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NOVEL CATALYTIC MECHANISMS FOR THE CHEMICAL REDUCTION OF CARBON DIOXID

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14. ABSTRACT
The objective of this work it to perform a combined theoretical and experimental study of CO2 reduction at metals, semiconductors and homogeneous electrocatalysts, and to understand at a detailed molecular level the catalytic processes involved in reducing CO2 to valuable energy-dense liquids. Of particular importance is to understand branching ratios and sources of selectivity. That is, how and why a catalyst or surface generates its particular products from CO2. A fundamental understanding of the underlying mechanisms and characteristics of CO2 reduction catalysts will allow the development of more robust, active, and selective catalysts using earth-abundant materials. A primary goal is to understand the interfaces of heterogeneous and homogeneous systems and develop an understanding of how a homogeneous co-catalyst can be coupled with a heterogeneous metal electrode or semiconductor in order to reduce reaction barriers and increase the overall activity and selectivity for the reduction of CO2 to liquid fuels.

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MURI 10 SIXTH YEAR (No Cost Extension period) REPORT

NOVEL CATALYTIC MECHANISMS FOR THE CHEMICAL REDUCTION OF CARBON DIOXIDE TO ENERGY-DENSE LIQUIDS

AFOSR Grant No: FA9550-10-1-0572

TITLE: NOVEL CATALYTIC MECHANISMS FOR THE CHEMICAL REDUCTION OF CARBON DIOXIDE TO ENERGY-DENSE LIQUIDS

PRINCIPAL INVESTIGATOR: Professor Clifford Kubiak

LEAD INSTITUTION: UC San Diego

AFOSR PROGRAM MANAGER: Dr. Michael Berman, AFOSR, (703) 696-7781,
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PROGRAM OBJECTIVE: The objective of this work it to perform a combined theoretical and experimental study of CO_2 reduction at metals, semiconductors and homogeneous electrocatalysts, and to understand at a detailed molecular level the catalytic processes involved in reducing CO_2 to valuable energy-dense liquids. Of particular importance is to understand branching ratios and sources of selectivity. That is, how and why a catalyst or surface generates its particular products from CO_2. A fundamental understanding of the underlying mechanisms and characteristics of CO_2 reduction catalysts will allow the development of more robust, active, and selective catalysts using earth-abundant materials. A primary goal is to understand the interfaces of heterogeneous and homogeneous systems and develop an understanding of how a homogeneous co-catalyst can be coupled with a heterogeneous metal electrode or semiconductor in order to reduce reaction barriers and increase the overall activity and selectivity for the reduction of CO_2 to liquid fuels. The structural and electronic effects of interfacing homogeneous catalysts and co-catalysts with specific types of semiconductor and metal electrode surfaces are not well understood, and we seek to elucidate the critical considerations of interfaces in CO_2 reduction systems.

SCIENTIFIC APPROACH: The approach we are taking to address the program objective is to combine theory and experiment to understand the challenge of understanding mechanisms at heterogeneous and homogeneous catalysts. On the experimental side, we are examining surfaces and semiconductors using electrochemical techniques such as cyclic voltammetry and bulk electrolysis. Spectroscopic techniques such as XPS and SEM are used to probe surface composition and morphology to understand how they affect catalyst activity and selectivity. The various CO_2 reduction products and their faradaic efficiencies are analyzed by performing bulk electrolysis and probing the solution and gas phase products with nuclear magnetic resonance (NMR) spectroscopy and gas chromatography (GC). Homogeneous catalysts and co-catalysts are similarly being examined using electrochemical techniques including bulk electrolysis followed by product analysis with NMR and GC. In addition, catalytically relevant species are examined in-situ using UV-Vis and Infrared spectroelectochemistry (UV-Vis-SEC and IR-SEC), and chemical reductions have been used to synthesize and isolate catalytically relevant intermediates, which are then characterized via spectroscopy and X-ray crystallography. Synchrotron radiation techniques such as EXAFS and XANES are being used to characterize the structure and composition of catalytically relevant metal and semiconductor surfaces under CO_2 reduction conditions. Synchrotron techniques are also being applied to study homogeneous electrocatalysts in order to understand their structure and electronic ground states in solution. Theoretical investigations of catalysts and surfaces are being performed using first-principles quantum mechanical and density functional theory (DFT) calculations. These calculations can be used to study intermediates and reaction mechanisms that cannot be directly observed through experimental approaches, as well as illuminating the interpretation of experimental data. The group has developed a computational approach that allows for reaction mechanisms to be elucidated in a potential-dependent manner, which is much more accurate for describing electrocatalytic

reaction mechanisms than standard methods. Surface morphologies of semiconductors and their reactions with CO_2 are also being explored via computational methods. The MURI team is performing calculations on surfaces as well as homogeneous compounds, and has developed methods for accurately predicting the acidity and reduction potentials of catalytically relevant species.

MOST RECENT GOVERNMENT REVIEWS AND GOVERNMENT PARTICIPANTS:

22 November 2010 - Kickoff Meeting for AFOSR MURI, Arlington, VA with Michael Berman (AFOSR), Marie Sandrock (DARPA), Kathleen Covert (NSF), Carol Bessel (DOE).

15-16 May 2011 - 2011 Air Force Office of Scientific Research (AFOSR) Molecular Dynamics Contractor's Program Review, Pasadena, CA, with Michael Berman (AFOSR), Jeffrey Owrutsky (AFOSR)

8 December 2011 - First MURI Annual Review Meeting, La Jolla, CA, with Michael Berman (AFOSR), Jeffrey Owrutsky (AFOSR), Marie Sandrock (DARPA), Brian Holloway (DARPA).

22-24 May 2012 - 2012 Air Force Office of Scientific Research (AFOSR) Molecular Dynamics Contractor's Program Review, Arlington, VA, with Michael Berman (AFOSR), Jeffrey Owrutsky (AFOSR)

8-10 August 2012 - MURI Program Review, Arlington VA with Michael Berman (AFOSR), Robin Staffin (Office of Basic Research, ASD Research Directorate)

7 December 2012 - Second MURI Annual Review Meeting, La Jolla, CA, with Michael Berman (AFOSR)

9 December 2013 - Third MURI Annual Review Meeting, La Jolla, CA with Michael Berman (AFOSR)

20 January 2015 – Fourth MURI Annual Review Meeting, La Jolla, CA with Michael Berman (AFOSR)

25 January 2016 – Fifth MURI Annual Review Meeting, La Jolla, CA with Michael Berman (AFOSR)

MURI CONSORTIUM RESEARCH TEAM MEMBERS:
Clifford Kubiak (UCSD)
Andrew Bocarsly (Princeton)
Emily Carter (Princeton)
Nate Lewis (Caltech)
Anders Nilsson (Stanford, SLAC)
Jens Nørskov (Stanford, SLAC)

FINANCIAL EXECUTION:

3-YEAR BASE PERIOD – FY10: $ $195,039 (2 months) **FY11:** $1,367,870 (12 months)
FY12: $1,494,927 (12 months) **FY13:** $ 1,442,172 (10 months)

2-YEAR OPTION PERIOD - FY13: $58,269 (2 months) **FY14:** $1,500,445 (12 months)
FY15: $1,441,278 (10 months)

As of 2/29/2015, total expenditures have been $5,351,317.81. This amount includes subcontract invoices through 2/29/2015 which have not yet hit the UCSD ledgers. Total expenditures represent approximately 90% of the Base Period funds.

ACCOMPLISHMENTS:

Work in the **Kubiak** laboratory has been focused on developing and studying homogeneous CO_2 reduction catalysts in order to elucidate novel mechanisms for CO_2 reduction. The **Kubiak** lab continues

to study the highly active and selective Re(bpy-R)$(CO)_3$X and Mn(bpy-R)$(CO)_3$X catalyst families, which perform a proton-coupled reduction of CO_2 to CO and H_2O. We have used a variety of spectroscopic techniques to fully elucidate the mechanisms for each of these catalysts. Some of these studies include using chemical reducing agents to independently, chemically synthesize the states leading up to the active catalysts, using X-Ray Absorption Spectroscopy (in collaboration with the Nilsson group) to directly probe the electronic structures of the active catalysts, using IR and UV-Vis spectroscopies in tandem with fast stopped-flow mixing to directly observe the interacts of the active states with CO_2 and protons, and a variety of in situ electrochemical techniques in tandem with IR spectroscopy. Through collaboration with the Carter group, we have used computational studies to elucidate the full mechanism for the proton-dependent electrocatalytic reduction of CO_2 by both the Re and Mn catalysts, and we directly compare the two mechanisms. These calculations are in complete agreement with all of our experimental data to date. The information gained from these comprehensive mechanistic studies will be a valuable lesson for the development of novel, selective catalysts for the reduction of CO_2 in the presence of protons.

The **Kubiak** group has developed an internal collaboration between members supported by this grant and those supported by AFOSR Basic Research Initiative (BRI) grant FA9550-12-1- 0414. With the eventual goal of incorporation of Re(bpy)$(CO)_3$X catalysts into biomolecules, this ambitious project has successfully drawn upon knowledge gained by the CO_2 MURI to understand complex electrochemical mechanisms enabled by hydrogen bonding between singly-reduced catalyst species ("Supramolecular Assembly Promotes the Electrocatalytic Reduction of Carbon Dioxide by Re(I) Bipyridine Catalysts at a Lower Overpotential." Machan, C.H.; Chabolla, S.A.; Yin, J.; Gilson, M.K.; Tezcan, F.A.; Kubiak, C.P. *J. Am. Chem. Soc.*, **2014**, *136*(41) 14598-14607.)

The **Kubiak** group has also utilized synthetic modification of the bpy ligand to significantly alter the electrochemical and electrocatalytic behavior of our Mn catalysts. We synthesized a bulky bipyridine ligand, 6,6´-dimesityl-2,2´-bipyridine (mesbpy), and we used this ligand to synthesize the corresponding Mn complex, Mn(mesbpy)$(CO)_3$X. Unlike previously reported Mn bipyridine catalysts, these Mn complexes exhibit a single, two-electron reduction wave under nitrogen, with no evidence for dimerization. In previously reported Mn(bpy-R)$(CO)_3$X complexes, two irreversible one-electron reductions typically occur and fast dimerization occurs directly after the first reduction. This dimerization pathway contributed to the overpotential for two-electron reduction and inhibits catalysis. In Mn(mesbpy)$(CO)_3$X, the usual second reduction has been shifted positive by ~300 mV and incorporated into a two-electron couple near the potential of the first reduction. This bulky Mn catalyst is among the most active for the two-electron reduction of CO_2 to CO, with turnover frequencies reaching ~5000 s–1 with added TFE (~14 times more active than the previous best Mn(bpy-R)$(CO)_3$Br catalyst!). Although this bulky Mn catalyst binds CO_2 with a proton at a 300 mV more positive potential than Mn(bpy)(CO)3Br, fast catalytic rates do not occur until the resulting Mn–COOH complex is reduced at a ~400 mV more negative potential. However, slow catalysis does occur at this lower potential. We used infrared-spectroelectrochemistry (IR-SEC) to gain insight into this unusual "over-reduction" that was necessary to push catalysis forward. Furthermore, the Mg^{2+} has successfully been used as a lewis acid in order to eliminate the need for this "over-reduction."

In the **Kubiak** group, the homogeneous electrochemical reduction of CO_2 by the molecular catalyst $[Ni(cyclam)]^{2+}$ was studied by electrochemistry and infrared spectroelectrochemistry. The electrochemical kinetics were probed by varying CO_2 substrate and proton concentrations. Products of CO_2 reduction are observed in infrared spectra obtained from spectroelectrochemical experiments. The two major species observed were a Ni(I) carbonyl, $[Ni(cyclam)(CO)]^+$, and a Ni(II) coordinated bicarbonate, $[Ni(cyclam)(CO_2OH)]^+$. The rate-limiting step during electrocatalysis was determined to be CO loss from the deactivated species, $[Ni(cyclam)(CO)]^+$, to produce the active catalyst, [Ni(cyclam)]+. Another macrocyclic complex, $[Ni(TMC)]^+$, was deployed as a CO scavenger in order to inhibit the deactivation of $[Ni(cyclam)]^+$ by CO. Addition of the CO scavenger was shown to dramatically increase the catalytic current observed for CO_2 reduction. Evidence for the [Ni(TMC)]+ acting as a CO scavenger includes the observation of $[Ni(TMC)(CO)]^+$ by IR. DFT calculations probing the optimized geometry of the $[Ni(cyclam)(CO)]^+$ species are also presented. These findings have implications on the increased activity for CO_2 reduction when $[Ni(cyclam)]^+$ is adsorbed on a mercury electrode. By the study of the $[Ni(cyclam)(CO)]^+$ structure we learned that there is significant distortion of the Ni center out of the plane

of the cyclam nitrogens. This distortion strengthens the Ni-CO interaction by increasing backbonding interactions. This leads to the hypothesis that the mercury surface, through Hg-Ni interactions, prevents the distorted geometry seen in solution leading to a more planar geometry. This helps to destabilize the carbonyl adduct which inhibits the extent of CO poisoning of the adsorbed catalyst. This work was reported in the recently accepted publication: Froehlich, J. D.; Kubiak, C. P. J. Am. Chem. Soc. 2015 [Accepted – DOI: 10.1021/ja512575v]

The **Kubiak** group has further developed a novel synthesis of P_2N_2 ligands that allow for functionalization of these important and versatile electrocatalysts in vastly new ways. Ni-P_2N_2 complexes are among the best electrocatalysts for the proton-coupled electron transfer reactions of hydrogen evolution and oxidation, formate oxidation, and oxygen reduction. This new synthesis involves the Michael Addition of a non-toxic, non-volatile phosphine starting material to a number of carbonyl-based compounds. These ligands and their metal complexes are being characterized for their electrocatalytic activity and their potential for heterogenization and further functionalization.

The **Kubiak** group has begun to incorporate N-heterocyclic carbene (NHC) ligands into its studies of Ni-based reductive electrocatalysis. These studies have yielded the first isolated Ni(0) tetracarbene complexes, which show unusual geometric distortion, high uv-visible absorption, and extreme reducing power. These complexes have been characterized by single crystal x-ray diffraction, and modeled by density functional theory (DFT) calculations. This class of compounds has also been expanded by incorporation of a propyl-linked bis-NHC ligand, which allows for asymmetric substitution at Nickel. The synthetic variety afforded by this approach is being explored in order to tune the strength of hydride donation by Ni-H complexes of this type.

The **Kubiak** group has also explored the production of methanol from carbon dioxide by dividing the overall six electron, six proton reduction or hydrogenation into smaller two electron, two proton reduction or hydrogenation steps. The first step from CO_2 to formic acid has been studied amply, but further reduction or hydrogenation of formic acid has been elusive. In light of a recent groundbreaking publication from the Goldberg group (Miller, A. J. M.; Heinekey, D. M.; Mayer, J. M.; Goldberg, K. I. *Angew. Chem. Int. Ed.* ***2013****,* 52: 3981–3984) where methanol was produced via transfer hydrogenation of formic acid catalyzed by $[Cp^*Ir(bpy)]^{2+}$, a series of analogous catalysts with differently substituted bipyridine ligands (4,4'-di-R-bpy; R= OMe, tBu, Me, H, CF_3) were synthesized and studied for their methanol producing abilities for fixed time periods under mild temperatures.

While the alkyl substituted bipyridine complexes displayed slightly higher turnover frequencies for methanol production, the unsubstituted bipyridine complex actually displayed the best selectivity for methanol (the selectivity of this reaction being hindered by an unfortunate side reaction producing hydrogen). Both the more donating (methoxy) and more withdrawing (trifluoromethyl) substituents resulted in low turnovers and selectivities for methanol production. In terms of formic acid consumption, the complexes showed a rather linear trend between the electron donating abilities of the bipyridine substituent, as estimated by the Hammett parameter, and the amount of formic acid consumed over the fixed reaction period. From this data, it is posited that complexes with more withdrawing substituents simply do not have enough driving force to react much, whereas complexes with more donating substituents simply react with protons even more quickly to make hydrogen, thus decreasing methanol formation selectivity.

The **Carter** group at Princeton University has made several significant insights into pyridinium-catalyzed CO_2 reduction on p-GaP photoelectrodes using first-principles quantum mechanics (QM) calculations. We have studied the nature of the p-GaP photoelectrode/water interface, the acid-base and electrochemical properties of pyridinium cations and CO_2 (and related species) in solution, as well as those same properties for species adsorbed on GaP(110). Special attention was devoted to characterizing the adsorption state of pyridine and the associated reactivity. Furthermore, we have calculated the band edge positions of GaP(110) to determine which reduction reactions can occur on this surface. We also collaborated with the Kubiak group to study the electrocatalytic CO_2 reduction mechanisms of homogeneous rhenium and manganese catalysts. Information gleaned from these works help clarify how to direct future experimental and theoretical studies of photoelectrocatalysis. QM calculations (using

density functional theory within the generalized gradient approximation (DFT-GGA)) correctly predict the GaP(110) surface as being the most stable amongst GaP low-index surfaces in vacuum. Water molecules were then added to this surface to determine the lowest-energy water structure at the solid/liquid interface. Although solvation energies are often sufficiently treated with the addition of a single monolayer of water molecules at surfaces, the interfacial structures of GaP(110) and water undergoes a qualitative change when the number of water monolayers is greater than two. Above two monolayers of water, we showed that it becomes energetically favorable to dissociate half of the water layer nearest to the surface to form adsorbed H and OH intermediates, which in turn changes the electronic structure of the surface. Bader charge analysis revealed a hydride-like H species, similar to those expected on electrodes with low overpotentials for hydrogen evolution. This is a very important finding (see Muñoz-García, A. B.; Carter, E. A. *J. Am. Chem. Soc.* **2012**, *134*, 13600–13603), as it reveals the reactive nature of the GaP surface in the presence of water, opening opportunities for more-focused mechanistic investigations while helping elucidate the fundamental nature of this semiconductor/water interface. Recently, we have further investigated the GaP(110)/water interface in collaboration with an experimental group at Princeton University and found that our prediction of the formation of hydride-like species is confirmed by XPS experiments. Moreover, our recent DFT study conducted within this collaboration shows that water dissociation on the surface is favored even without additional solvation layers, when co-adsorbed water molecules stabilize adsorbed OH species via hydrogen bonding. These adsorbed species and their interaction were also confirmed by XPS experiments (Kronawitter C. X.; Lessio M.; Zhao P.; Riplinger C.; Boscoboinik A.; Starre D.; Sutter P.; Carter E. A.; Koel B. E., *J. Phys. Chem. C*, **119**, 17762 (2015)). Finally, we have used DFT to compute a surface Pourbaix diagram that shows that all these adsorbed species (hydride-like H species, OH and water molecules) should be present under the experimental conditions (pH and applied potential).

QM calculations utilizing mixed explicit/implicit solvation models also provided important insights. We completed a thorough *ab initio* and hybrid-DFT benchmarking study to find a practical calculation scheme to predict gas and aqueous phase pyridinium deprotonation energies (data needed for pKa calculations). After benchmarking these computational schemes, we used the same schemes to predict deprotonation energies for radical analogs that were not yet known by either experiment or theory. We found that the pKa calculation scheme established in the literature encounters unexpected inconsistencies when unstable radical anions are involved, and these inconsistencies can result in errors larger than 10 kcal/mol. In our work (see Keith, J. A.; Carter, E. A. *J. Chem. Theory Comput.* **2012**, *8*, 3187–3206), we prescribe a consistent treatment to avoid these errors. Our work also reached an unexpected conclusion: pyridinyl radicals originally considered to be participants in the relevant acid-base chemistry are not acidic at all, and therefore such molecules in solution cannot be considered active participants in the catalysis of CO_2 reduction. Using the same benchmarked calculation methods, we reported reduction potentials for pyridinium, and these results were even more surprising. The thermodynamic one-electron reduction potential for pyridinium in solution was found to be roughly 1 V more negative than the experimental reduction potential (-0.58 V vs. SCE on Pt electrodes), which has been attributed for decades to the one-electron reduction of solvated pyridinium (see Keith, J. A.; Carter, E. A. *J. Am. Chem. Soc.* **2012**, *134*, 7580–7583). Note that this conclusion was made after showing one-electron reductions for a variety of solvated N-substituted pyridinium molecules were calculated within 0.3 V compared to experiment. Thus, the same pyridinium species that plays a crucial role in the photoelectroreduction of CO_2 also is a significant outlier compared to other molecules with similar chemical moieties, suggesting that the species being measured cannot be simply solvated pyridinium. The actual species being reduced at -0.58 V is not yet known for certain, but we have investigated further possibilities by considering other molecules formed in acid-base and electrochemical reactions under ambient conditions. For example, our calculated standard reduction potentials are in reasonable agreement with experiment when considering a two-electron reduced species: dihydropyridine (DHP). However, we found barriers for H/CO_2 exchange in solution for DHP, as well as the previously suggested pyridinyl radical, are far too high to be accessible (~30 kcal/mol). Thus, we suggested that the reaction must be occurring on the electrode surface. (see Keith, J. A; Carter, E. A. *Chem. Sci.*, **2013**, *4*, 1490), consistent with the observation that not all electrodes can induce this chemistry to occur. We also used first principles quantum chemistry calculations to model GaP photoelectrode surfaces with GaP(110) surface cluster models, which must be constructed with care to properly capture the donor-acceptor character of the electronic structure of GaP. We benchmarked molecular adsorption energies on these clusters against results from calculations using

periodic boundary calculations (see Keith, J. A; Muñoz-García, A. B.; Lessio M.; Carter,*Top. Catal.*, **2015**, *58*, 46). The cluster models facilitate the consideration of charged adsorbates and continuum solvation. Most importantly, we find that it is thermodynamically possible to reduce surface-bound pyridine to DHP in a $2e^-$ reduction step at moderate applied potentials. Interestingly, DHP has similar chemical groups and redox properties as nicotine amide adenine dinucleotide (NADH), a ubiquitous biological redox cofactor. Their redox potentials are sufficient to drive the reduction of CO_2 to a variety of products. On the basis of these results, we proposed a new and general reaction mechanism that explains the performance of nitrogen-heterocycle cocatalysts for semiconductor-based (photo-) electrochemical CO_2 reduction (Keith, J. A; Carter, E. A., *J. Phys. Chem. Lett.*, **2013**, *4*, 4058; *J. Phys. Chem. Lett*., **2015**, *6*, 568). Recently, we started using these cluster models to predict acidity constants and reduction potentials of adsorbed species. We used the computed acidity constants to predict the acidity of the surface under experimental conditions. We found that protons that develop partial hydride character upon adsorption will likely be present on the surface, and can be reduced to react with adsorbed pyridine under these conditions. These results can help us gain new insights into the mechanism of CO_2 reduction in this system and further characterize the surface under experimental conditions. Furthermore, we computed the band edge positions of the GaP(110) surface (see Lessio, M.; Carter, E. A. *J. Am. Chem. Soc.* **2015**, *137*, 13248–13251). By comparing their values to the reduction potential of a specific reaction, we can determine whether or not the latter can occur through the transfer of photoexcited electrons from this surface. We found that the homogeneous reduction of pyridinium to the pyridinyl radical is not energetically feasible on the GaP(110) surface under illumination, however very recent, more refined computations (to be published) of the electrode work function in the presence of the adsorbed water layer indicates it may be possible to form pyridinyl in solution, though this pathway is still much less favorable than reduction to adsorbed pyridine and hydrogen. We also considered the possibility that pyridinium might adsorb on the negatively charged photoelectrode surface and that adsorption might catalyze its reduction to pyridinyl. However, we also found that pyridinium does not adsorb either on neutral- or negatively charged surface. Thus, we investigated alternative pathways for pyridinium reduction on GaP(110). We found pyridinium can be reduced to an adsorbed pyridine and a hydrogen atom by photoexcited electrons. Interestingly, these are the reactants needed to form adsorbed dihydropyridine. In a recent collaboration with an experimental group at Princeton University, we investigated the adsorbed state of pyridine on the GaP(110) surface using scanning tunneling microscopy (STM) and DFT (see Kronawitter C. X., Lessio M., Zahl P., Muñoz-García A. B., Sutter P., Carter E. A., Koel B. E. *J. Phys. Chem. C*, **2015**, in press). The study characterized the unoccupied states of the adsorbed molecule to investigate its reactivity. We conclude that adsorption might favor subsequent pyridine reduction to dihydropyridine.

We are now extending our study of pyridinium-catalyzed CO_2 reduction to other semiconductor surfaces that have demonstrated promising results. Since semiconductor surfaces may readily reconstruct during operation, verification of thermodynamically stable reconstructions is essential for deriving proper surface models, especially ones that accurately represent adsorption sites participating in the heterogeneous mechanism. As such, we employed the formalism of *ab initio* thermodynamics to compute the relative free energies of GaP, CdTe, and $CuInS_2$ surface reconstructions, thus establishing which surface reconstructions are likely to occur during catalytic operation. Having established plausible surface models, we are employing the cluster model approach to investigate adsorption trends across the GaP, CdTe, and $CuInS_2$ surfaces, lending insight into key adsorption sites and intermediate species that may play a role in the Py-catalyzed reaction mechanism.

The **Carter** group is also contributing to the understanding of homogeneous electrocatalytic CO_2 reduction by a homogeneous Re(bpy = 2,2'-bipyridine)$(CO)_3Cl$ catalyst. in collaboration with the **Kubiak** group. This catalyst selectively reduces CO_2 to CO. Careful analysis of the electronic structure of the reaction intermediates reveals that the bpy ligand plays a non-innocent role in this reduction, serving as a source and sink for electrons (see *Angew. Chem. Int. Ed.*, **2013**, *52*, 4841). Moreover, its special electronic structure provided the insight into a likely origin of its selectivity for CO_2 rather than proton reduction. Our subsequent mechanistic study identified potential reaction intermediates and reaction pathways, while validating our computations against available experimental one-electron reduction potentials, non-aqueous pK_as, and reaction free energies. We proposed a complete reaction mechanism that is consistent with all experimental data and sheds light onto this catalyst's selectivity. Specifically, we find that even though the thermodynamic energy for binding CO_2 is slightly less favorable than

protonation, CO_2 binding is highly favored kinetically – with a reaction barrier that is lower by about 10 kcal/mol. This kinetics effect determines the catalyst's high selectivity (see *J. Am. Chem. Soc.*, **2013**, *135*, 15823). Protonation and then reduction of a metastable Re-CO_2 intermediate anion precedes Brønsted acid catalyzed C–O cleavage and then rapid release of CO at negative applied potentials. The strong C-O double bond of free CO_2 is weakened during CO_2 binding to the catalyst. The CO_2 adduct with its weakened C-O bond is stabilized by protonation. The subsequent C-O bond cleavage is facilitated by further reduction of the complex and is initiated by Brønsted acid addition. The Brønsted acid stabilizes C-O bond cleavage by stabilizing the released OH- species.

The **Carter** group has also collaborated with the **Kubiak** group to understand homogeneous electrocatalytic CO_2 reduction by the Mn(bpy)$(CO)_3$Br catalyst. This catalyst is, except for the metal center, chemically identical to the Re(bpy = 2,2'-bipyridine)$(CO)_3$Cl catalyst, but differs in observed redox potentials, turnover rates, Brønsted acid dependence and catalyst inactivation through dimerization. Using hybrid-DFT calculations we modeled the reaction mechanism of the manganese catalyst and comparing the results to those of the rhenium catalyst. Our calculations show that in the catalytically active oxidation states, the rhenium catalyst has a higher binding affinity to a sixth ligand than the manganese complex. This yields different computed redox potentials, and ultimately the two catalysts follow different reaction pathways under the simulated electrochemical conditions. Different ligand binding affinities also explain the higher tendency of the manganese catalyst to dimerize (see Riplinger C.; Sampson M. D.; Ritzmann A. M.; Kubiak C. P.; Carter E. A., *J. Am. Chem. Soc.*, **2014**, *136*, 16285). In order to test the effect of these properties on the overall reaction outcome, we performed microkinetics simulations, giving us the turnover frequencies (TOFs) for CO_2 reduction by both catalysts at different applied potentials, as well as the corresponding intermediate distributions. The TOFs are in agreement with the experimental data to within about one order of magnitude, when correlated wavefunction theory is used instead of DFT to compute the barriers. The intermediate distribution shows that the Re catalyst needs higher overpotentials than the Mn catalyst because of its more negative reduction potential of the singly reduced state. The TOFs of both catalysts depend on the type of Brønsted acid used, with the Mn catalyst exhibiting no catalytic turnover without added Brønsted acid. We then investigated these differences by modeling the reaction pathways with all experimentally used Brønsted acid (see Riplinger C.; Carter E. A., *ACS Catalysis*, **2015**, *5*, 900). We find that some of the experimentally used acids are too weak to protonate CO_2 or to stabilize CO_2 binding - catalysis with these acids requires more negative applied potentials or higher acid concentrations compared to catalysis with stronger acids. This trend is more pronounced for the Mn catalyst than for the Re catalyst. The latter can work at maximum turnover with acids that work at submaximum turnover with the Mn catalyst. We investigated the solvent acetonitrile and the electrolyte as possible proton sources for the experimental scenario without added Brønsted acid. Neither appear to be responsible for turnover, based on both thermodynamics and kinetics. Water produced during catalysis might be responsible for completing the reaction cycle in the absence of acid.

The **Carter** group has recently started working in collaboration with the **Kubiak** group to understand what properties make the bpy ligand effective for CO_2 reduction. For this purpose, we are currently studying how substituting bpy with various ligands affects the catalyst reduction potential, the distribution of extra electrons in the reduced catalyst, and CO_2 versus proton binding strength.

For metal-catalyzed C_2 product formation, the **Nørskov** group showed the existence of a CO dimer on both Cu(111) and Cu(100), stabilized by a charged water bilayer. We expect the barrier for this dimerization process to be lower on Cu(100) than that on Cu(111), consistent with experimental observations, where the former has lower overpotentials for C-C coupling. Moreover, we observed this effect for cations other than H^+, consistent with the pH independence of C_2 product formation on Cu. We also extended these barrier calculations to (211) surfaces and showed CO-CO coupling to be feasible on all 3 [(111), (100), (211)] facets. We hypothesize that overall selectivity is determined by coverage, and are working toward detailed Pourbaix diagrams as well as a CO reduction kinetic model that includes adsorbate-adsorbate interactions/field effects. Moreover, using the same explicit-solvation model, we find that the protonation of oxygen to be trivial compared to protonation of carbon and C-O scission-inducing protonation of R-OH species. We revise the free energy diagram for the reduction of CO_2 to methane on

Cu(211) to include these observations. We believe it to be likely that the dominant pathway includes *CHOH and *CH as intermediates rather than $*OCH_3$.

We described the electrocatalytic reduction of CO_2 on polycrystalline gold surfaces, which have high activity and selectivity for CO evolution. We analyzed the thermodynamics of potential mechanisms for the production of CO, H_2, formate, and methanol using DFT. We suggested one mechanism that explains gold's selectivity towards methanol and is consistent with the generally unreactive nature of the Au surface. We expect to further the development of more efficient catalysts with this finding. Moreover, we presented DFT calculations highlighting how the C-C coupling barrier depends on the CO binding energy via a scaling relation. We attributed the increased selectivity to OH-terminated C_2 and C_3 species due to the strengthened binding of the CO and CH_2O intermediate at the gold and copper interfaces.

Explicit-solvation barrier calculations are expensive, and become prohibitively so when larger unit cells are used. In lieu of the computationally costly potential-extrapolation model, we developed a novel method to determine constant potential energetics for simple charge transfer reactions. Our new method requires only a single barrier calculation in an electrochemical environment, and the corresponding surface charge at the initial, transition, and final states. An accurate determination of charge is required to utilize this capacitor model. However, DFT delocalization error gives the charge of a hydronium (H_3O^+) ion in the outer Helmholtz plane to be not +1 but rather +0.6. We are currently working toward a correction scheme to obtain the correct charge in the outer Helmholtz plane in order to thoroughly implement the new extrapolation scheme using the capacitor model.

We also obtained insights into the CO_2 reduction mechanism on oxide surfaces. On RuO_2(110), we found CO-covered surfaces to be stable under the relevant electrochemical environment. We identified the lowest free energy pathways for CO_2 reduction to formic acid, methanol, and methane on partially reduced RuO_2(110) at different coverages of CO* and found that the potential-limiting step is dependent upon on CO-coverage. At 0.25 ML CO-coverage, the most thermodynamically difficult step is the reduction of formate (OCHO*) to formic acid, with a limiting potential of −0.43 V vs. RHE. At 0.5 ML CO-coverage, however, we found the limiting potential to be −0.25 V vs. RHE, where the reduction of formic acid to H_2COOH* is the most thermodynamically difficult step. Thus, we show CO-coverage to be a possible parameter in tuning the CO_2 reduction activity on RuO_2.

Lastly, the **Nørskov** group investigated the effects of liquid additives on the activity and selectivity of electrochemical CO_2 reduction. In the first step toward understanding the mechanism by which an ionic liquid cation, 1-methyl-3-ethylimidazolium ($EMIM^+$), enhances CO_2 reduction, we constructed Pourbaix diagrams $EMIM^+$ at the Ag(111)|water interface. We showed that $EMIM^+$ adsorbs specifically to the silver surface and is expected to have a high coverage under experimental conditions. We expect this to have important implications for the CO_2 reduction mechanism on Ag(111).

The **Nilsson** group has studied the reactivity a stepped Cu(211) single crystal surface for the adsorption and dissociation of CO, an important intermediate in the formation of hydrocarbons from CO_2 reduction. After dosing CO on a Cu(211) surface cooled to 100K and annealing the Cu crystal to 150K we observed a significant decrease of the molecular CO species on the surface. Simultaneously there was an appearance of graphitic and carbidic carbon in the C 1s spectrum and atomic oxygen in the O 1s spectrum. The fact that we detect carbidic carbon and atomic oxygen on the Cu surface is a direct implication of CO dissociation. In addition we have also dosed CO on a flat Cu(111) surface at 100K and annealed it up to 150K. We only detected the adsorption of molecular CO at 100K and most of which desorbs at 150K. This implies that the adsorption of CO is even weaker on Cu(111) than Cu(211) and CO dissociation is not feasible on the flat Cu(111). The Norskov group is currently investigating this system theoretically to find possible explanations for this unusual reactivity.The outcome of this comparison clearly shows that the stepped surface plays a crucial role in CO dissociation on Cu and could offer important new insights into the mechanism of CO_2 reduction.

To study the activity of single crystal surfaces for CO_2 reduction, the **Nilsson** group has built a mass spec system for integration with an electrochemical cell with sensitivity for products in the μA range. The system will allow us to compare the activity of different Cu surfaces and novel metal alloys identified in the

theoretical screening of the Nørskov group. The surfaces will be investigated using x-rays before and after reaction. Studying the well-defined surfaces of single crystals will allow for better characterization of the active site the leads to high activity and selectivity for hydrocarbon and alcohol production.

With the completion of the online electrochemical mass spectrometer (OLEMS), the **Nilsson** group has investigated a wide array of copper surfaces as electrode catalysts for CO2 reduction. Three different single crystals, Cu(211), (111), and (100), were compared to determine which lattice structure is most active/selective. In the past, theoretical results from the Norskov group suggested the Cu(211) surface could be particularly active for CO2 reduction, and APXPS work in the Nilsson group has shown CO to readily dissociate on the Cu(211) surface. The OLEMS results, however, showed Cu(211) to be similar to Cu(111) in methane and ethylene production, while the Cu(100) was in fact the most interesting single crystal surface investigated as it had the highest selectivity for ethylene. Looking at several literature reports by Hori, this result is no surprise, as his work showed similar trends in ethylene:methane ratio for a range of single crystals. More recent work by the Norskov group has helped to explain the enhanced selectivity of the Cu(100) surface for a two carbon product such as ethylene.

The **Nilsson** group discovered a unique, nanostructured copper surface that is decorated with 30-100 nm cubes (CuCube) and is highly selective for ethylene production. The onset potential for ethylene, compared to polycrystalline copper, is shifted by ~150 mV more positive, and the overall intensity of ethylene production is increased by about a factor of 2. Perhaps more importantly, the methane production on the CuCube surface is essentially turned off through the potential region investigated (0 to -1.15 V vs RHE), pushing the ethylene to methane ratio nearly 2 orders of magnitude higher than any other surface we have investigated (CuPoly and the single crystals mentioned above).
The CuCube surface itself is formed by cycling a typical polycrystalline copper electrode oxidative and reductive in 0.1 M KHCO3 with the critical addition of 4 mM KCl. The specific potentials and sweep speed are important, and it was found that 5 mV/sec between +0.9 and -1.15 V vs RHE is ideal for creating a reproducible, stable CuCube electrode with high ethylene selectivity.

In order to determine the mechanism for the CuCube growth, spectroscopic studies were performed across several beamlines at both the Stanford Synchrotron Radiation Lightsource (SSRL) and the Advanced Lightsource (ALS). Since forming the CuCube surface depends on the presence of 4 mM KCl, one conjecture is that a copper chloride forms, resulting in the final cubic shape on the surface. Experiments at SSRL BL 14-3 followed the Cl K-edge in situ, during the CuCube formation (during the oxidative-reductive cycling). Throughout this process, the Cl K-edge remained unchanged and never showed signs of forming a copper chloride phase. The same experiment was performed at SSRL BL 7-3 to track the Cu K-edge through the CuCube formation, and it was determined that a thick Cu2O phase is formed during oxidation, and is reduced back to copper metal during the reduction. Under the same conditions but without KCl, a much thinner CuO phase is formed, resulting in a slightly roughened surface that has reactivity identical to unoxidized polycrystalline copper. It appears the 4 mM KCl helps catalyze the formation of an unusually thick Cu2O film, which after reduced back to metallic copper, retains the cubic shape, resulting a metallic copper catalyst that is highly selective for ethylene.

Several ambient pressure X-ray photoelectron spectroscopy (APXPS) beam times at ALS BL 9-3-1 confirmed that a stable copper chloride phase is not formed, but instead a thick Cu2O layer is grown. After reduction, the copper appears to again be metallic, but a continued excess of oxygen suggests its persistent presence and possible role in the increased selectivity of the CuCube catalyst. Theoretical work to determine how residual oxygen can affect the reaction pathway is in progress. Future APXPS experiments at SSRL BL 13-2 are planned to investigate reaction intermediates. Membrane electrode assemblies are being tested now that would allow for *operando* experiments tracking the binding energy of carbon intermediate species as the potential-driven reaction is occurring. Lastly, a scanning tunneling electron microscopy (STEM) project is underway to further investigate the presence of residual oxygen in the CuCube and other oxide-derived catalysts. Coupling with electron energy loss spectroscopy (EELS), we will investigate where the residual oxygen is located in the CuCube sample, and whether the oxidation state of copper in that area is unchanged.

The discovery of a CO dissociation pathway (2CO* + C* —> 2C* + CO2) on a stepped Cu(211) has inspired the **Nilsson** group to explore the hydrogenation of dissociated CO on Cu at room temperature. For exploring this reaction avenue, we exposed a clean Cu(211) surface to a mixture of CO and H2O at room temperature. The in-situ C and O 1s core level spectra were mapped as a function of time using APXPS. Under this forward water gas shift condition, we observed the steady production of gas phase CO2 and a gradual growth of a surface product that can be hydrogenated carbon. The reaction energetics are confirmed by DFT calculations. Both experimental and calculated XPS binding energy of the hydrogenated carbon species are comparable.

For understanding the intriguing phenomena of CO and CO2 electroreduction over Cu catalysts, we have compared the fundamental impact of CO respective CO2 adsorption on Cu oxides. Oxides were formed by dosing molecular O2 on a Cu(211) surface at room temperature. Our observation seems to follow this general redox reaction: CuxO + CO <—> Cu(x+1)O + CO2, i.e. CO reduces Cu while CO2 oxidizes Cu, from Cu (I) to C (II). A prolong exposure of a Cu oxide surface to CO will convert all surface oxides to oxygenated carbon while CO2 will result in a mixture of CuO and oxygenated carbon. CO has the tendency to form more carboxylate species while CO2 forms more carbonates.

The **Bocarsly** Group continues to probe the mechanism of CO_2 reduction, using pyridinium and other aromatic amines as catalysts, at various semiconductor and metal electrodes. The underpinning philosophy driving this work is that a critical understanding of the charge transfer mechanism will lead to improved electrocatalytic processes. Recent proposals from several theory groups caused us to re-evaluate and collect new electroanalytical data related to the pyridinium catalyzed reduction of CO_2 on both platinum and p-GaP electrode interfaces. Based on this new data, and support from the groups of Carter, Musgrave, and Batista we now have concluded that the proposed initial charge transfer to the pyridinium □*-system is not correct. Rather, the initial charge transfer is to the acidic proton of pyridinium. In this regard, we find Batista model most compelling when a platinum electrode is employed. In this model a one-electron charge transfer to pyridinium yields pyridine and a surface platinum hydride. In the absence of CO_2 this species reacts a second proton source to generate H_2. Cyclic voltammetric analysis of this process using isotopic labeling in comparison to quantum simulations indicates two processes occur, one that is surface controlled and one that is diffusion limited. It appears that the primary steps in H_2 formation directly relate to the reduction of CO_2 when it is present. This conclusion is based on a cyclic voltammetric study of a wide range of weak acids (Yan, Y.; Zeitler, E. L.; Gu, J.; Hu, Y.; Bocarsly, A. B., *J Am Chem Soc* **2013,** *135*, 14020-14023 and Zeitler, E.L., “Mechanism of Acid Reduction at Low and High Overpotential Metal Electrodes in the Presence and Absence of CO_2: Implications for CO_2 Reduction by N-Heterocycles”, Princeton University, Ph.D. Dissertation, 2014). The key finding here is that the formation of a surface Pt-hydride is a necessary but not sufficient process for CO_2 reduction. After hydride formation, the aromatic amine catalyst (or a second equivalent of catalyst) must complex with carbon dioxide to form an adduct that can react with the surface hydride to form formate. Additionally, we find that this latter reaction is quite pH sensitive. Only when a solution pH gradient is present at the electrode surface that drops the pH below ~4 can the formate continue to accept electrons, eventually forming methanol. In the coming year, we intend to extend this mechanistic/kinetic study to other metallic electrode surfaces that have higher overpotentials for H_2 formation and thus are more favorable for CO_2 reduction. These studies will continue to be collaborative with the Batista group.

A second mechanism put forth by Carter and endorsed with some modification by Musgrave is the formation of a dihydropyridine as the redox product of pyridinium reduction, followed by a hydride transfer from this NADH-like species to CO_2. Though, our analysis of pyridinium reduction on platinum rules out this mechanism on that electrode surface (see: Zeitler, E.L., “Mechanism of Acid Reduction at Low and High Overpotential Metal Electrodes in the Presence and Absence of CO_2: Implications for CO_2 Reduction by N-Heterocycles”, Princeton University, Ph.D. Dissertation, 2014) this mechanism may operate at other electrode interfaces. In particular Carter and Keith have suggested that this intermediate might be specific to a GaP surface. To that end, we are evaluating the charge transfer chemistry of 2,6- and 3,5-lutidines at illuminated p-GaP photoanodes. Our findings to date, suggest that the acidic proton must be present for CO_2 catalysis to occur in this system. That is methylation of the N-position destroys catalytic activity, and we have ruled out a steric effect as the source of this inactivation. Work on this

system continues, using a series of in situ spectroelectrochemical approaches to study the intermediates involved.

In a very different set of experiments, motivated by Kubiak and Carter's works on molecular catalysis we have initiated a project evaluating the mechanism by which [$BrMn(CO)_3bpy$] electrocatalyzes the reduction of CO_2 to CO. We hypothesize that a key step in the reduction of carbon dioxide in this system is the formation of a hydrogen bond to the metal bound CO_2. To test this hypothesis we have placed a phenol group on the bipyridine ligand as shown in the figure below. Placement is such that the phenolic proton is directed at the CO_2 ligand. In this system we find an enhanced catalytic rate for CO formation in support of our mechanism. In theory the observed enhancement might also be due to a simple increase in effective local concentration of protons. We will test this issue in the coming months by moving the phenolic group around the bipyridine ring to enhance or decrease the hydrogen bonding geometry while observing the electrocatalytic rate constant. Based on our observations to date, this approach will not only reveal a key mechanistic attribute in this system, but is likely to lead to significantly enhanced catalytic rates.

Work in the **Lewis** group has applied our synthetic capabilities to the growth of polycrystalline thin films of layered transition-metal dichalcogenides (MX_2s). This work is motivated by recent experimental work showing that the hydrogen-evolution activity of MX_2s can be suppressed by ionic liquids [Asadi et al., *Nat. Comm*., 2014]. The **Lewis** group has synthesized thin films of WS_2 and MoS_2 by sputter-depositing thin metal films (~ 5 nm) onto Si substrates and subsequently sulfurizing the films. The thickness of the metal layer and temperature of sulfurization can be tuned to select for edge-rich or edge-poor crystal orientations in the films. The electrocatalytic activity of the films for CO_2 reduction was tested in contact with an aqueous ionic liquid (EMIM BF_4). At an applied potential of -1.23 V versus a Ag/AgCl reference electrode (-0.8 V vs RHE), the MoS_2 thin film exhibited a Faradaic efficiency, FE, for hydrogen evolution of < 25%. Both the WS_2 and MoS_2 films yielded methane with FE of ~15%. The MoS_2 film also yielded significant amounts of ethylene (> 10% FE) and methanol (~ 5% FE).

The **Lewis** group has also explored intermetallic compounds in an effort to identify new classes of materials potentially capable of electrochemically reducing CO_2. Recent experimental work has demonstrated that nanoparticles of intermetallic Ni–Ga nanoparticles of various stoichiometries are highly active for the thermochemical gas-phase hydrogenation of CO_2 [Studt et al., *Nat. Chem*., 2014]. The **Lewis** group has synthesized films of NiGa, Ni_5Ga_3, and Ni_3Ga using a temperature-programmed reduction method. The electrocatalytic activities of the films were evaluated as a function of potential in contact with an aqueous, CO_2-saturated 0.1 M $NaHCO_3$ solution. Gas-phase products were evaluated using gas chromatography and liquid-phase products were analyzed using nuclear magnetic resonance. The onset potential for CO_2 reduction was -0.48 V versus RHE. The three phases of Ni–Ga produced ethylene and ethane as well as methane, and similar product distributions and onset potentials were observed for the three Ni–Ga stoichiometries tested. At low current densities, the onset potential for CO_2 reduction to C_2 products by the Ni–Ga compounds tested was > 250 mV more positive than for polycrystalline copper and approximately equal to single crystals of copper.

SUMMARY:

- Mn(bpy-*t*Bu)$(CO)_3$Br complexes act as robust, selective, and efficient catalyst precursors for the reduction of CO_2 to CO. These catalysts are exciting because they operate at lower overpotentials and are much more earth-abundant than the corresponding Re catalysts. (J. M. Smieja, M. D. Sampson, K. A. Grice, E. E. Benson, J. D. Froehlich, C. P. Kubiak. *Inorg. Chem.* 2013, 52, 2484–2491)
- Cationic $[Re(bpy\text{-}R)(CO)_4]^+$ species spontaneously labialize a CO ligand upon exposure to a reducing potential, forming $[Re(bpy\text{-}R)(CO)_3(MeCN)]^+$ species, which provides insights into the catalytic mechanism for these Re catalysts (K. A. Grice, N. X. Gu, M. D. Sampson, C. P. Kubiak. *Dalton Trans.* 2013, 42, 8498–8503)
- Spectroscopic and structural comparisons are made between Re anions with bpy-R ligands spanning a wide range of electron-withdrawing and donating abilities. The X-ray characterization of mono-

reduced, $[Re(bpy\text{-}CF_3)(CO)_3Cl]^-$, is a rare example of a structurally characterized "19 e^-" intermediate formed in the electrochemical reduction of $Re(bpy\text{-}R)(CO)_3Cl$ complexes. (E. E. Benson, K. A. Grice, J. M. Smieja, C. P. Kubiak. *Polyhedron*, 2013, 58, 229–234)

- X-Ray Absorption Spectroscopy of Re(bpy) complexes has enabled us to determine that $[Re(bpy\text{-}R)(CO)_3]^-$ anions, the catalytically-active complexes, possess $Re^0(bpy^-)$ ground states, which helps explain the mechanism of CO_2 activation by these catalysts and explain their unique selectivity for CO_2 reduction in the presence of high concentrations of protons. (E. E. Benson, M. D. Sampson, K. A. Grice, J. D. Froehlich, D. Friebel, J. A. Keith, E. A. Carter, A. Nilsson, C. P. Kubiak. *Angew. Chem. Int. Ed.* 2013, 52, 4841–4844)
- A complete mechanism for the proton-dependent electrocatalytic reduction of CO_2 to CO by $Re(bpy)(CO)_3Cl$ has been developed using first principles quantum chemistry, which is consistent with all of our previous experimental observations. (J. A. Keith, K. A. Grice, C. P. Kubiak, E. A. Carter. *J. Am. Chem. Soc.* 2013, 135, 15823–15829)
- This mechanism has been fully compared and contrasted with corresponding calculations for $Mn(bpy)(CO)_3Br$.
- Stopped-flow IR spectroscopy provides the first *in situ* observation of the CO_2 reduction product, $Re(bpy\text{-}R)(CO)_3(CO_2H)$, formed in the reaction between catalytically-active $[Re(bpy\text{-}R)(CO)_3]^-$ and CO_2/H^+. (M. D. Sampson, J. D. Froehlich, J. M. Smieja, E. E. Benson, I. D. Sharp, C. P. Kubiak. *Energy Environ. Sci.* 2013, Advanced Article, DOI: 10.1039/C3EE42186D)
- Used synthetic modification to alter the electron donating and withdrawing ability of the bpy ligand and study its effects on catalytic activity of the $Mn(bpy\text{-}R)(CO)_3Br$ catalysts. (Sampson, M.D.; Nguyen, A.D.; Grice, K.A.; Moore, C.E.; Rheingold, A.L.; Kubiak, C.P. J. Am. Chem. Soc. **136**, 5460-5471 (2014).
- Used a bulky bpy ligand, 6,6'-dimesityl-2,2'-bipyridine, to inhibit unwanted dimerization after the first reduction for $Mn(bpy\text{-}R)(CO)_3Br$ catalysts. Eliminating dimerization shifts the formation of the catalytically-active catalyst by over +300 mV and increases catalytic activity.
- The aforementioned catalyst can be further improved by addition of a Mg^{2+} lewis acid promoter.
- The aforementioned catalyst is the fastest Mn-based HER catalyst reported.
- Characterization of Ni(I)(cyclam) + CO_2 reaction products.
- Determination of catalytic rate limiting step: self-poisoning.
- Improved turn-over frequency by addition of a CO sponge.
- Characterization of the products of Ni(I)(cyclam) catalysed reduction of CO_2 by IR-SEC and electrochemistry.
- Determined that CO poisoning is the major limitation of catalytic rates by employing a CO scavenger
- Discovered a probable reason for the increased activity of $[Ni(cyclam)]^+$ on mercury: destabilization of the CO adduct by maintaining a more planar geometry .
- New synthetic techniques expanding the scope of P_2N_2 chemistry.
- Isolation and characterization of the first group 10 M(0) tetracarbene complexes.
- Found that Mo and W(bpy-R)(CO)4 complexes are active for the reduction of CO_2, highlighting the need for one bpy, one metal based reductions for more effective catalysis as seen in the Re and Mn based complexes.
- Investigated the mechanism of pyridinium reduction at platinum through voltammetry and spectroelectrochemistry.
- Studied effect of ring substitutions on pyridine in the electrochemical reduction of CO_2 at p-GaP semiconductor electrodes.
- Studied use of ionic liquids as solvents for CO_2 reduction.
- Theoretical modeling of the GaP(110) semiconductor/ water interface requires multiple monolayers of water molecules to capture its lowest-energy interfacial structure: a GaP(110) surface covered OH* and H* species arising from water dissociation (see A. B. Muñoz-García, E. A. Carter, J. Am. Chem. Soc. 134, 13600 (2012)).
- The presence of these adsorbed species was confirmed by XPS experiments and more detailed DFT simulations suggest that their formation does not require multiple solvation layers. Moreover, the adsorbed hydride species was shown to be very strongly adsorbed, offering a possible reason for why GaP is so selective to methanol rather than hydrogen evolution (C. X. Kronawitter; M. Lessio; P.

Zhao; C. Riplinger; A. Boscoboinik; D. Starre; P. Sutter; E. A. Carter; B. E. Koel, *J. Phys. Chem. C*, **119**, 17762 (2015))

- A GaP(110) surface Pourbaix diagram was computed showing that these same species will be present under experimental pH and applied potential (to be published).
- Calculating physically consistent radical deprotonation energies (energies needed for acid dissociation constants) may require characterizing excited states for radical anions. Not characterizing these states can lead to errors larger than 10 kcal/mol. Pyridinyl molecules furthermore have very low acidities in aqueous solution, and they are therefore highly unlikely to participate in any kind of acid-base chemistry under ambient electrochemical conditions (see J. A. Keith, E. A. Carter, *J. Chem. Theory Comput.* **8**, 3187 (2012))
- The observed reduction potential of pyridinium at ~-0.6 V vs. the SCE on Pt electrodes is not consistent with the one-electron reduction of solvated pyridinium but rather another presently unknown reduction process. (See J. A. K. Keith, E. A. Carter, *J. Am. Chem. Soc.* **134**, 7580 (2012))
- We predict that the actual form of the co-catalyst involved in pyridinium-based CO_2 reduction is not the long-proposed pyridinyl radical in solution, but is more probably a surface-bound dihydropyridine species (see J. A. Keith and E. A. Carter, *Chem. Sci.*, **4**, 1490 (2013)).
- It is possible to describe the interaction of electrocatalysts with GaP via judiciously constructed cluster models that are then capable of accounting for solvation and charging (see J. A. Keith, A. B. Muñoz-García, M. Lessio, and E. A. Carter, *Top. Catal*., **58**, 46 (2015)).
- Calculations show that proton or pyridinium reduction is energetically unfavorable on GaP, even at very negative electrode potentials. Reduction of a surface-bound pyridine to dihydropyridine is thermodynamically favorable, even at moderate potentials (see J. A. Keith and E. A. Carter *J. Phys. Chem. Lett*., **4**, 4058 (2013); *J. Phys. Chem. Lett*., **6**, 568 (2015).).
- Using the cluster models to compute acidity constant values, we found that protons with hydride character will likely be reduced and react with adsorbed pyridine under experimental conditions (to be published).
- Computed band edge positions of GaP(110) and adsorption energy values confirm that pyridinium reduction to the pyridinyl radical cannot occur through the transfer of photoexcited electrons from the bare surface. Instead, reduction to an adsorbed pyridine and an adsorbed hydrogen atom is energetically feasible (see Lessio, M.; Carter, E. A. *J. Am. Chem. Soc.* **2015**, *137*, 13248–13251). Very recent refined electrode work function computations in the presence of a dissociated water layer on the GaP surface suggest that pyridinyl might be able to form under illumination but that it is much less favorable than the proposed reduction above to adsorbed pyridine and hydrogen (to be published).
- A combined experimental and computational study shows that adsorption of pyridine on the surface might favor its reduction to dihydropyridine (see Kronawitter C. X., Lessio M., Zahl P., Muñoz-García A. B., Sutter P., Carter E. A., Koel B. E. *J. Phys. Chem. C*, **2015**, in press).
- Relative free energy diagrams, derived with *ab initio* thermodynamics, predict stable reconstructions of GaP(111), CdTe(111) , and CuInS2(112) surfaces (to be published).
- The cluster approach is extended to model the reconstructed GaP(111), CdTe(111), and CuInS2(112) surfaces. Similar to GaP(110), pyridine and dihydropyridine adsorption are thermodynamically favorable on these surfaces, while pyridinium adsorption is not.
- Calculations strongly suggest that bipyridine is a non-innocent ligand taking over the additional electrons during reduction of the Re(bpy)(CO)3Cl catalyst. The active catalyst thus comprises of a Re0 species (see E. E. Benson, M. D. Sampson, K. A. Grice, J. M. Smieja, J. D. Froehlich, D. Friebel, J. A. Keith, E. A. Carter, A. Nilsson, and C. P. Kubiak Angew. Chem. Int. Ed. 52, 4841 (2013)).
- Calculations indicate that the selectivity of the rhenium catalyst for CO_2 reduction over H_2 generation is determined by the lower reaction barrier for CO_2 binding to the active catalyst compared to the barrier for protonation of the active catalyst. C-O bond cleavage is catalyzed by a Brønsted acid (see J. A. Keith, K. A. Grice, C. P. Kubiak, and E. A. Carter J. Am. Chem. Soc. 135, 15823 (2013)).
- Calculations indicate that the lower redox potentials observed for the Mn(bpy)(CO)3Br, compared to the Re(bpy)(CO)3Cl catalyst, can be explained by its lower binding affinity for a sixth ligand. This leads to different active pathways under catalytic conditions. Experimentally observed manganese complex dimerization is also determined by the lower binding affinity (see Riplinger C.; Sampson M. D.; Ritzmann A. M.; Kubiak C. P.; Carter E. A., *J. Am. Chem. Soc.*, **2014**, *136*, 16285)

- Microkinetic simulations show that the Re(bpy)(CO)3Cl catalyst works under higher overpotentials because of its more negative reduction potential of the singly reduced state. These simulations also elucidate the effect of the Brønsted acid. If the Brønsted acid is to weak, a higher acid concentration or a higher applied potential are required for both catalysts; however, this trend is more pronounced for Mn(bpy)$(CO)_3$Br (see Riplinger C.; Carter E. A., *ACS Catalysis*, **2015**, *5*, 900).
- Cu electrodes produce methane, ethylene, hydrogen, ethanol, and n-propanol as reported in the literature
- Oxidized Cu produces reduced amounts of methane and increased amounts of ethanol, and n-propanol.
- Cu/TiO2 electrodes and Cu/Al2O3 electrodes do not reduce CO_2 efficiently.
- Cu/ZnO electrodes reduce CO_2 efficiently, but only after a significant activation period.
- Observed CO dissociation on the stepped Cu(211) surface, suggesting a possible pathway to the formation of hydrocarbons during CO_2 reduction. (manuscript submitted).
- Built a system to study the activity of single crystal electrodes with high sensitivity for hydrocarbon products.
- The online electrochemical mass spectrometry (OLEMS) system was successfully built and is currently operational. It is most effective at detecting gas-phase products such as hydrogen, methane, and ethylene, with a small sensitivity towards detecting alcohols. Its main advantage over typical detection methods is the ability to detect products in real time as the potential is sweeping.
- Of the three copper single crystals studied, the Cu(100) surface has the best ethylene:methane selectivity, followed by Cu(211) and Cu(111). Calculations by the Norskov group suggest this is due to the increased affinity for CO coupling to occur on the Cu(100) surface.
- A nanostructured copper surface can be created with the addition of 4 mM KCl to 0.1 M KHCO3 and cycled between oxidative and reductive potentials. The resulting surface is covered with 30-100 nm cubic shapes (CuCube).
- This CuCube surface is several orders of magnitude more selective for ethylene over methane compared to its polycrystalline copper counterpart. While the absolute ethylene production only appears to increase by about a factor of 2, the methane production is essentially nonexistent over the potential range investigated.
- Spectroscopic investigations reveal that a thick Cu2O layer (not a copper chloride) is formed during the oxidation-reduction process, giving rise to the cubic shape. The presence of residual oxygen, even after thorough electrochemical reduction was detected with ambient pressure XPS and will be further investigated as a potential explanation for the increased selectivity of oxide-derived catalysts.
- Co-dosing CO and H2O on a Cu(211) surface results in the formation of CO2 and the growth of a C-H species on the copper surface.
- Dosing CO and CO2 on a preoxidized Cu(211) surface results in either a more reduction surface (CO dose) or more oxidized surface (CO2 dose). CO forms carboxylate species, while CO2 forms carbonates.
- The stepped (211) surface is more active for CO_2 reduction than (111) for metals that bind CO weakly (Cu, Ag and Au), whereas (111) is more active than (211) for metals that bind CO strongly (Pt, Ni, Rh and Ir).
- The reduction of CO is thermodynamically difficult on both steps and terraces of transition metals, which gives rise to a significant overpotential.
- The poor selectivity for CO_2 reduction in transition metals that bind CO strongly arises primarily from their high activity for hydrogen evolution, rather than a very high overpotential for CO_2 reduction.
- The reduction of CO_2 and methanediol H2C(OH)2 share no common reaction intermediates. Contrary to suggestions in the literature, the reduction of aqueous CH_2O to CH_3OH does not rule out that adsorbed CH_2O is formed as a short-lived reaction intermediate in CO_2 reduction to CH_4 on Cu.
- The protonation of CO to COH and CHO on Pt(111) and Au(111), respectively, has small to moderate barriers when the protonation reaction is close to thermoneutral.
- Thin films of layered transition-metal dichacolgenides have been synthesized and shown to electrocatalytically reduce CO_2 to methane at ~15% Faradaic efficiency (FE) when in contact with an ionic liquid. Thin films of MoS_2 also yielded significant amounts of ethylene (> 10% FE) and methanol (~5% FE).

- Intermetallic Ni–Ga compounds have been synthesized and shown to electrochemically reduce CO_2 to methane, ethylene, and ethane when in contact with an aqueous CO_2-saturated sodium bicarbonate solution and biased to -0.48 V versus RHE. These compounds offer a promising new class of materials for electrochemical CO_2 reduction. (Torelli, D. A.; Francis, S. A.; Crompton, J. C.; Javier, A.; Thompson, J. R.; Brunschwig, B. S.; Soriaga, M. P.; Lewis, N. S., Nickel-Gallium-Catalyzed Electrochemical Reduction of CO2 to Highly Reduced Products at Low Overpotentials, submitted for publication.)
- a CO dimer exists on both Cu(111) and Cu(100), stabilized by a charged water bilayer
- the barrier for this dimerization process is expected to be lower on Cu(100) than that on Cu(111), consistent with experimental observations
- CO-CO coupling is shown to be feasible on (111), (100), and (211) facets
- the barrier for protonation of oxygen is small compared to protonation of carbon and C-O scission-inducing protonation of R-OH species
- the dominant pathway on Cu(211) likely includes *CHOH and *CH as intermediates rather than *OCH_3
- we analyzed the thermodynamics of potential mechanisms for the production of CO, H_2, formate, and methanol using DFT on Au
- one mechanism explains gold's selectivity towards methanol and is consistent with the generally unreactive nature of the Au surface
- the C-C coupling barrier depends on the CO binding energy via a scaling relation on a Cu/Au surface
- the increased selectivity to OH-terminated C_2 and C_3 species may be due to the strengthened binding of the CO and CH_2O intermediate at the gold and copper interfaces
- we developed a novel method to determine constant potential reaction energetics for simple charge transfer reactions
- this requires only a single barrier calculation in an electrochemical environment and the corresponding surface charge at the initial, transition, and final states
- DFT delocalization error currently prevents the successful implementation of this model; a correction scheme is being investigated
- the potential-limiting step for CO_2 reduction on RuO_2(110) is dependent upon CO-coverage
- limiting potentials of −0.43 V and −0.25 V vs. RHE were obtained at 0.25 ML and 0.5 ML CO coverage, respectively
- CO-coverage is a possible parameter in tuning the CO_2 reduction activity on RuO_2
- Pourbaix diagrams of $EMIM^+$ interaction at the Ag(111)|water interface were constructed
- $EMIM^+$ adsorbs specifically to the silver surface and is expected to have a high coverage under experimental conditions

PLANS FOR THE COMING YEAR:

During the No Cost Extension (NCE) period the **Kubiak** group continued to expand our understanding and utilization of bpy-based ligand frameworks by expanding into new metals. We will employ a similar approach to attempt to successfully interface P_2N_2-based complexes with carbon dioxide. Future work on the $[Ni(cyclam)]^{2+}$ catalyst system will focus on verifying the hypothesis that the CO poisoned catalyst, $[Ni(cyclam)(CO)]^+$, is destabilized on a mercury surface. It has also been hypothesized in the literature that the adsorbed catalyst is in a different conformation than exists in solution. Computational studies and empirical data is needed to determine the true identity of the highly active version of $[Ni(cyclam)]^+$ adsorbed on mercury. Generation of this special version of the catalyst without such a toxic substance as mercury will be of great importance.

The **Kubiak** group also further optimized the use of Lewis acids to promote catalysis at low overpotentials with the $Mn(mesbpy)(CO)_3X$ system. This will include investigations of chelating agents to maintain Mg^{2+} solubility over longer periods of time as well as the use of other Lewis acids. Finally, the **Kubiak** group will continue to explore the structural diversity of Ni(bis-NHC) complexes, with a focus on the generation of strong nickel hydride species for the reduction of CO_2 to formate.

The **Kubiak** group examined the question of pre-activation of CO_2 for its reduction to methane by NHC complexes. The recent report that $[Ni(cyclam)]^{2+}$ in conjunction with NHCs leads to the 8-electron reduction of CO_2 to CH_4 will be considered mechanistically. Key mechanistic details that are revealed will be used to extend the concept of pre-activated CO_2 and to optimize the effect's activity and selectivity.

The **Kubiak** group will seek funding from AFOSR and other agencies to continue to work on promising systems first discovered under the MURI program, including proton dependent selective CO2 reduction, reduction of CO2 to more complex organic fuels, catalytic Metal Organic Frameworks (MOF), catalysts with carbene ligands, studies of hydricity.

The **Carter** group continued studies of nitrogen heterocyles on GaP, aiming at a more-refined understanding of potential adsorbed intermediates and attendant electrochemical reduction reactions. In particular, mechanistic pathways and barriers to DHP formation on GaP will be calculated, as well as examining the potential for proton/hydride coupled reduction of CO_2, potentially facilitated by DHP. We will continue our work, in collaboration with the Kubiak group, to understand the role of bpy in CO_2 reduction by the Mn(bpy = 2,2'-bipyridine)$(CO)_3Br$ and the Re(bpy)$(CO)_3Cl$ catalysts.

The **Nørskov** group will focus on full micro-kinetic models of CO_2/CO reduction on Cu surfaces based on calculated reaction energetics. These models will seek to explain the activity and selectivity of various Cu facets towards hydrogen evolution and C1 and C2 products. Furthermore, in view of a fundamental understanding of selectivity towards hydrogen evolution and CO_2 reduction, they will investigate the reaction energetics of hydrogen evolution in basic solutions, where the intrinsic hydrogen evolution activity is dramatically suppressed. They will also investigate the impact of imidazolium additives on the activation energies for hydrogen evolution and CO_2 reduction.

The **Nilsson** group continued to study surface intermediates formed during CO_2 reduction using ambient pressure XPS, which should allow for the in situ characterization of reaction intermediates as a function of potential. Using this system and other x-ray techniques, we also plan to study pyridinium catalysts in collaboration with the Bocarsly group to better understand the roll of the pyridinium in changing the selectivity and overpotential of the CO_2 reduction reaction. Our observation of CO dissociation on Cu raises many questions about the mechanism which requires further study. We hypothesize the adatom-like Cu and unsaturated carbon species on the (211) surface is important to the formation of graphitic carbon which could further facilitate C-O bond cleavage. We will also evaluate the activity and selectivity of a number of alloys predicted from the Nørskov group using our mass spectroscopy system and in-situ measurements on various beamlines. We have also started to pursue CO reduction on ultrafast timescales using the new x-ray laser (LCLS) at SLAC with a focus to detect CHO intermediates.

Several ongoing studies in the **Bocarsly** group have already been noted in the section above. In addition, we plan to expand our studies of semiconducting systems to GaAs and $BiVO_4$. GaAs is of interest because of its similarities to GaP. However, this material has a smaller band gap and as a result a less negative conduction band edge. We anticipate this will influence the interactions of this interface with our aromatic amine catalysts, producing a different product distribution than previously observed. This should both be of pragmatic interest and shield light on the mechanistic details associated with the aromatic amine catalyzed CO_2 reduction on III-V semiconductor surfaces. Bismuth vanadate has been reported to photoreduce CO_2 to ethanol when in a powered form. We will fashion this material as an electrode so that kinetic data can be obtained from this system. Since this system is quite different from the III-V materials studied to date, we expect very different surface interactions with aromatic amines. The reports on bismuth vanadate to date seem to suggest it is an unstable system. Given that pyridinium stabilizes the GaP interface, we wish to determine if there are aromatic amines that stabilize the bismuth vanadate system allowing for kinetic control over the observed products, in particular, products that have multiple carbons since these species represent true solar fuels.

During the NCE period, the **Lewis** group plans to continue to study the role that deposition conditions play in electrolytic CO_2 reduction on dendritic Cu electrodes. The literature regarding Cu electrodeposition suggests that the ligand structure around Cu2+ ions is significantly influenced by solution pH, which in turn influences the crystallographic orientation of growth during electrodeposition.

We will use SEM and XRD to study the initial growth of Cu electrodeposition as a function of pH in order to infer the mechanistic differences between electrodes. We will also use metal nanocatalysts on semiconductors to prepare photoelectrodes that possess catalytic specificity. Through pulsed electrodeposition, we can control the size, structure, and areal density of catalyst nanoparticles. This maintains the best feature of each component: the semiconductor substrate equilibrates with solution, while the catalyst imparts selectivity that is not necessarily inherent to the semiconductor with minimal perturbation to the photovoltaic properties of the electrodes.

TRANSITION PLANNING:
The research in this program has been and will continue to be disseminated in peer-reviewed publications, as well as presentations to a global audience (*vida infra*). This allows for an increased awareness in the scientific community of the work in our MURI program, including members of industry working on CO_2 reduction. The information we are disseminating will be invaluable for the development of an integrated device for the production of liquid fuels from sunlight and CO_2 using a heterogeneous or homogeneous catalyst, or a combination of the two. We have been in contact with companies interested in using systems similar to those we are studying in the MURI program (e. g. PSIcorp Inc.). We plan on continuing discussions with companies and government organizations interested in the development of applied systems for CO_2 reduction. In addition, we will be pursuing patents for any discoveries in the MURI Program that would be applicable for a CO_2 reduction device.

PUBLICATIONS, PRESENTATIONS, AND INDIVIDUAL AWARDS:

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Presentations

C.P. Kubiak, "If you make a solar fuel from CO_2, what should it be?" Duke University, Durham, North Carolina, November 14, 2016.

C.P. Kubiak, "Non-covalent interactions and co-catalysts in the electrochemical reduction of CO_2" ***COST*** | European Cooperation in Science and Technology Meeting, Milazzo, Italy, September 3-6, 2016 (invited lecture).

C.P. Kubiak, "Molecular electrocatalysts for the reduction of CO_2 and the effects of bioinspired, secondary-sphere interactions on mechanism" National Meeting of the American Chemical Society, San Diego, CA, March 16, 2016, (invited symposium lecture).

C. P. Kubiak, "If you are going to make a solar fuel from CO_2, what should it be?" Gordon Research Conference on Renewable Energy: Solar Fuels, Lucca, Italy, February 28-March 4, 2016.

C. P. Kubiak, "Carbon dioxide reduction by manganese bipyridine complexes: Lowering overpotentials and enhancing stability." International Congress of the Pacific Basin Societies (Pacifichem 2015), Honolulu, HI, December 15-20, 2015, (invited symposium lecture).

C. P. Kubiak, "Electrochemical reduction of CO_2: Hydricities and reduction potentials control switching between CO_2reduction to formate, CO_2 reduction to CO, and formate oxidation." International Congress of the Pacific Basin Societies (Pacifichem 2015), Honolulu, HI, December 15-20, 2015, (invited symposium lecture).

C. P. Kubiak, Basolo Medal Award Lecture, Northwestern University, October 30, 2015, (invited lecture).

C. P. Kubiak, "Carbon dioxide reduction by earth abundant artificial catalysts in solar fuels applications: New mechanistic insights and challenges." Michigan State University, October 5, (invited lecture).

C. P. Kubiak, "Electrocatalytic Reduction of Carbon Dioxide", University of California, Los Angeles, September 30, 2015, (invited lecture).

C. P. Kubiak, "New nickel(0) complexes supported by chelating N-heterocyclic carbene ligands: Unusual structures and small molecule activation." National Meeting of the American Chemical Society, Boston, MA, August 18, 2015, (invited symposium lecture).

C. P. Kubiak, "Solar Fuels: The conversion of CO_2 to liquid fuels." International Union of Pure and Applied Chemistry (IUPAC), 45th World Chemistry Congress, Busan, Korea, August 11, 2015, (Keynote address).

C. P. Kubiak, “Catalytic Reduction of CO_2.” Center for Enabling New Technologies through Catalysis (CENTC) Summer School on Catalysis, University of Washington, July 23, 2015, (invited lecture).

C. P. Kubiak, “Manganese Catalysts with Bulky Bipyridine Ligands for the Electrocatalytic Reduction of Carbon Dioxide: Eliminating Dimerization and Altering Catalysis.” Virtual Inorganic Pedagogical Electronic Resource (VIPER): A community for teachers and students of inorganic chemistry workshop in catalysis, University of Washington, June 30, 2015, (invited lecturer and participant).

C. P. Kubiak, “Carbon dioxide reduction by earth abundant artificial catalysts in solar fuels applications: New mechanistic insights and challenges.” First International Conference on Solar Fuels (ISF-1), Uppsala, Sweden, May 1, 2015, (plenary lecture).

C. P. Kubiak, “Carbon dioxide reduction by earth abundant artificial catalysts in solar fuels applications: New mechanistic insights and challenges.” Stanford University, April 20, 2015, (invited lecture).

C. P. Kubiak, "Homogeneous reduction of CO_2 by $[Ni(cyclam)]^+$, poisoning by CO, detoxification by CO sponge, and useful conversion of CO by tandem catalysis.” National Meeting of the American Chemical Society, Denver, CO, March 24, 2015, (invited symposium lecture).

C. P. Kubiak, “Photoelectrochemical reduction of CO_2.” Joint Center for Artificial Photosynthesis (JCAP) All-Hands Meeting, Asilomar, CA, March 13, 2015, (plenary lecture).

C. P. Kubiak, “Mechanistic studies of the electrocatalytic reduction of CO_2. Supramolecular approaches to lowering the overpotential.” Gordon Research Conference in Mechanistic Inorganic Chemistry, Galveston, TX, March 4, 2015, (invited lecture).

C. P. Kubiak, “Carbon dioxide reduction by earth abundant catalysts in artificial photosynthesis: Mechanistic insights and challenges.” International Conference on Artificial Photosynthesis (ICARP 2014), Awaji Island, Japan, November 26, 2014, (plenary lecture).

C. P. Kubiak, “Earth-Abundant Transition Metal Catalysts for the Conversion of CO_2 to CO, HCOOH, and Liquid Fuels.” SUSTEC Summit in Sustainable Technology, UC, Santa Barbara, September 30, 2014, (plenary lecture).

C. P. Kubiak, “Electrochemical and photoelectrochemical reduction of CO_2.” Gordon Research Conference on Electrochemistry, Ventura, CA, January 8, 2014, (invited lecture).

C. P. Kubiak, “Carbon dioxide reduction by rhenium and manganese bipyridyl complexes: Mechanistic insights and new strategies to lower overpotentials.” Julia S. and Edward C. Lee Memorial Lecture, University of Chicago, November 18, 2013.

C. P. Kubiak “Electrochemical and Photoelectrochemical Reduction of CO_2”. International CECAM Workshop “Future Challenges in CO_2 Reduction”, University of Bremen, Breman, Germany, October 8 – 12, 2012.

C. P. Kubiak “Electrochemical and Photoelectrochemical Reduction of CO_2”. The 19th International Conference on Photochemical Conversion and Storage of Solar Energy, Pasadena, CA, July 30 – August 3, 2012.

C. P. Kubiak “Electrochemical and Photoelectrochemical Reduction of CO_2”. The 243rd National Meeting of the American Chemical Society, Symposium on Sustainable Inorganic Chemistry, San Diego, CA, March 26, 2012.

C. P. Kubiak “An artificial formate dehydrogenase that bypasses a metal hydride in order to oxidize formate faster and at lower potential.” Experts Workshop in Metal Hydrides in Biology, Oxford University, Oxford, England, March 14-15, 2012.

C. P. Kubiak “Electrochemical and Photoelectrochemical Reduction of CO_2”. Solar Fuels. Science, Engineering, and Policy, Duke University, Durham, NC, January 11-12, 2012.

C. P. Kubiak “Electrochemical and Photoelectrochemical Reduction of CO_2”. Natural and Artificial Photosynthesis Conference, Rensselaer Polytechnic Institute, Troy, NY, November 4-5, 2011.

C. P. Kubiak “Electrochemical and Photoelectrochemical Reduction of CO_2” University of Uppsala, Uppsala, Sweden, August 26, 2011.

C. P. Kubiak “Electrochemical and Photoelectrochemical Reduction of CO_2” (3 Lectures). C1 Chemistry Summer Course, University of Hamburg, Hamburg, Germany, August 22-24, 2011.

C. P. Kubiak “Electrochemical and Photoelectrochemical Reduction of CO_2”. Max Planck Institute for Bioinorganic Chemistry, Muelheim, Germany, August 19, 2011.

C. P. Kubiak “Electrochemical Reduction of CO_2.” Challenges in Renewable Energy (ISACS 4), MIT, Cambridge, MA, July 5-8, 2011.

C. P. Kubiak “Sungas: Solar Syngas” Gordon Research Conference on Renewable Energy: Solar Fuels, Ventura, CA, January 21, 2011.

E. A. Carter, “Modelling Heterogeneous Photoelectrocatalysis from First Principles,” at the Pacifichem 2015 Congress, Honolulu, HI, Dec. 19, 2015.

E. A. Carter, “Theoretical Characterization of Photoelectrochemistry of GaP,” at the 2015 MRS Fall Meeting, Boston, MA, Dec. 1, 2015.

E. A. Carter, “Quantum Mechanical Evaluation of Photoelectrocatalysis,” at the Dorothy Crowfoot Hodgkin (DCH) Symposium, Zurich, Switzerland, Oct. 5, 2015.

E. A. Carter, “How Quantum Mechanics Can Help Provide a Sustainable Energy Future,” plenary lecture at the SCF'15 Conference on Chemistry and Energy Transition, Lille, France, July 7, 2015

E. A. Carter, “Mechanisms of rhenium – and manganese-catalyzed electrochemical reduction of CO2 from theory,” at the 249th ACS Spring National Meeting, Denver, CO, Mar. 26, 2015.

E. A. Carter, “What theory can reveal about carbon dioxide reduction and the role of molecular catalysts,” at the 249th ACS Spring National Meeting, Denver, CO, Mar. 24, 2015

E. A. Carter, “How Quantum Mechanics Can Help Solve the World's Energy Problems,” at the 2015 AAAS Meeting, San Jose, CA, Feb. 14, 2015.

E. A. Carter, “Building a Sustainable Energy and Environmental Future,” Dreyfus Teacher-Scholar Symposium, New York Academy of Sciences, New York, NY, Oct. 24, 2014.

E. A. Carter, “Mechanisms for heterogeneous and homogeneous reduction of carbon dioxide from first principles,” at the 248th ACS Fall National Meeting, San Francisco, CA, Aug. 12, 2014.

E. A. Carter, “First Principles Quantum Simulations of Renewable Energy Phenomena,” at the Gordon Research Conference on Atomic Molecular Interactions, Easton, MA, July 13, 2014.

E. A. Carter, “Evaluation and Design of Photoelectrochemical Materials from First Principles,” at the 2014 MRS Spring Meeting, San Francisco, CA, Apr. 24, 2014.

E. A. Carter, “First principles quantum simulations of (photo)electrocatalysis at semiconductor surfaces,” at the 247th ACS Spring National Meeting, Dallas, TX, Mar. 19, 2014.

E. A. Carter, “Quantum Mechanics and the Future of the Planet,” Mathematics of Planet Earth 2013 Simons Public Lecture at the Institute for Pure and Applied Mathematics, Los Angeles, CA, November 4, 2013.

E. A. Carter, “Mechanisms of (Photo)Electrochemical Reduction of Carbon Dioxide From First Principles,” keynote lecture at the 224th Electrochemical Society Meeting, San Francisco, CA, October 28, 2013.

E. A. Carter, "Mechanisms of Photoelectrochemical Reduction of Carbon Dioxide and Water Splitting from First Principles,” at the Avogadro Colloquium) on Challenges for theoretical and computational chemistry in Horizon2020, Pisa, Italy, September 27, 2013.

E. A. Carter, “How Quantum Mechanics Can Help Solve the World's Energy Problems,” plenary lecture at the Applied Mathematics, Modeling and Computational Science (AMMCS) 2013 International Conference, Waterloo, ON, Canada, August 27, 2013.

E. A. Carter, “Materials Genome Initiative: Hard Condensed Matter for Energy Applications,” at the NSF Materials Genome Initiative Workshop, Arlington, VA, December 13, 2012.

E. A. Carter, “Quantum Mechanical Design and Evaluation of New Solar Energy Conversion Materials,” keynote lecture at the SPIE Optics & Photonics 2012, San Diego, CA, August 14, 2012.

E. A. Carter, “Quantum Mechanical Evaluation of Photoelectrochemical and Solid Oxide Fuel Cells,” keynote lecture at the 11th Spring Meeting of the International Society of Electrochemistry, Washington, DC, May 25, 2012.

E. A. Carter, “Novel Catalytic Mechanisms for the Chemical Reduction of Carbon Dioxide to Energy-Dense Liquids (MURI),” at the AFOSR Molecular Dynamics Contractor’s Meeting, Arlington, VA, May 23, 2012.

E. A. Carter, “Quantum Mechanical Evaluation of New Solar Energy Conversion Materials,” at the ACS Spring 2012 National Meeting & Exposition, San Diego, CA, March 25, 2012.

J. K. Nørskov, *A Theory of transition metal Heterogeneous Catalysis,* CHAINS 2015: Chemistry Matters for the Future, Veldhoven, The Netherlands, December 2015

J. K. Nørskov, *A Theory of transition metal Heterogeneous Catalysis,* 2015 AICHE Annual Meeting, Salt Lake City, November 2015

J. K. Nørskov, *Zhang Dayu Lecture—A Theory of transition metal Heterogeneous Catalysis,* Zhang Dayu Lectureship, Dalian Institute of Chemical Physics, Chinese Academy of Sciences
Dalian, China, May 2015

J. K. Nørskov, *Dodge Series Lecture—A predictive theory of transition metal surface catalysis,* Yale University, Department of Chemical & Environmental Engineering, New Haven, April 2015

J. K. Nørskov, *Irving Langmuir Prize Lecture—A predictive theory of transition metal surface catalysis,* APS March Meeting, San Antonio, Texas, March 2015

J. K. Nørskov, *Electrochemical CO2 Reduction: Theoretical Investigations,* MURI (Multi-University Research Initiative) 2014 Review of the project Novel Catalytic Mechanisms for the Chemical Reduction

of Carbon Dioxide to Energy-Dense Liquids, La Jolla, California, January 2015

J. K. Nørskov, *Electronic Structure Theory, Interface Science, and Catalysis*, 1st International Symposium on Interactive Materials Science, Osaka, Japan, November 2014.

J. K. Nørskov, *Understanding Activity and Selectivity Trends In Electrocatalysis: Energy Conversion Process,* International Symposium on Electrocatalysis: Explorations of the Volcano Landscape, Whistler, British Columbia, October 2014.

J. K. Nørskov, *Catalysis for Sustainable Energy and In-Search of the Catalyst Genome,* University of Pittsburg, Pittsburg, Pennsylvania, October 2014.

J. K. Nørskov, *Catalysis for sustainable Energy*, Daegu Gyeongbuk Institute of Science and Technology, Korea, September 2014.

J. K. Nørskov, *Concepts and trends in surface reactivity*, The 2014 CAMD Summer School on Electronic Structure Theory and Materials Design, Technical University of Denmark, Copenhagen, Denmark, August 2014.

J. K. Nørskov, *Reactivity of nanoparticles for more efficient and sustainable energy conversion,* The 2014 CINF Summer School, Technical University of Denmark, Kobaek-Strand, Denmark, August 2014.

J. K. Nørskov, *Theory of transition metal surface catalysis*, International Symposium onInorganic Insights into Catalysis, Berlin, Germany, July 2014.

J. K. Nørskov, *Catalysis for sustainable energy,* ESOF 2014 (Euroscience Open Forum), Copenhagen, Denmark, June 2014.

J. K. Nørskov, *In Search of the Catalyst Genome*, BASF Corporation North America, Newark, New Jersey, March 2014.

J. K. Nørskov, *Catalysis for sustainable energy,* 247th ACS National Meeting & Exposition, Chemistry & Materials for Energy, Dallas, Texas, March 2014.

J. K. Nørskov, *In Search of the Catalyst Genome*, The 17th SANKEN International Symposium 2014, Osaka, Japan, January 2014.

J. K. Nørskov, DGIST Distinguished Lectureship, Daegu Institute of Science and Technology, South Korea, 2014.

J. K. Nørskov, Bayer Distinguished Lectureship at the Swanson School of Engineering, University of Pittsburgh, 2014.

J. K. Nørskov, *In Search of the Catalyst Genome*, 2013 AIChE Annual Meeting, Global Challenges for Engineering a Sustainable Future, San Francisco, California, USA, November 2013.

J. K. Nørskov, *Electro Catalysis for Sustainable Energy*, The Electrochemical Society, 224th ECS Meeting, San Francisco, California, USA, October - November 2013.

J. K. Nørskov, *Fuels from Sunlight*, IPAM Workshop (Institute for Plan and Applied Mathematics), Los Angeles, California, USA, October 2013.

J. K. Nørskov, *In Search of the Catalyst Genome*, EuropaCat, XIth European Congress on Catalysis, Lyon, France, September 2013.

J. K. Nørskov, *Electro- Catalysis*, SLAC/Stanford Summer Institute 2013, Heterogenous Catalysis for Energy Transformations, Menlo Park, California, USA, August 2013.

J. K. Nørskov, *In Search of the Catalyst Genome*, 23rd North American Meeting of the Catalysis Society, Louisville, Kentucky, USA, June 2013.

J. K. Nørskov, *Nanostructured Catalysts for Conversion of Chemical Energy*, Gordon Research Conference, Nanomaterials for Applications in Energy Technology, Ventura, USA, February 2013.

J. K. Nørskov, "(Photo-)electro-catalytic fuel production," The 63rd Annual Meeting of the International Society of Electrochemistry: Electrochemistry for Advanced Materials, Technologies and Instrumentation, Prague, Czech Republic, August 2012.

J. K. Nørskov, "Catalysis for sustainable energy," 243rd ACS National Meeting, San Diego, USA, March 2012.

J. K. Nørskov, "Activity descriptors for CO_2 electroreduction to methane on transition-metal catalysts," 243rd ACS National Meeting, San Diego, USA, March 2012.

J. K. Nørskov, "Tailoring Surface Chemical Properties Using Electronic Structure Theory," APS March Meeting, Boston, USA, February 2012.

J. K. Nørskov, "(Photo-)electro-catalytic CO_2 Reduction," MRS 2011 Fall Meeting, Boston, USA, Nov 2011.

J. K. Nørskov, "From descriptive to predictive models of surface reactions," 100 year Anniversary Symposium for the Fritz-Haber Institute, Berlin, Germany, October 2011.

J. K. Nørskov, "Catalysis for Sustainable Energy," DOE SCGF 2011 Annual Research Meeting, Oak Ridge, TN, USA, July 2011.

J. K. Nørskov, "Catalysis for Sustainable Energy," 22nd North American Catalysis Society Meeting, Detroit, USA, June 2011.

J. K. Nørskov, "Understanding selectivity in syngas reactions," 241st ACS National Meeting, Anaheim, USA, March 2011.

J. K. Nørskov, "Understanding catalytic and electro-catalytic CO_2 reduction," Gordon Research Conference on Chemical Reactions at Surfaces, Ventura, USA, February 2011.

J. K. Nørskov, "Catalysis for sustainable Energy," Welch Foundation 2010 Conference on Chemical Research: Green Chemistry and Sustainable Energy, Houston, USA October 2010.

J. K. Nørskov, "Understanding electrochemical CO_2 reduction," Fall Symposium on Future Directions in CO_2 Conversion Chemistry, Princeton University, USA, October 2010.

J. K. Nørskov, "Fuels from sunlight – a challenge to electronic structure theory," Psi-k 2010 Conference, Berlin, Germany, September 2010.

J. K. Nørskov, "Fuels from Sunlight: The Role of Theory," Symposium honoring Juergen Hafner, University of Vienna, Austria, September 2010.

J. K. Nørskov, "Catalysis for sustainable energy," ACS 240th National Meeting, Boston, USA, August 2010.

A. Nilsson, “Spectroscopy for Catalysis with LCLS II” LCLS II Chemistry Workshop, SLAC/Stanford (2015).

A. Nilsson, “Spectroscopy for Catalysis with FLASH II” Workshop on the future of chemistry at FLASH, Hamburg (2015).

A. Nilsson, “Operando X-ray Studies of Electrocatalysis” Photocatalysis Workshop at EMPA, Zurich (2015).

A. Nilsson, “Ultrafast X-ray Spectroscopic Probing of Catalytic Surface Chemical Reactions using LCLS” 16th XAFS conference, Karlsruhe, Germany (2015).

A. Nilsson, “Chemical Energy Transformation at Interfaces” RACIRI summershool, Rugen Island, Germany (2015).

A. Nilsson, “Catalysis in Real Time and Fluctuations on Various Length Scales in Water” Symposium on Assessing the Future of Physical Chemistry, Fritz Haber Institute, Berlin (2015).

A. Nilsson, “Fundamental Studies in electrocatalysis using x-rays” American Chemical Society meeting, Dallas (2014).

A. Nilsson, “X-ray Studies of ElectroCatalysis” Heraeus-Seminar From Sunlight to Fuels, Physikzentrum Bad Honnef, Germany (2014).

A. Nilsson, “Ultrafast Surface Chemistry and Catalysis using Soft X-rays at LCLS” 23rd Congress and General Assembly of the International Union of Crystallography, Montreal (2014).

A. Nilsson, “Ultrafast Surface Chemistry and Catalysis” Summer School, Korbaek strand, Denmark (2014).

A. Nilsson, “Probing structure and dynamics of water and chemical reactions on surfaces; early experience from LCLS” Maxlab user meeting, Lund, Sweden (2014).

A. Nilsson, “Fundamental Studies of ElectroCatalysis using X-rays” Materials for tomorrow, Chalmers, Gothenburg, Sweden (2014).

A. Nilsson, “Ultrafast Surface Chemistry and Catalysis” 3rd Ertl symphosium, Berlin, Germany (2014).

A. Nilsson, “Ultrafast Surface Chemistry and Catalysis using Soft X-rays at LCLS” XFEL user meeting, Hamburg, Germany (2014).

A. Nilsson, “In-situ X-ray studies of Photo and Electrocatalysis” American Chemical Society meeting, New Orleans (2013).

A. Nilsson, “In-Situ X-ray Studies of Photo-and ElectroCatalysis” Summer School on Reactivity of Nanoparticles for more Efficient and Sustainable Energy Conversion, Korbaek, Denmark, August 2012.

A. Nilsson, “In-Situ X-ray Studies of Photo-and ElectroCatalysis” The 34th Solar Photochemistry Research Conference, Annapolis, Maryland, USA, June 2012.

A. B. Bocarsly. The University of Delaware, *A Chemist's Solution To Excessive Atmospheric CO_2: Catalytic Solar-Driven Reduction Of Aqueous CO_2 To Organics* (November 2014).

A. B. Bocarsly. Sydney Ross Lecturership at Rensselaer, *Electrocatalytic Solar-Driven Conversion of Aqueous CO_2 to Organics: Pyridinium an Unexpected Catalyst for Carbon Dioxide Reduction* (October 2014).

A. B. Bocarsly. Monash University, Melbourne, Australia, *Electrocatalytic Solar-Driven Conversion of Aqueous CO_2 to Organics: Pyridinium an Unexpected Catalyst for Carbon Dioxide Reduction* (October 2014).

A. B. Bocarsly, Cole, E., Kaczur, J., White, J.L., Majsztrik, P.W., *Carbon dioxide as an abundant feedstock replacement for fossil fuels*. Abstracts of Papers of the American Chemical Society, 2014. 248.

A. B. Bocarsly, *New Materials for Solar Fuels from CO_2: From Chemical Concept to Real World Applications*, ACS Green Chemistry and Engineering Conference, 2014, invited talk.

A. B. Bocarsly, Pander, J.E., Zeitler, E., Yan, Y., Liao, K.*, Pyridinium as an electrocatayst for the reduction of carbon dioxide to C_1 products: Mechanistic considerations*. Abstracts of Papers of the American Chemical Society, 2014. 248. invited talk.

A. B. Bocarsly. Columbia University, *CO_2 Conversion to Fuels* (April 2014).

A. B. Bocarsly. Peking University, Bejing, PRC, 利用新型材料（p型半导体光阴极）和新型催化剂生成"日光燃料: *New Materials and Catalysts for Solar Fuels: p-Type Semiconductors as Photocathodes*, (April 2014).

A. B. Bocarsly. Nanjing University, Nanjing, PRC, *New Materials for Solar Fuels: p-Type Semiconductors as Photocathodes*, (April 2014).

A. B. Bocarsly. Georgia Tech and Emory University (Separate Talks), Catalytic *Photoelectrochemical Reduction of Aqueous Carbon Dioxide to Organics: A Chemist's Solution to Excessive Atmospheric CO_2* (February, 2014).

A. B. Bocarsly. Queens College (CUNY), *A Chemist's Solution to Excessive Atmospheric CO_2: Catalytic Photoelectrochemical and Electrochemical Generation of Alcohols* (December 2013).

A. B. Bocarsly, *Pyridinium Catalyzed Reduction of CO_2*. New York Catalysis Society Symposium, 2013, invited talk.

A. B. Bocarsly, *Electrocatalytic Reduction of CO_2 to Alcohols*, Clearwater Clean Coal Conference, 2013, invited talk.

A. B. Bocarsly, Zeitler, E., Liao, K., He, Y., Gu, J., Yan, Y., Shaw, T.W., L'Esperance, R.P. *Electrochemical conversion of CO_2 to organic products in an aromatic amine catalyzed environment.* Abstracts of Papers of the American Chemical Society, 2013. 245. invited talk.

A. B. Bocarsly, Gu, J., Yan, Y., Watkins, J., Zeitler, E., Detweiler, Z., Hu, Y., Liao, K., White, J., Baruch, M., Pander, J., Wuttig, A*. Non-innocence of the electrode interface in low overpotential reduction of CO_2 to organic products*. Abstracts of Papers of the American Chemical Society, 2013. 246. invited talk.

A. B. Bocarsly, *Solar Fuels from Carbon Dioxide and Water: Catalytic Photoelectrochemical and Electrochemical Generation of Alcohols*, Wissenschaftsforum Chemie 2013, invited talk.

A. B. Bocarsly, "CO_2 Reduction," Gordon Research Conference on Green Chemistry, (lead off talk) Lucca, Italy, July 2012.

A. B. Bocarsly, "Visible light driven photoelectrochemical conversion of carbon dioxide to reduced carbon products" Pacifichem 2010 International Meeting, Honolulu, Hawaii, Dec 2010.

A. B. Bocarsly, "Development of electrode materials and soluble catalysts for the efficient optical conversion of carbon dioxide to liquid fuels," Henkel-SAB, Bridgewater, NJ, September 2010.

X-ray studies of electrocatalyst, from sunlight to fuels - novel materials and processes for photovoltaic and (photo)catalytic applications. WE-Heraeus-Seminar, Physikzentrum Bad Honnef, Germany, May 2014.

Ultrafast Surface Chemistry and Catalysis, 3rd Ertl Center Symposium, Berlin November 2014.

N. S. Lewis, May 12, 2015, Keynote Speaker, Ohio State University.

N. S. Lewis, May 6, 2015, Guest Speaker at 31st PSI Electrochemistry Symposium, Germany.

N. S. Lewis, May 5, 2015, Mechanical Engineering Department Guest Speaker, EPFL, Switzerland.

N. S. Lewis, April 27, 2015, Physical Chemistry Seminar, UCLA.

N. S. Lewis, April 8, 2015, Student-Selected Electrochemical Seminar, Indiana University.

N. S. Lewis, March 22-23, 2015, 249th Meeting of the American Chemical Society, Denver.

N. S. Lewis, March 17, 2015, Third Biennial Carbon Dioxide Workshop, Princeton University.

N. S. Lewis, February 22, 2015, Invited Speaker, Gordon Research Conference, Ventura.

N. S. Lewis, February 17, 2015, Emory University, Chemistry Department Research Seminar.

N. S. Lewis, February 13, 2015, University of Cincinnati, Spring Seminar Series.

N. S. Lewis, January 27, 2015, VerdeXchange 2015 Conference, Commercialization of Clean Technology: Extracting Value from Universities and National Labs.

N. S. Lewis, January 20, 2015, NRC Chemical Sciences Round Table with the National Academy of Sciences.

N. S. Lewis, January 14, 2015, UC Riverside Materials Science and Engineering Colloquium.

N. S. Lewis. Nov. 17, 2014, USC, Decarbonizing California - The Promise of Photosynthesis.

N. S. Lewis. Nov. 09, 2014, Falling Walls Conference - Breaking the Wall of the Global Energy Challenge.

N. S. Lewis. Nov. 08, 2014, 9th Berlin Debate on Science and Policy - From Truth to Power: Translating Science into a Better World.

N. S. Lewis. Oct. 24, 2014, UC Berkeley - Here Comes the Sun: The New Energy Future.

N. S. Lewis. Aug. 07, 2014, GRC – Rhode Island - Global Energy Perspectives.

N. S. Lewis. July 29, 2014, IPS-20 Conference - Sunlight-Driven Hydrogen Formation by Membrane-Supported Photoelectrochemical Water Splitting.

N. S. Lewis. May 22, 2014, MIT, Solar Study - Solar Photovoltaic Technologies.

N. S. Lewis. May 01, 2014, UC Berkeley - Sunlight-Driven Hydrogen Formation by Membrane-Supported Photoelectrochemical Water Splitting.

N. S. Lewis. Apr. 22, 2014, Materials Research Society - Sunlight-Driven Hydrogen Formation by Membrane-Supported Photoelectrochemical Water Splitting.

N. S. Lewis. Apr. 08, 2014, Sacramento Municipal Utility District - Reduction of Carbon Dioxide Emissions.

N. S. Lewis. Apr. 08, 2014, Clean Energy States Alliance - Clean Energy Efforts.

N. S. Lewis. Apr. 08, 2014, California Energy Commission - An Understanding of the Promise of Artificial Photosynthesis.

N. S. Lewis. Mar. 25, 2014, ICTAS New Horizons Seminar - Using Sunlight to Turn Water and Carbon Dioxide in Fuel.

N. S. Lewis.Mar. 17, 2014, 247th American Chemical Society National Meeting - Powering the Planet: The Future Energy in the World.

N. S. Lewis. Mar. 2, 2014, APS/GERA Energy Research Workshop, Energy for Transportation - Sunlight-Driven Hydrogen Formation by Membrane-Supported Photoelectrochemical Water Splitting.

N. S. Lewis. Feb. 25, 2014, Aspen Energy Workshop - Artificial Photosynthesis to Hydrogen Fuel: Technical Progress and Energy System Implications.

Talks from Postdocs and students:

Reineke, M.H., Kubiak, C.P. "$^{Me}C^{prop}C^{Me}Ni^{2+}$ as a Synthon for Novel Ni^{2+} Complexes: Structural Diversity and Small Molecule Activation." Poster, Organometallic Chemistry Gordon Research Conference, Newport, RI. July 12-17, 2015.

Sampson, M.D., Kubiak, C.P. "Carbon dioxide reduction by manganese complexes with bulky bipyridine ligands: Eliminating dimerization and altering catalysis." Poster, Organometallic Chemistry Gordon Research Conference, Newport, RI. July 12-17, 2015.

Karen Chan. "Theoretical Investigations of CO2 Reduction." Manufacturing Green Fuels, Roskilde, Denmark, April 2015 *(Invited)*

Karen Chan, Chuan Shi, Joseph Montoya, Robert Sandberg, Xinyan Liu, Xin Hong, Charlie Tsai, Jens Nørskov. "Theoretical Investigations of CO2 Reduction: The Thermochemical Perspective and Beyond." CIFAR 2015, San Francisco, USA

Leanne D. Chen, Alan C. Luntz, Karen Chan, Jens K. Nørskov. "Electrochemistry with DFT: Metal-Air Batteries and Constant-Potential Energies." CIFAR 2015, San Francisco, USA

M. Lessio "Pyridine-catalyzed CO2 reduction on p-GaP electrodes: new insights on the role of pyridinium from theoretical investigations," poster at the 4th Annual Meeting of the Princeton E-ffiliates Partnership, Princeton, NJ, Nov. 20, 2015.

M. Lessio "Pyridine-catalyzed CO2 reduction on p-GaP photoelectrodes: First-principles investigation of possible reaction mechanisms," talk at the 249th ACS Spring National Meeting, Denver, CO, Mar. 26, 2015.

M. Lessio "Py-catalyzed CO2 Reduction on GaP Electrodes: Can Surface Hydrogen Atoms Play a Role?," poster at the Third Biennial CO2 Workshop, Princeton, NJ, Mar. 16, 2015

M. Lessio "Py-catalyzed CO_2 Reduction on GaP Electrodes: Can Surface Hydrogen Atoms Play a Role?," poster at the AFOSR MURI Annual Review Meeting, San Diego, CA, Jan. 20, 2015.

M. Lessio "Pyridine-catalyzed CO_2 Reduction on p-GaP Electrodes: New Mechanistic Insights from Theoretical Investigations," talk at the Tokyo Tech ACEEES Forum: 3rd International Education Forum on Environment and Energy Science, Perth, Australia, Dec. 16, 2014.

C. Riplinger "Understanding the Differences between Rhenium- and Manganese-Catalyzed Electrochemical Reduction of CO_2," poster at the 3rd Annual Meeting of the Princeton E-ffiliates Partnership, Princeton, NJ, Nov. 14, 2014.

M. Lessio "New insights into the mechanism of Py-catalyzed CO_2 reduction on GaP electrodes," poster at the 3rdAnnual Meeting of the Princeton E-ffiliates Partnership, Princeton, NJ, Nov. 14, 2014.

K. Chan, C. Tsai, H.A. Hansen, J. K. Nørskov, Molybdenum Sulfides and Selendies as Possible Electrocatalysts for CO_2 Reduction, ECAT Symposium, Whistler, BC, Oct. 2014.

An unusual CO dissociation on Cu(211) at ambient pressures. ECOSS, Turkey, September 2014.

M. Lessio “New insights into the mechanism of Py-catalyzed CO_2 reduction on GaP electrodes,” poster at the American Conference on Theoretical Chemistry (ACTC) 2014, Telluride, CO, July 22, 2014.

C. Riplinger “Understanding the Differences between Rhenium- and Manganese-Catalyzed Electrochemical Reduction of CO_2,” poster at the Gordon Research Conference on Atomic Molecular Interactions, Easton, MA, July 16 & July 17, 2014.

J. A. Keith “First-principles descriptors for molecular heterocycles that promote CO_2 reduction,” invited talk at the 247th ACS Spring National Meeting, Dallas, TX, Mar. 16, 2014.

J. Montoya, C. Shi, K. Chan, J. K. Nørskov, The Koper Effect: CO dimerization in CO_2 electroreduction on Cu, ECAT Symposium, Whistler, BC, 2014.

J. Montoya, A. Peterson, J. K. Nørskov, Computational insights into C-C coupling on copper surface in CO_2 electroreduction, 247th ACS National Conference, Dallas, TX, 2014.

M. Doud, C. Kubiak. Electrocatalysis with phosphine-functionalized P2N2 complexes in proton-coupled electron transfer processes. ACS San Francisco, San Francisco, CA. 2014.

M.D. Sampson, A. Nguyen, K. Grice, C. Moore, A. Rheingold, C. Kubiak. Carbon dioxide reduction by manganese bipyridyl complexes: Synthetic modification and mechanistic insights. ACS San Francisco, San Francisco, CA. 2014.

White, J.L., Bocarsly, A.B., *Electroreduction of carbon dioxide on indium-based nanoparticles*. Abstracts of Papers of the American Chemical Society, 2014. 248.

M. Lessio “Towards understanding pyridine-catalyzed photocatalytic reduction of CO_2 on GaP electrodes,” poster at the AFOSR MURI Annual Review Meeting, La Jolla, CA, Dec. 9, 2013

C. Riplinger "Understanding the Differences between Rhenium- and Manganese-Catalyzed Electrochemical Reduction of CO_2,” poster at the AFOSR MURI Annual Review Meeting, La Jolla, CA, Dec. 9, 2013

C. Riplinger “Towards Understanding the Differences Between Rhenium- and Manganese-Catalyzed Electrochemical Reduction of CO_2,” poster at the 2nd Annual Meeting of the Princeton E-ffiliates Partnership, Princeton, NJ, Nov. 15, 2013

M. Lessio “Pyridine-Catalyzed Photocatalytic Reduction of CO_2 on GaP Electrodes,” poster at the 2nd Annual Meeting of the Princeton E-ffiliates Partnership, Princeton, NJ, Nov. 15, 2013

Chuan Shi, Heine A. Hansen and Jens K. Nørskov. “Activity Descriptors for CO_2 Reduction On Transition Metal Surfaces.” 2013 AIChE Annual Meeting, San Francisco, California, USA, November 2013.

J. A. Keith, "Modeling Photoelectrochemical Water Oxidation and CO_2 Reduction With DFT+U, DFT+D, and Heterogeneous Solvation,” talk at the *2013 AIChE Annual Meeting*, San Francisco, CA, November 5, 2013.

J. A. Keith, “Quantum mechanical insights into photoelectrochemical CO_2 reduction processes,” talk at the *246th ACS National Meeting Physical Chemistry of Solar Energy Conversion*, Indianapolis, IN, September 9, 2013.

J. A. Keith, “Quantum Mechanical Insights into Photoelectrochemical Reduction of CO_2 with Pyridinium Catalysts,” talk at the *12th International Conference on Carbon Dioxide Utilization (ICCDU)*, Alexandria, VA, June 25, 2013.

H. A. Hansen “DFT Studies of CO_2 Electroreduction on Pure Elements and Alloys.” 23rd North American Catalysis Society Meeting, Louisville, Kentucky, USA, June 2013.

Chuan Shi, Heine A. Hansen, Christopher P. O'Grady, Andrew A. Peterson and Jens K. Nørskov. “Kinetics of Electrochemical CO_2 Reduction on Pt(111). ” 23rd North American Catalysis Society Meeting, Louisville, Kentucky, USA, June 2013.

J. H. Montoya, A. A. Peterson, J. K. Nørskov. "Mechanisms of carbon-carbon coupling in CO_2 electroreduction on Cu(211)," 23rd North American Catalysis Society Meeting, Louisville, Kentucky, USA, June 2013.

Baruch, M., Detweiler, Z., Gu, J., Hu, Y., Liao, K., Pander, J. Shaw T., Watkins, J., White, J., Yan, Y. and Zeitler, E., *Electrocatalytic Reduction of CO_2 to Oxygenated Organics*, ICCDU-XII, 2013. invited talk

Baruch, M., Detweiler, Z., Gu, J., Hu, Y., Liao, K., Pander, J. Shaw T., Watkins, J., White, J., Yan, Y. and Zeitler, E., *Electrocatalytic Reduction of CO_2 to Oxygenated Organics*, ICCDU-XII, 2013. invited talk

Gu, J., Wuttig, A., Krizan, J., Cava, R.J., Bocarsly, A.B. *Development of p-type $CuFeO_2$ photoelectrodes: Potential semiconductor electrodes for CO_2 reduction.* Abstracts of Papers of the American Chemical Society, 2013. 245.

Yan, Y., Bocarsly, A.B. *Electrochemistry of aqueous pyridiniums: A key component in the electrocatalytic reduction of carbon dioxide to methanol.* Abstracts of Papers of the American Chemical Society, 2013. 245.

Dominey, R.N., Goldman, E.W., Abdul-Satar, R., Faust, K., Griswold, J., Guglielmo, D., Elia, C., Wilson, S., Newman, M., Bocarsly, A.B., Zeitler, E. *Poly-substituted pyridines: Probing structural/electronic influences on catalytic activity of the “Bocarsly” pyridinium-based catalyst system for reduction of CO_2 to methanol.* Abstracts of Papers of the American Chemical Society, 2013. 245.

J. A. Keith, “Quantum Mechanical Insights into Photoelectrochemical Reduction of CO_2 with Pyridinium Catalysts,” poster at the *2012 MURI Review Meeting*, San Diego, CA, December 7, 2012.

N. Alidoust, L. Isseroff, and J. A. Keith, “New Solar Energy Conversion Materials,” talk at *Celebrate Princeton Invention 2012*, Princeton, NJ, November 29, 2012.

J. A. Keith, “Quantum Mechanical Insights into Photoelectrochemical Reduction of CO_2 with Pyridinium Catalysts,” poster at the *Second Biennial CO_2 Workshop*, Princeton, NJ, November 9, 2012.

J. A. Keith, “Quantum Mechanical Insights into Photoelectrochemical Reduction of CO_2 with Pyridinium Catalysts,” talk at the CECAM Workshop on Future Challenges in CO_2-Reduction, Bremen, Germany, October 12, 2012.

Z. M. Detweiler, S. L. Bernasek, A. B. Bocarsly, “Mechanistic study of heterogeneous carbon dioxide reduction at metal electrodes.” 244 ACS national meeting, Philadelphia, PA, August 2012.

E. L. Zeitler, A. B. Bocarsly ”Aromatic nitrogen heterocycle catalysts for CO_2 reduction: Key mechanistic studies of the multielectron pathway”. 244 ACS national meeting, Philadelphia, PA, August 2012.

J. Gu, T. W. Shaw, A. J. Morris, A. B. Bocarsly, “Photochemical reduction of carbon dioxide to formate using 4,4’-bipyridnium and pyridinium derivatives as electron transfer mediators.” 244 ACS national meeting, Philadelphia, PA, August 2012.

A. A. Peterson, “Trends in the transition metals for electrochemical CO_2 reduction,” International Society of Electrochemistry Spring Meeting 2012, Washington DC, USA, May 2012.

A. A. Peterson, H. A. Hansen and J. K. Nørskov “Alloy electrocatalysts for CO_2 reduction,” CASE review meeting, Technical University of Denmark, Lyngby, Denmark, May 2012.

J. A. Keith “First-principles Prediction of Substituted Pyridinium Ion and Pyridinyl Radical pKas: Implications for Photoelectrocatalytic Reduction of CO_2,” talk at the ACS Spring 2012 National Meeting & Exposition, San Diego, CA, March 29, 2012

A. B. Muñoz-García “First-principles Study of Pyridine and Water Interactions with p-GaP (110) Surfaces: Implications for Photocatalytic Reduction of Carbon Dioxide,” talk at the ACS Spring 2012 National Meeting & Exposition, San Diego, CA, March 29, 2012.

C. Shi, C. P. O'Grady. A. A. Peterson, H. A. Hansen and J. K. Nørskov "CO_2 Reduction on Pt(111) - Modeling the Electrified Metal-Water Interface" SUNCAT Scientific Advisory Committee meeting, Stanford University, Stanford, California, USA, January 2012.

H. A. Hansen, L. C. Grabow, D. Lee, J. Montoya, C. P. O’Grady, A. A. Peterson, C. Shi, J. V. Varley and J. K. Nørskov “Electroreduction of CO_2”, SUNCAT Scientific Advisory Committee meeting, Stanford University, Stanford, California, USA, January 2012.

A. B. Muñoz-García “Interaction of H_2O and Pyridine on Pure and Zn-Doped GaP(110) Surfaces: New Insights From First-Principles Calculations,” poster at the First Annual DOD-MURI Meeting on CO_2 Conversion to Energy Dense Liquids, San Diego, CA, December 8, 2011.

J. A. Keith “First-Principles Determination of Electrochemical Stabilities of Pyridinium Ions and Pyridinyl Radicals for Photoelectrocatalytic CO_2 Reduction,” poster at the First Annual DOD-MURI Meeting on CO_2 Conversion to Energy Dense Liquids, San Diego, CA, December 8, 2011.

A. A. Peterson “Mechanisms and trends in electrochemical CO_2 reduction on transition metal catalysts,” invited seminar at the Fritz Haber Institute of the Max Planck Society, Berlin, Germany, November 10, 2011.
A. A. Peterson “Design criteria for effective electrocatalysts in the electrochemical reduction of CO_2,” invited seminar at the Risø DTU National Laboratory, Roskilde, Denmark, on November 7, 2011, and at the *Technical University of Denmark*, Lyngby, on November 8, 2011.

R. N. Dominey, E. W. Goldman, K. Humphrey, M. Newman, A.B. Bocarsly, A.J. Morris, and E. Zeitler, “Rational design to increase the activity of the "Bocarsly catalyst" for reduction of carbon dioxide to reduced forms of carbon.” 241 ACS national meeting, Anaheim, CA, March 2011.

A. J. Morris, A.B. Bocarsly, “Carbon dioxide reduction at pyrite photoelectrodes for solar fuel production.” 241 ACS national meeting, Anaheim, CA, March 2011.

S. Wilson, S., R.N. Dominey, E.W. Goldman, B. Allen, K. Jobes, A.B. Bocarsly, A.J. Morris, and E. Zeitler, “Naphthyridine series: Probing steric effects with the "Bocarsly" pyridinium-based catalyst system for reduction of CO_2 directly to methanol.” 241 ACS national meeting, Anaheim, CA, March 2011.

E. L. Zeitler, A.J. Morris, P.S. Lakkaraju, E.B. Cole, and A.B. Bocarsly, “Aromatic amine electrocatalysts for the coupling of CO_2 to form multicarbon alcohols: Electrode surface and substituent effects.” 241 ACS national meeting, Anaheim, CA, March 2011.

INDIVIDUAL AWARDS:

C.P. Kubiak, Oscar Rice Lecture, University of North Carolina, November 10, 2016.

C. P. Kubiak, Sheldon Shore Lecture, Ohio State University, April 15, 2016.

C. P. Kubiak, Reilly Lectures, University of Notre Dame, February 8-12, 2016.

C. P. Kubiak, Basolo Medal for Outstanding Research in Inorganic Chemistry, 2015.

C. P. Kubiak, Invited Visiting Professor, Université Paris Diderot (Paris 7), 2014.

C. P. Kubiak, Elected, American Academy of Arts & Sciences, 2014.

C. P. Kubiak, Woodward Lecturer, Harvard University, 2014.

C. P. Kubiak, Inter-American Photochemical Society Award in Photochemistry, 2013.

C. P. Kubiak, Frontiers Lecture in Catalysis Science and Engineering, Pacific Northwest National Laboratory, 2013.

C. P. Kubiak, Hans B. Jonassen Endowed Lecture, Tulane University, 2013.

C. P. Kubiak, William H. Nichols Distinguished Symposium, New York, 2013.

C. P. Kubiak, Linus Pauling Medal Symposium, Portland, Oregon, 2013.

C. P. Kubiak, Scialog: Solar Energy Conversion, 4th Annual Conference, Plenary Lecturer, Tuscon, Arizona, 2013.

C. P. Kubiak, Oesper Award Symposium, Cincinnati, Ohio, 2013.

C. P. Kubiak, Julia S. and Edward C. Lee Memorial Lecture, University of Chicago, 2013.

C. P. Kubiak, 2012 ACS Award in Inorganic Chemistry, ACS Spring Meeting, San Diego, CA, 2012.

C. P. Kubiak, Fellow of the American Chemical Society, 2012.

C. P. Kubiak, Aldrich Chemical Inorganic Award Lecture, Northwestern University, 2012.

E. A. Carter, 2015-16 Joseph O. Hirschfelder Prize in Theoretical Chemistry, Theoretical Chemistry Institute at the University of Wisconsin, Madison, 2015.

E. A. Carter, Fellow, National Academy of Inventors, 2014.

E. A. Carter, Malcolm Dole Distinguished Summer Lecturer in Physical Chemistry, Northwestern University, 2014.

E. A. Carter, 2014 Ira Remsen Award, Maryland Section of the American Chemical Society, Johns Hopkins University, 2014.

E. A. Carter, 2014 Linnett Visiting Professor of Chemistry, University of Cambridge, 2014.

E. A. Carter, 2013 Hoyt C. Hottel Lecturer in Chemical Engineering, Massachusetts Institute of Technology, 2013.

E. A. Carter, Kenneth S. Pitzer Lecturer, Department of Chemistry, University of California, Berkeley, 2013.

E. A. Carter Mathematics of Planet Earth 2013 Simons Public Lecturer, Institute for Pure and Applied Mathematics, UCLA, 2013.

E. A. Carter, Lord Lecturer, Department of Chemistry, Allegheny College, 2013.

E. A. Carter, Sigillo D'Oro (Golden Sigillum) Medal Recipient, Italian Chemical Society, Scuola Normale Superiore, Pisa, Italy, 2013.

E. A. Carter, Article selected for *The Journal of Chemical Physics* 80th Anniversary Collection (Chen Huang and Emily A. Carter, "Potential-functional embedding theory for molecules and materials," *J. Chem. Phys.*, **135**, 194104 (2011).), 2013.

E. A. Carter, Francis Clifford Phillips Lectureship, Xi Chapter of the Phi Lambda Upsilon National Honorary Chemical Society and the Department of Chemistry, University of Pittsburgh, 2013.

E. A. Carter, Tedori-Callinan Lectureship, Department of Mechanical Engineering and Applied Mechanics, University of Pennsylvania, 2013.

E. A. Carter, W. Allan Powell Lectureship, Virginia Section of the American Chemical Society and the University of Richmond, 2013.

E. A. Carter, Molecular Foundry Distinguished Lecturer, Lawrence Berkeley National Laboratory, 2012.

E. A. Carter, Doctor Honoris Causa, Ecole Polytechnique Fédérale de Lausanne, 2012.

E. A. Carter, Fellow of the American Chemical Society, 2012.

E. A. Carter, Honorary Mathematical and Physical Sciences Distinguished Lecturer, National Science Foundation, 2012.

E. A. Carter, Dean's Distinguished Lecture, College of Science and Technology, Temple University, 2012.

E. A. Carter, MIT Distinguished Speaker in Computational Science and Engineering, Massachusetts Institute of Technology, 2011.

E. A. Carter, August Wilhelm von Hofmann Lecture Award, German Chemical Society, 2011.

E. A. Carter, Jerome B. Cohen Lecturer in Materials Science and Engineering, Northwestern University, 2011.

E. A. Carter, Ernest Davidson Lecturer in Theoretical Chemistry, University of North Texas, 2011.

E. A. Carter, Gerhard R. Andlinger Professor in Energy and the Environment, Princeton University, 2011.

J. K. Nørskov, the Carlsberg Foundation Research Prize, Royal Danish Academy of Science and Letters, 2015

J. K. Nørskov, Honorary Professor of the Dalian Institute of Chemical Physics, Chinese Academy of Sciences, 2015

J. K. Nørskov, the Rigmor and Carl Holst-Knudsen Award, Aarhus University, 2015

J. K. Nørskov, Irving Langmuir Prize in Chemical Physics, American Physical Society, 2015

J. K. Nørskov, The Hageman Medal, Technical University of Denmark, 2013.

J. K. Nørskov, Michel Boudart Award for the Advancement of Catalysis, North American Catalysis Society and the European Federation of Catalysis Societies, 2013.

J. K. Nørskov, Dr. Honoris Causa, Norwegian University of Science and Technology, Trondheim, Norway, May 2012.

J. K. Nørskov, Giuseppe Parravano Memorial Award for Excellence in Catalysis Research, Michigan Catalysis Society, 2011.

J. K. Nørskov, Donald L. Katz Lectureship in Chemical Engineering, University of Michigan, 2011.

C. Shi, 2013 Kokes Award for the 23rd North American Catalysis Society (NACS) meeting.

J. Montoya, 2013 Kokes Award for the 23rd North American Catalysis Society (NACS) meeting.

M. Lessio, Third Year Seminar Hubbell ’47 Prize, Princeton University, Princeton, NJ, May 29, 2015.

M. Lessio, Best presentation award, Tokyo Tech ACEEES Forum: 3rd International Education Forum on Environment and Energy Science, Perth, Australia, Dec. 16, 2014.

M. Lessio, Journal of Physical Chemistry award for outstanding poster presentation, American Conference on Theoretical Chemistry (ACTC) 2014, Telluride, CO, July 24, 2014.

A. Nilsson, Honorable Doctorate at the Danish Technical University (DTU), May 2015.

STUDENT and POST DOCs SUPPORTED:
5 Undergraduate students have been supported by the MURI grant.
28 Graduate students have been supported by this MURI grant.
20 Post Docs have been supported by this MURI grant.
4 Staff scientists have been supported by this MURI grant.

Undergraduates
Sterling Chen
Robert T. McGibbon
Justin Rock
James Shee
Anna Wuttig

Graduate Students Funded:
Baruch, M.
Travis Blane
Chen Chen
Leanne D. Chen

Melissa Clark
Zach M. Detweiler
Victoria Dix
Michael Doud
Jesse D. Froehlich
Jacob Good
Hu, Y.
Kate Keets (presently research scientist at Liquid Light Inc.)
Martina Lessio
Kuo Liao
Alyssia Lilio
Felix Mbuga
Joseph Montoya (NSF Fellowship)
Mark Reineke
Matt Sampson
Robert Sandberg
Alissa Sasayama
Candace Seu
Travis Shaw
Chuan Shi
Victoria Tan
White, J.
Elizabeth L. Zeilter
Jessica Frick

Degrees Granted:
Chen Chen (PhD)
Melissa Clark (MS)
Zach Detweiler (MA)
Michael Doud (PhD)
Jesse Froehlich (PhD)
Kate Keets (PhD)
Kuo Lian (MA)
Felix Mbuga (PhD)
Robert T. McGibbon (BS)
Mark Reineke (MS)
Matt Sampson (MS, PhD)
Alissa Sasayama (MS, PhD)
Elizabeth Zeitler (MA, PhD)

Post-Docs Funded (Current Position):
Karen Chan
Sangwan Cho
Rob Coridan (University of Arkansas)
Kyle Grice (Assistant Professor, DePaul University)
Jing Gu (Current position is at NREL)
Heine A. Hansen
Jimmy John
Mohammadreza Karamad
John A. Keith (Assistant Professor, University of Pittsburgh)
Kendra Kuhl
Prasad Lakkaraju (Professor at Georgian Court College)
Amanda J. Morris (Assistant Professor at Virginia Tech.)
Ana Belen Muñoz-García (Assistant Professor, University of Naples Federico II)

May Ling Ng
Andrew A. Peterson (Assistant Professor, Brown University)
Christoph Riplinger (Postdoctoral Fellow, Max Planck Institute for Chemical Energy Conversion)
F. Sloan Roberts
Thomas P. Senftle
Watkins, J (Current position is at NETL)
Yong Yan

Staff Scientists
Esta Abelev
Daniel Friebel
Chris O'Grady
Makoto Urushihara

ISSUES OF CONCERN:

None

AFOSR Deliverables Submission Survey

Response ID:7369 Data

1.

Report Type

Final Report

Primary Contact Email

Contact email if there is a problem with the report.

ckubiak@ucsd.edu

Primary Contact Phone Number

Contact phone number if there is a problem with the report

8588222665

Organization / Institution name

University of California, San Diego

Grant/Contract Title

The full title of the funded effort.

NOVEL CATALYTIC MECHANISMS FOR THE CHEMICAL REDUCTION OF CARBON DIOXIDE TO ENERGY-DENSE LIQUIDS

Grant/Contract Number

AFOSR assigned control number. It must begin with "FA9550" or "F49620" or "FA2386".

FA9550-10-1-0572

Principal Investigator Name

The full name of the principal investigator on the grant or contract.

Clifford P. Kubiak

Program Officer

The AFOSR Program Officer currently assigned to the award

Michael Berman

Reporting Period Start Date

09/15/2010

Reporting Period End Date

09/14/2016

Abstract

This report covers the No Cost Extension period as well as the 5 year MURI performance period. Publications, presentations, and other sections of the report have been updated from the 5 year report.

Distribution Statement

This is block 12 on the SF298 form.

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Explanation for Distribution Statement

If this is not approved for public release, please provide a short explanation. E.g., contains proprietary information.

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Archival Publications (published) during reporting period:

See report.

New discoveries, inventions, or patent disclosures:
Do you have any discoveries, inventions, or patent disclosures to report for this period?

No

Please describe and include any notable dates

Do you plan to pursue a claim for personal or organizational intellectual property?

Changes in research objectives (if any):

Change in AFOSR Program Officer, if any:

Extensions granted or milestones slipped, if any:

AFOSR LRIR Number

LRIR Title

Reporting Period

Laboratory Task Manager

Program Officer

Research Objectives

Technical Summary

Funding Summary by Cost Category (by FY, $K)

	Starting FY	FY+1	FY+2
Salary			
Equipment/Facilities			
Supplies			
Total			

Report Document

Report Document - Text Analysis

Report Document - Text Analysis

Appendix Documents

2. Thank You

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