity. Dr. Lai has studied E-AB sensors for vascular endothelial growth factor (VEGF) detection, cocaine detection, and insulin detection. Additionally, she is researching electrochemical ion sensors (E-Ion) for Hg(II), glutathione, and Cr(VI), as well as electrochemical peptide-based sensors (E-PB) for HIV detection. Ongoing goals for both Dr. Lai and the field of biosensing include improving the LOD (limit of detection) for various biosensors, as well as developing more electrochemical-based methods for analysis (and consequently optimization) of electrochemical biosensors.

Minshu Du and **Allen Bard**, *The University of Texas at Austin*
"Mechano-electrochemistry and Strain Effects"

Dr. Allen Bard and his visiting scholar Dr. Minshu Du co-presented a talk on the effect of mechanical energy (including strain and triboelectric processes) on the thermodynamics and kinetics of electrochemical processes.

For example, crystal growth in epitaxial vs. non-epitaxial layers can give rise to strain. Dr. Bard and his group have been working to make direct measurements of strain and correlate that to electrocatalytic properties. For example, compressive strain on two Pt atoms can in a sense "push" the d orbitals closer together, and this can make a better catalyst for some applications.

To modify the strain, there are several possible strategies, including: (1) *in-situ* bending or stretching of an electrode, within elastic limits to avoid plastic deformation, (2) lattice mismatch, and (3) alloying. In practice these can be achieved through core-shell structures, or monolayers deposited on a dissimilar metal, although one must unravel mixed electronic or ligand effects and strain effects.

Drs. Du and Bard are exploring another way, using the two-way shape memory effect of NiTi shape-memory alloys (SMA). This can serve to isolate the strain effect from the ligand effect. NiTi phase transitions with temperature, but it can also be maintained at room temperature in three different states: pristine, with an intrinsic compressive stress, or with an intrinsic tensile stress.

The method presented was to make an NiTi electrode, put a layer of 5-10 nm Pt on this material, then test oxygen reduction (ORR) on these electrodes with compressive or tensile stresses. Low-angle XRD demonstrated that the strain of the substrate is at least partially communicated to the Pt layer. That is, about 1-2% strain was measured in the Pt layer, compared to 7.5% strain in the underlying NiTi.

These electrodes were tested as macroelectrodes in a three-electrode cell, with 0.5 M H_2SO_4 either Ar- or O_2-saturated. Under compressive strain, kinetics increased slightly, and under tensile strain, kinetics decreased slightly (both measurements > 2σ). These effects were larger on the 5 nm film compared to the 10 nm film.

Poster Session

Saturday 5:15-7:45p Welch Hall, Grand Hallway

Nirupam Aich	*Assessing Environmental Sustainability of Novel Carbon Nanotube-Titania-Platinum Nano-hybrid Electrocatalysts*
Victoria Basile	*Synthesis and Effects of Modifying Extended Phenylene Wire Lengths on a Silicon(111) Surface*
Brent Bennett	*The Bromine/Nitrobenzene Flow Battery and the* Br^-/Br_2 *Reaction Mechanism in Nitrobenzene*
Nataraju Bodappa	*Temperature-Dependent Transport Properties of a Redox-active Ionic Liquid with a Viologen Group*
Francisco Carrillo	*Operating Principles of Electrochemically Mediated Water Desalination*
Alma Castaneda	*Electrocatalytic Amplification of Nanoparticle Collisions at Electrodes Modified with Polyelectrolyte Multilayer Films*
Will Chemelewski	*Electrodeposition of Ni-doped FeOOH Oxygen Evolution Catalyst and Application to Photoelectrochemical Water Oxidation*
Qing Chen	*The Quinone-bromide Flow Battery*
Pedro de Souza	*Modified Coin Cell for* In situ *Optical Characterization of Dendrites*
Jeffrey Dick	*Specific Electrochemical Detection of Biologically Relevant Analytes by Monitoring Discrete Collisions at Ultramicroelectrodes*
Robin Forslund	*Perovskites as Electrocatalysts for the Oxidation of Urea*
Hoang Gang	*Lithium Storage Enhancement of Micro-sized Sn/Se Anode*
William Hardin	*Perovskite Electrocatalysts for Oxygen Reduction and Water Oxidation*
Caleb Hill	*Tunneling in Passivated Ultramicroelectrode Systems*
Hsien-Yi Hsu	*Electrochemiluminescence of Platinum Acetylide Complex*
Harkjin Kim	*Platinum-Enhanced Electron Transfer and Surface Passivation through Ultra-thin Film Aluminum Oxide* (Al_2O_3) *on* $Si(111)–CH_3$ *Photoelectrodes*
Jiyeon Kim	*Electrochemical Imaging of Bacterial Quorum Sensing by Scanning Electrochemical Microscopy*
Jun Myung Kim	*Covalent Decoration of Graphene Oxide With Dendrimer-encapsulated Nanoparticles for Universal Attachment of Multiple Nanoparticles on Chemically Converted Graphene*
Kyle Klavetter	*Germanium Microparticles Stabilized by Incorporation of Substoichiometric Selenium as a High Tap Density Lithium-ion Battery Anode Material*
Molly Kogan	*Paper Diagnostic Devices for Electrochemical Detection of Biological Weapons*
Felicia Konopka	*Building Molecular Wires for Optimal Electron Transport Through Passivating Metal Oxide Layers on Si(111) Substrates*

Dillon Kopecky	*Electrochemistry on Single Crystal Au Bead Electrode*
Luc Le	*The Effect of Passivation Layer* TiO_2 *and Catalyst Pt on the Photoelectrochemical Cells of Modified Si Working Electrode*
Estelle Lebegue	*Catalytic Effects of Derivative Aqueous Pyridinium Cations in the Electrochemical Reduction of* CO_2 *on Different Electrode Materials*
Xiang Li	*Paper Microfluidic Device Based DNA Detection Using Silver Anodic Stripping Voltammetry*
Long Luo	*Low Voltage Paper-based Electrophoretic Devices*
Tyler Mefford	*The Role of Oxygen Vacancies and Cobalt Oxidation State in Sr-Doped* $La_{1-x}Sr_xCoO_{3-\delta}$ *for Bifunctional Oxygen Electrocatalysts*
Ryan Pekarek	*Functionalization of Si(111) Photocathodes: Interplay Between Steric Spacing of Molecular Linkers and ALD-deposited Metal Oxide Films*
Emily Powell	*Synthesis of* GeS_x *for Use as a Battery Anode Material*
Christophe Renault	*Mapping of Sub-micron-sized Electro-active Defects by Spectroelectrochemistry*
Alex Rettie	*Anisotropic Small-polaron Hopping and Electron Drift Mobility in* $W:BiVO_4$ *Single Crystals*
Donald Robinson	*Lowering the Detection Limit of Particle Impact Electroanalysis with Magnetically Guided Pt-decorated Iron Oxide Nanoparticles*
Junhyeok Seo	*Hybrid Organic / Inorganic Band-Edge Modulation of p-Si(111) Photoelectrodes: Effect of R, Metal Oxide and Pt on* H_2 *Generation*
Shannon Stauffer	*Computational Study of Lithium Intercalation Mechanism of* $LiTi_2O_4$ *Slab*
Sean Wood	*Electrochemical Evidence of Polyselenide Shuttle Reaction During (De)Lithiation of PbSe Anodes*
Eunsoo Yoon	*Electrochemically Mediated Desalination*
Liang Zhang	*Correlating Structures and Functions for Alloy Nanoparticles Catalysts*
Yuebing Zheng	*Rational Design of Nanostructured Semiconductors, Electrocatalysts, and Plasmonic Nanostructures for High-performance Solar Water Splitting*
Ji Zhao	*Photo-active Silicon Layer Deposited on Silver* via *Molten Salt Electrolysis*
Cindy Zoski	*Electrochemical Collisions of Metal Nanoparticles*