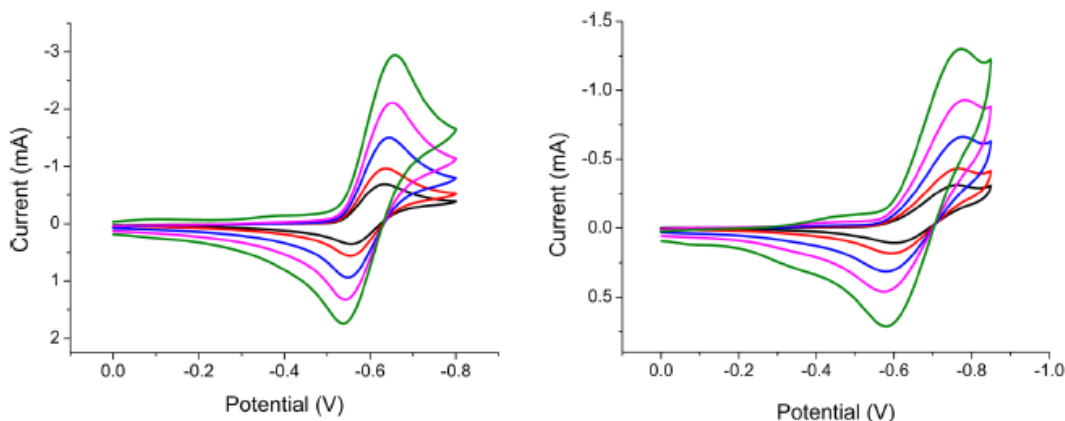


**Final Report to the AFOSR:**  
Photoelectrochemical Conversion of Carbon Dioxide to Alcohols: Formation of Carbon-  
Based Fuels Via Carbon Bond Formation  
May 2010-August 2013  
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In 2008, we reported<sup>1</sup> the photoelectrochemical reduction of CO<sub>2</sub> in an aqueous electrolyte at a p-GaP interface, demonstrating that pyridinium efficiently catalyzed the multielectron reduction of CO<sub>2</sub> to methanol. This result represented the first report that CO<sub>2</sub> could be reduced to methanol in a purely light driven system. In other words, this was the first example that one could store solar energy as a methanol fuel using a semiconductor based system. Further, the reduction by 6-electrons and 6-protons in near quantitative yield was unprecedented. The catalytic activity of pyridinium ran contrary to the standard thinking that CO<sub>2</sub> reduction would best be achieved using a multielectron charge transfer reagent (pyridinium is a one-electron, one-proton reagent). Thus, a major focus of our AFOSR research has been to develop an energetic and mechanistic understanding of this pyridinium catalyzed process as well as to expand this chemistry to other semiconductors, catalysts and electrolytes with the aim of increasing the available product distribution. The work reported here involved the activities of three postdoctoral fellows and two graduate students producing four papers of which three are either published or in press. Several undergraduate researchers also supported the project.

*Research Accomplishments*

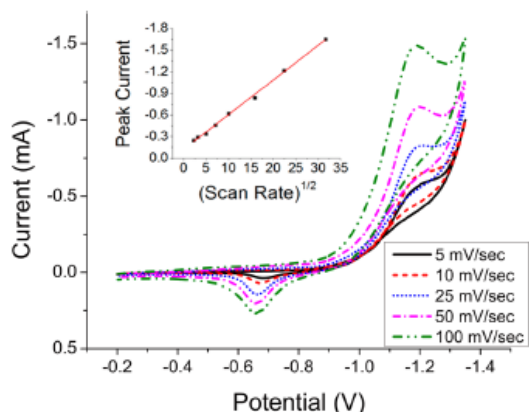
To further explore the detailed mechanistic role of the aromatic amine electrocatalyst, we initially elected to carry out a comparative mechanistic study of pyridinium versus imidazolium catalyzed reduction of CO<sub>2</sub> using both platinum and p-FeS electrodes. In the latter case, the p-FeS behaved as a photocathode when exposed to visible light (0.9 eV or greater energy). We adopted this approach since the platinum electrode allowed us to apply well-established electroanalytical analyses (i.e. Nicholson and Shain cyclic voltammetric analysis) along with digital simulation of the scan rate dependent current-voltage response as illustrated in Figure 1, while the p-FeS system provided a robust photoelectrochemical response as shown in Figure 2.



**Figure 1:** (Left) CVs of 10 mM pyridine in an aqueous solution of 0.5 M KCl at pH 5.3 under an Ar atmosphere at a Pt electrode. (Right) CVs of 10 mM imidazole in an aqueous solution of 0.5 M KCl at pH 5.68 under an Ar atmosphere at a Pt electrode. The scan rates shown are 5 (black), 10 (red), 25 (blue), 50 (magenta), and 100 (green) mV/s. (From Ref. 2)

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| 14. ABSTRACT                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                           |                                    |                                     |                                    |                                          |                                 |
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This study led to an improved understanding of the molecular dynamics associated with the aromatic amine catalyzed reduction of CO<sub>2</sub>. The results were reported in the journal ACS Catalysis.<sup>2</sup> In addition, this work provided the first report indicating that imidazolium was an electrocatalyst for the reduction of CO<sub>2</sub>.



**Figure 2:** Scan rate dependence of the reduction of pyridine at an illuminated pyrite electrode under a CO<sub>2</sub> atmosphere. (Inset) The linear dependence of cathodic peak current with the square root of the scan rate from 5 to 1000 mV/s indicates a diffusion limited electrochemical reaction. (From Ref. 2)

Through this and related work we have suggested that the catalytic reduction of CO<sub>2</sub> to formic acid and methanol proceeds through a mediated charge transfer process as follows:

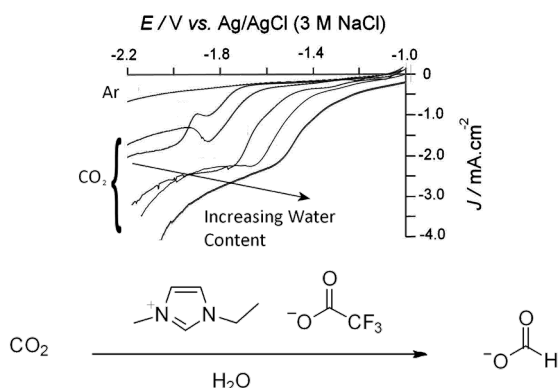
1. Reduction of the aromatic amine via a mechanism that involves formation of a surface hydride species.
2. Reaction of the surface hydride with available amine to form the catalytically active species.
3. Reaction of the active species with CO<sub>2</sub> to form formate.
4. An iterative process in which a second equivalent of activated aromatic amine reacts with formate to produce formaldehyde followed by methanol.

It was also noted that the reaction mechanism is heavily branched and different branches are favored depending on the electrode material employed. This mechanism along with key energetic requirements were discussed in an article published last year.<sup>3</sup>

A corollary to these findings is that not all semiconductor electrodes present viable interfaces for the aromatic amine catalyzed reduction of CO<sub>2</sub>. In general, we find that III-V materials provide interfaces having both the energetics and kinetics to accomplish the reactions of interest, as does p-type iron pyrite. However, other p-type electrodes have yielded little reactivity at reasonable potentials (p-Si and p-CdTe for example). Typically, pyridinium reduction occurs through a specific surface interaction, in contrast to an “outer sphere” type charge transfer from the semiconductor conduction band. The nature of this interaction needs to be understood in order to design higher efficiency interfaces for the amine catalyzed reduction of CO<sub>2</sub>, and the work reported here has taken us several steps closer to understanding the key interfacial details.

Perhaps the most exciting finding made during the current grant period is the observation that the direct reduction of CO<sub>2</sub> to formate can be accomplished using the ionic liquid 1-ethyl-3-methylimidazolium trifluoroacetate (EMIM TFA) as the electrolyte. When a heavy post-transition metal electrode, such as indium is employed in this system an aromatic amine co-catalyst need not be added. However, we found that the activity of the system was highly water

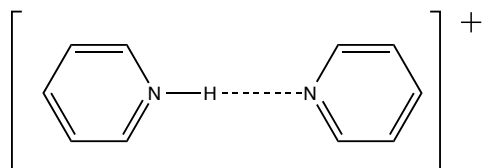
dependent as shown in Figure 3, with a decrease in the required potential and increased current with addition of up to 30% water.



**Figure 3:** Water enhances CO<sub>2</sub> reduction rates when using a mixed EMIM TFA/water matrix to facilitate the conversion of CO<sub>2</sub> into formate on indium electrodes. Addition of greater amounts of water lowers the overpotential for the reduction of CO<sub>2</sub> as well as increases the rate of CO<sub>2</sub> reduction as shown by these linear sweep voltammograms taken at 100mV/s with water attention from 1% to 30%.

This result has just been reported.<sup>4</sup> With a follow up result, showing that this type of system can be used to generate methyl-formate by adding methanol to the electrolyte.<sup>5</sup> The interaction between methanol and water is very non-linear and will be the subject of future studies. The big advantage of the EMIM TFA system is that CO<sub>2</sub> is dramatically more soluble in this electrolyte than in water. Thus, much higher reaction rates can be sustained in this system compared to an aqueous electrochemical cell.

In addition to the purely electrochemical studies reported above we also introduced a hybrid technique into our studies with the development of a raman/electrochemical cell. Preliminary studies led to the conclusion that both raman and resonance raman spectroscopies are not sufficiently sensitive to see the low concentrations of active catalyst anticipated to exist at the electrode-electrolyte interface. Thus, we fabricated a surface enhance raman (SERS) electrochemical interface base on a nanostructured gold electrode and 860nm optical excitation. This system allows us to see adsorbed pyridine and pyridinium at the electrode surface in a CO<sub>2</sub> purged aqueous electrolyte. On going studies are evaluating the charge transfer chemistry of interest using this system. In addition, we have developed a mixed gold/platinum nanostructured interface to study the chemistry of interest at a platinum electrode. One early outcome from these studies is the observation that at electrolyte pH values near the pyridinium pK<sub>a</sub> value, pyridinium species hydrogen bond selectively to pyridine (over water) generating the dimeric species shown below, which must be considered during evaluation of the catalytic cycle.



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