NOVEL CATALYTIC MECHANISMS FOR THE CHEMICAL REDUCTION OF CARBON DIOXID

Clifford Kubiak
UNIVERSITY OF CALIFORNIA SAN DIEGO
9500 GILMAN DR DEPT 621, OFFICE OF CONTRACT & GRANT ADMIN. 09
LA JOLLA, CA 92093-0621

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Final Report
The objective of this work is 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, michael.berman@afosr.mil

PROGRAM OBJECTIVE: The objective of this work is to perform a combined theoretical and experimental study of CO\textsubscript{2} reduction at metals, semiconductors, and homogeneous electrocatalysts, and to understand at a detailed molecular level the catalytic processes involved in reducing CO\textsubscript{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\textsubscript{2}. A fundamental understanding of the underlying mechanisms and characteristics of CO\textsubscript{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\textsubscript{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\textsubscript{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\textsubscript{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 spectroelectrochemistry (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\textsubscript{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 \( \text{CO}_2 \) 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 Owratisky (AFOSR)

8 December 2011 - First MURI Annual Review Meeting, La Jolla, CA, with Michael Berman (AFOSR), Jeffrey Owratisky (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 Owratisky (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 \( \text{CO}_2 \) reduction catalysts in order to elucidate novel mechanisms for \( \text{CO}_2 \) reduction. The Kubiak lab continues
to study the highly active and selective Re(bpy-R)(CO)₃X and Mn(bpy-R)(CO)₃X catalyst families, which perform a proton-coupled reduction of CO₂ to CO and H₂O. 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 CO₂ 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 CO₂ 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 CO₂ 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)₃X catalysts into biomolecules, this ambitious project has successfully drawn upon knowledge gained by the CO₂ 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)₃X. 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)₃X 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)₃X, 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 CO₂ to CO, with turnover frequencies reaching ~5000 s⁻¹ with added TFE (~14 times more active than the previous best Mn(bpy-R)(CO)₃Br catalyst!). Although this bulky Mn catalyst binds CO₂ with a proton at a 300 mV more positive potential than Mn(bpy)(CO3)Br, 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 Mg²⁺ 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 CO₂ by the molecular catalyst [Ni(cyclam)]²⁺ was studied by electrochemistry and infrared spectroelectrochemistry. The electrochemical kinetics were varied by CO₂ substrate and proton concentrations. Products of CO₂ reduction were 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)(CO₂OH)]²⁻. 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 CO₂ reduction. Evidence for the [Ni(TMC)]⁺ acting as a CO scavenger includes the observation of [Ni(TMC)(CO)]²⁻ 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 CO₂ 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$_2$N$_2$ ligands that allow for functionalization of these important and versatile electrocatalysts in vastly new ways. Ni-P$_2$N$_2$ 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 CO₂ 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 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. 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
positions of the GaP(110) surface (see Lessio, M.; Carter, E. A. further characterize the surface under experimental conditions. Furthermore, we computed the band edge These results can help us gain new insights into the mechanism of CO 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 CO₂ 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-Garcia 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 CO₂ 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 \textit{ab initio} thermodynamics to compute the relative free energies of GaP, CdTe, and CuInS₂ 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 CuInS₂ surfaces, lending insight into key adsorption sites and intermediate species that may play a role in the Py-catalyzed reaction mechanism.

The \textit{Carter} group is also contributing to the understanding of homogeneous electrocatalytic CO₂ reduction by a homogeneous Re(bpy = 2,2'-bipyridine)(CO)₃Cl catalyst. in collaboration with the \textit{Kubiak} group. This catalyst selectively reduces CO₂ 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 \textit{Angew. Chem. Int. Ed.}, 2013, 52, 4841). Moreover, its special electronic structure provided the insight into a likely origin of its selectivity for CO₂ 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 pHs, 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 CO₂ is slightly less favorable than
protonation, CO₂ 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 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 CO₂ is weakened during CO₂ binding to the catalyst. The CO₂ 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 CO₂ reduction by the Mn(bpy)(CO)₃Br catalyst. This catalyst is, except for the metal center, chemically identical to the Re(bpy = 2,2'-bipyridine)(CO)₃Cl 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 CO₂ 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 CO₂ or to stabilize CO₂ 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 CO₂ 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 CO₂ versus proton binding strength.

For metal-catalyzed C₂ 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 C₂ 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 CO₂ 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 *OCH₃.

We described the electrocatalytic reduction of CO₂ 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, H₂, 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 C₂ and C₃ species due to the strengthened binding of the CO and CH₂O 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 (H₃O⁺) 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 CO₂ reduction mechanism on oxide surfaces. On RuO₂(110), we found CO-covered surfaces to be stable under the relevant electrochemical environment. We identified the lowest free energy pathways for CO₂ reduction to formic acid, methanol, and methane on partially reduced RuO₂(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 H₂COOH* is the most thermodynamically difficult step. Thus, we show CO-coverage to be a possible parameter in tuning the CO₂ reduction activity on RuO₂.

Lastly, the Nørskov group investigated the effects of liquid additives on the activity and selectivity of electrochemical CO₂ reduction. In the first step toward understanding the mechanism by which an ionic liquid cation, 1-methyl-3-ethylimidazolium (EMIM⁺), enhances CO₂ 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 CO₂ 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 CO₂ 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 CO₂ reduction.

To study the activity of single crystal surfaces for CO₂ 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\(^+\) \rightarrow 2C\(^+\) + CO\(_2\)) 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 H\(_2\)O 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 CO\(_2\) 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 CO\(_2\) electroreduction over Cu catalysts, we have compared the fundamental impact of CO respective CO\(_2\) adsorption on Cu oxides. Oxides were formed by dosing molecular O\(_2\) on a Cu(211) surface at room temperature. Our observation seems to follow this general redox reaction: CuxO + CO \rightarrow Cu(x+1)O + CO\(_2\), i.e. CO reduces Cu while CO\(_2\) 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 CO\(_2\) will result in a mixture of CuO and oxygenated carbon. CO has the tendency to form more carboxylate species while CO\(_2\) 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 \(\pi\)-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., \textit{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\(_2\) evolution.

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 spectr electrochemical approaches to study the intermediates involved.

In a very different set of experiments, motivated by Kubiak and Carter’s work on molecular catalysis we have initiated a project evaluating the mechanism by which [BrMn(CO)\textsubscript{3}bpy\textsuperscript{+}] electrocatalyzes the reduction of CO\textsubscript{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\textsubscript{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\textsubscript{2} ligand. In this system we find an enhanced catalytic rate for CO\textsubscript{2} 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\textsubscript{2}s). This work is motivated by recent experimental work showing that the hydrogen-evolution activity of MX\textsubscript{2}s can be suppressed by ionic liquids [Asadi et al., Nat. Comm., 2014]. The Lewis group has synthesized thin films of WS\textsubscript{2} and MoS\textsubscript{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\textsubscript{2} reduction was tested in contact with an aqueous ionic liquid (EMIM BF\textsubscript{4}). At an applied potential of -1.23 V versus a Ag/AgCl reference electrode (~0.8 V vs RHE), the MoS\textsubscript{2} thin film exhibited a Faradaic efficiency, FE, for hydrogen evolution of <25%. Both the WS\textsubscript{2} and MoS\textsubscript{2} films yielded methane with FE of ~15%. The MoS\textsubscript{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\textsubscript{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\textsubscript{2} [Studt et al., Nat. Chem., 2014]. The Lewis group has synthesized films of NiGa, Ni\textsubscript{5}Ga\textsubscript{3}, and Ni\textsubscript{3}Ga 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\textsubscript{2}-saturated 0.1 M NaHCO\textsubscript{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\textsubscript{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\textsubscript{2} reduction to C\textsubscript{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-\textsubscript{fBu})(CO)\textsubscript{3}Br complexes act as robust, selective, and efficient catalyst precursors for the reduction of CO\textsubscript{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-R)(CO)\textsubscript{4}]\textsuperscript{+} species spontaneously labialize a CO ligand upon exposure to a reducing potential, forming [Re(bpy-R)(CO)\textsubscript{3}(MeCN)]\textsuperscript{+} 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-

- X-Ray Absorption Spectroscopy of Re(bpy) complexes has enabled us to determine that [Re(bpy-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. Friebl, 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)$_3$Cl 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)$_3$Br.


- Used a bulky bpy ligand, 6,6'-dimesityl-2,2'-bipyridine, to inhibit unwanted dimerization after the first reduction for Mn(bpy-R)(CO)$_3$Br 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$_2$N$_2$ 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.


- 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.

Using the cluster approach to model the reconstructed 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 CO2 reduction over H2 generation is determined by the lower reaction barrier for CO2 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 too 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)3Br (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 CO2 efficiently.

Cu/ZnO electrodes reduce CO2 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 CO2 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 CO2 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 CO2 reduction in transition metals that bind CO strongly arises primarily from their high activity for hydrogen evolution, rather than a very high overpotential for CO2 reduction.

The reduction of CO2 and methanediol H2C(OH)2 share no common reaction intermediates. Contrary to suggestions in the literature, the reduction of aqueous CH2O to CH3OH does not rule out that adsorbed CH2O is formed as a short-lived reaction intermediate in CO2 reduction to CH4 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 dichalcogenides have been synthesized and shown to electrocatalytically reduce CO2 to methane at ~15% Faradaic efficiency (FE) when in contact with an ionic liquid. Thin films of MoS2 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$_2$O 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$_2$N$_2$-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)$_3$X 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 CO$_2$ reduction, reduction of CO$_2$ to more complex organic fuels, catalytic Metal Organic Frameworks (MOF), catalysts with carbene ligands, studies of hydricity.

The **Carter** group continued studies of nitrogen heterocycles 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)$_3$Br and the Re(bpy)(CO)$_3$Cl 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 Cu$_2$+ 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. PSIcon 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:

FULL LIST OF MURI PUBLICATIONS:


Sun, K.; Kuang, Y.; Verlage, E. A.; Brunschwig, B. S.; Tu, C. W.; Lewis, N. S., Sputtered NiOx Films for


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**Proceedings**


**Presentations**

C.P. Kubiak, “If you make a solar fuel from CO\textsubscript{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\textsubscript{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\textsubscript{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, “Electrochemical reduction of CO\textsubscript{2}: Hydricities and reduction potentials control switching between CO\textsubscript{2} reduction to formate, CO\textsubscript{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, “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\textsubscript{2} to liquid fuels.” International Union of Pure and Applied Chemistry (IUPAC), 45\textsuperscript{th} World Chemistry Congress, Busan, Korea, August 11, 2015, (Keynote address).


C. P. Kubiak, “Mechanistic studies of the electrocatalytic reduction of CO\textsubscript{2}. Supramolecular approaches to lowering the overpotential.” Gordon Research Conference in Mechanistic Inorganic Chemistry, Galveston, TX, March 4, 2015, (invited lecture).


C. P. Kubiak “Electrochemical and Photoelectrochemical Reduction of CO\textsubscript{2}”. International CECAM Workshop “Future Challenges in CO\textsubscript{2} Reduction”, University of Bremen, Breman, Germany, October 8 – 12, 2012.


C. P. Kubiak “Electrochemical and Photoelectrochemical Reduction of CO\textsubscript{2}”. The 243\textsuperscript{rd} National Meeting of the American Chemical Society, Symposium on Sustainable Inorganic Chemistry, San Diego, CA, March 26, 2012.


C. P. Kubiak “Electrochemical and Photoelectrochemical Reduction of CO₂” University of Uppsala, Uppsala, Sweden, August 26, 2011.


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


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


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


J. K. Nørskov, *Catalysis for sustainable energy*, ESOF 2014 (Euroscience Open Forum), Copenhagen, Denmark, June 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, *Fuels from Sunlight*, IPAM Workshop (Institute for Plan and Applied Mathematics), Los Angeles, California, USA, October 2013.


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


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, “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. 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\textsubscript{2}* (February, 2014).

A. B. Bocarsly. Queens College (CUNY), *A Chemist's Solution to Excessive Atmospheric CO\textsubscript{2}: Catalytic Photoelectrochemical and Electrochemical Generation of Alcohols* (December 2013).


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 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. 08, 2014, 9th Berlin Debate on Science and Policy - From Truth to Power: Translating Science into a Better World.
N. S. Lewis. May 01, 2014, UC Berkeley - 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.


**Talks from Postdocs and students:**


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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\textsubscript{2} reduction on GaP electrodes,” poster at the American Conference on Theoretical Chemistry (ACTC) 2014, Telluride, CO, July 22, 2014.


J. A. Keith “First-principles descriptors for molecular heterocycles that promote CO\textsubscript{2} reduction,” invited talk at the 247th ACS Spring National Meeting, Dallas, TX, Mar. 16, 2014.


J. Montoya, A. Peterson, J. K. Nørskov, Computational insights into C-C coupling on copper surface in CO\textsubscript{2} electroreduction, 247th ACS National Conference, Dallas, TX, 2014.


M. Lessio “Towards understanding pyridine-catalyzed photocatalytic reduction of CO\textsubscript{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\textsubscript{2},” poster at the AFOSR MURI Annual Review Meeting, La Jolla, CA, Dec. 9, 2013


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


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C. Shi, C. P. O’Grady, A. A. Peterson, H. A. Hansen and J. K. Nørskov “CO₂ Reduction on Pt(111) - Modeling the Electrified Metal-Water Interface” SUNCAT Scientific Advisory Committee meeting, Stanford University, Stanford, California, USA, January 2012.


A. A. Peterson “Mechanisms and trends in electrochemical CO₂ 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 CO₂,” 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.


INDIVIDUAL AWARDS:


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


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

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


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


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

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


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


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


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

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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, 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.

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. Zeitler
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
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.

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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)

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Report Document

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Report Document - Text Analysis

Appendix Documents

2. Thank You

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