The oxidation of water and the reduction of CO$_2$ to fuels

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Abstract
In this project, we are developing catalysts for CO$_2$ electroreduction and the oxygen evolution reaction (OER). We report our results in these areas, both experimental and computational. Three types of catalysts have been investigated in this study: transition metals, metal sulfides, and metal oxides. Significant advancements have been made both in terms of catalyst development as well as in providing the knowledge needed for expediting the development of future catalysts for these reactions.

Introduction
The objective of this project is to develop catalysts for two key energy conversion reactions: CO$_2$ electroreduction and the oxygen evolution reaction (OER). Developing catalysts for these reactions can enable technologies that can produce carbon-neutral fuels when coupled to renewable energy sources, e.g. wind and solar. Currently, there are no efficient catalysts for CO$_2$ reduction and the best OER catalysts are scarce precious metals. In order to produce better electrocatalysts, both experimental and theoretical approaches were taken. Experimentally, we studied 1) copper and other metal surfaces for CO$_2$ reduction, 2) metal sulfides for CO$_2$ reduction, 3) polymer-modified Pt surfaces for CO$_2$ reduction, and 4) manganese oxides as earth abundant and inexpensive OER catalysts.

Background
There have been several significant advances in CO$_2$ reduction catalysis by our labs as well as by others in recent times. For instance, at Leiden University in the Netherlands, research in the lab of Prof. Marc Koper used an on-line mass spectrometer to understand the mechanism of CO$_2$ reduction on Cu electrodes by comparing the products of the reduction of suspected reaction intermediates. At the University of Illinois, Prof. Paul Kenis and Richard Masel used ionic liquids as catalysts to electrochemically convert CO$_2$ to CO at extremely low overpotential. And at Stanford University, theoretical analysis by the group of Prof. Jens Nørskov explored the effect of different surfaces of Cu on the product distribution and developed activity descriptors for CO$_2$ reduction metal surfaces to guide the development of better catalysts. The group of Prof. Chorkendorff at the Technical University of Denmark worked with the Nørskov lab to experimentally confirm their prediction that a rougher surface would favor multi-carbon products. In this report, we describe our most recent advances which are setting a new standard in the field.
Results

CO₂ Electrolysis Reactor Design

One difficulty in studying CO₂ electroreduction is the need to measure both gas and liquid phase products. There is no 'standard' method in the field for conducting these kinds of studies, thus our first goal was to develop a method that would allow for high sensitivity in identifying and quantifying gaseous and liquid-phase products of reaction. To achieve this goal we ran electrolysis experiments for 1 hr at a range of potentials using a custom cell designed to have a large electrode area and small electrolyte volume to maximize product formation and concentration. CO₂ was constantly flowed through the cell during electrolysis to achieve good mass transport and gas phase products were measured by a gas chromatograph (GC) downstream of the electrolysis cell. Liquid phase products were measured by nuclear magnetic resonance (NMR) after electrolysis. Figure 1 shows a schematic of the cell and examples of the data used to quantify the products that were formed.

![Electrolysis cell used for CO₂ reduction with representative gas chromatograph and NMR data used to quantify products.](image)

**Figure 1.** Electrolysis cell used for CO₂ reduction with representative gas chromatograph and NMR data used to quantify products.

CO₂ Electrolysis on Cu Metal

The activity of Cu metal for CO₂ reduction is well known, so we began by benchmarking results obtained using our experimental setup against literature reports. CO₂ reduction on Cu is known to produce methane, ethylene, formate, CO, ethanol, acetaldehyde, propanol, propionaldehyde, and allyl alcohol along with hydrogen as a side product. In addition to these products, methanol and acetate have been detected in a few studies. With our newly developed methods, not only did we detect and quantify all of the previously detected products of CO₂ reduction on Cu our system ever reported in the literature (from all previous studies combined in one single set of experiments), were we
also able to detect a number of new, previously unreported products: glyoxal, ethylene glycol, glycolaldehyde, acetone, and hydroxyacetone. Importantly, we were also able to track the rates of production for each and every product across a wide potential window. Figure 2 shows the rates of formation of each product as a function of voltage, represented in terms of current efficiency, the fraction of current going towards each product, and in terms of partial current density, which scales linearly with turnover frequency (TOF).

![Figure 2](image-url)  
*Figure 2.* Current efficiency and Tafel plots of partial current going to products over the voltage range measured.

Several important observations can be made about the data in Figure 2. At low overpotential, CO₂ is reduced only to the CO and formate, which are believed to have lower kinetic barriers to formation than the more reduced products. At higher overpotential, where high kinetic barriers can be overcome, more reduced products appear. Ethylene and methane are the two major hydrocarbon products. At lower overpotential slightly more current goes to making ethylene than methane. But at greater overpotential this trend is reversed. The pathway to multi-carbon products must contain a C-C coupling step along with proton and electron transfers necessary to all products. As the overpotential increases, proton and electron transfers become more and more
favorable and eventually outcompete the C-C coupling step leading to the production of less multi-carbon products and more methane and hydrogen.

Another interesting observation is that the partial currents of products with multiple carbons tend to track each other across the voltage range, suggesting that these products share common mechanistic pathways. However, the observed multi-carbon products display a wide range of functional groups; alcohols, carboxylates, ketones, and double bonds are all present. As the first lab to have identified and quantified this more complete view of the reaction products and rates of production, we were able to provide deeper insights into reaction mechanisms that could potentially lead to such diverse products. An important insight was the realization that the products containing a carbonyl group have other possible forms. A carbonyl group can react with water to form a diol or tautomerize to an enol form. By looking at these other forms of the products, we realized that a plausible mechanism could proceed through the dehydroxylation of the enol or diol form of the various products. Figure 3 shows this hypothesized pathway in which the enol or diol form of the products in present as an intermediate on the electrode surface and either desorbs or is dehydroxylated leading to the formation of more reduced products.

Figure 3. Proposed pathway for multi-carbon product formation.

Studying CO₂ reduction on Cu allowed us to validate the new experimental methods we have developed and more importantly, led to several new insights into the reaction products and pathway. Understanding the mechanism of CO₂ reduction has the potential to allow for control of the product distribution of the reaction and engineer catalysts to selectively form the desired product depending on the application.
**CO₂ Reduction with Sulfides**

Taking inspiration from the enzyme carbon monoxide dehydrogenase (CODH), we explored the CO₂ reduction activity of Fe₄S₄ cubanes supported on highly oriented pyrolytic graphite (HOPG). While we were successful in attaching the cubanes to the surface and visualizing them with STM, XPS spectra taken before and after water exposure showed that the Fe₄S₄ complexes were unstable (Figure 4A).

We then moved on to exploring thin films of other sulfides. CO₂ electrolysis experiments were performed with thin films of FeS₂, FeS, MoS₂ and VS₂. Again, the Fe-S materials were unstable (Figure 4B) and hydrogen was the major product detected during CO₂ reduction. MoS₂ is a well known catalyst for hydrogen evolution and
produced mostly hydrogen, as did VS₂. Figure 5 shows that hydrogen was produced at high current efficiency at a range of potentials on the sulfides studied.

![Figure 5. Current efficiency to hydrogen production on metal sulfides.](image)

**Theoretical studies of CO₂ Reduction with Dehydrogenase enzymes**

To supplement and guide the experimental efforts on bioinspired systems, we have explored the relevant reaction mechanisms with first-principles calculations. To this end we have used the CO dehydrogenase enzyme (CODH) as a model system to study the redox reaction $\text{CO} + \text{H}_2\text{O} \leftrightarrow \text{CO}_2 + 2\text{H}^+ + 2\text{e}^-$. The active site of this metalloenzyme consists of a Ni and Fe₄S₄ cluster akin to a cubane system, which we have also investigated. Figure 6 shows a schematic of the studied structures, each of which provides insight into different mechanisms underlying the catalytic activity of the enzyme. These include the preferred adsorption sites on the cluster(s) and the role of the surrounding ligand environment in adsorbate stabilization and selectivity, both of which can ultimately offer routes to engineering superior catalysts.
In Figure 7 we show the relaxed atomic geometries of the adsorbed COOH* and CO* species and their energetics on one type of model the dehydrogenase species from the *Methanosarcina barkeri* bacteria (Mb-CODH).\textsuperscript{13} We have included the first-order ligand environment surrounding the active site to explicitly account for stabilization provided by hydrogen bonding, which we have found has a significant effect in the observed activity. The free energy diagram describing the \( \text{CO}_2 + 2\text{H}^+ + 2\text{e}^- \leftrightarrow \text{CO} + \text{H}_2\text{O} \) reaction is shown in Figure 7c, where we find a modest overpotential of -0.47 eV necessary to drive the reaction electrochemically, in excellent agreement with experiments on other CODH enzymes.\textsuperscript{10} We find that the effect of the different cluster atoms also contribute to the binding energies, as can be see from the COOH* where the C binds to Ni and an O forms a secondary bond to Fe (Figure 7a). Our future plans include exploiting this as a design principle for breaking scaling relations between adsorbates that bind via C or O, as recently detailed in Ref \textsuperscript{5}.

**Figure 6.** A) Model of a CODH dehydrogenase enzyme with the immediate ligand environment as determined by high-resolution X-ray crystallography.\textsuperscript{13} B) Model of a CODH enzyme without the ligand environment. C) Model cubane structures of different Ni-Fe-S stoichiometry. Light green atoms represent Ni, orange represents Fe, and yellow represents S in all clusters shown.
We have previously shown for a variety of transition metal surfaces that the CO* and COOH* binding energies both determine the activity in CO₂ reduction and follow scaling relations.¹⁴ We have combined our current results on CODH and cubane systems with ongoing work in a project studying metal surfaces for the same reaction into a microkinetic model as seen in Figure 8, where we find that both the hydrogen bonding due to ligands and the “alloyed” surfaces of the CODH and cubanes can lead to deviations from the transition metal scaling relations. Such deviations can lead to enhanced activity, as seen by some of the cubane and CODH points that fall closer to the top of the Volcano Plot in Figure 8. The enhanced activity exhibited by the Mb-CODH and the Ni₂Fe₂S₄ cubane cluster are being analyzed to further characterize the relative importance of the geometry (stoichiometry) and stabilization effects of surrounding ligands.

**Figure 7.** A) Most stable configuration of COOH* and B) CO* adsorbed on the model CODH dehydrogenase enzyme. C) Gibbs free energy diagram for CO₂ reduction to CO* and H₂O. The black curve shows no applied potential, while the red curve shows the minimum potential necessary to make the reaction exergonic.
As was recently discovered experimentally\textsuperscript{15,16}, variants of the nitrogenase enzyme were found to synthesize a wide variety of hydrocarbons from CO and CN. In addition to the ammonia synthesis they are known for, this makes nitrogenases extremely promising catalysts for Fischer-Tropsch synthesis under ambient conditions. The ability to catalyze such a diverse set of products from simple and abundant reactants makes the nitrogenase another crucial model system to study for the development of superior bio-inspired catalysts.

Studies of electrochemical reduction of CO\textsubscript{2} on other transition metals

In order to further our understanding of CO\textsubscript{2} reduction we studied a variety of transition metals. The activity Au, Ag, Pt, Zn, Fe, Al, Ti, and Ni plus carbon have been tested so far and the results are comparable to previous literature reports\textsuperscript{17} with the addition of several products that are detectable using our sensitive experimental methods, many of which have previously gone unreported.

Figure 9a shows the current-voltage data for the tested metals. Clear differences can be seen in the current generated in a CO\textsubscript{2} saturated environment. Figure 9b shows the percentage of the current that goes to reduce CO\textsubscript{2} into any product as opposed to...
hydrogen. These figures show that although iron and platinum generate high currents at low overpotential they mostly reduce protons to hydrogen. Although gold, copper and silver have a moderate total current, they are able to reduce CO₂ more effectively than platinum or iron which generates higher currents overall. Table I shows the products of the different metals where red highlights those that are produced on the metal. Currently, we are conducting deeper investigations into iron, platinum, and gold.

![Figure 9: (a) Current-voltage data for 9 transition metals: Cu, Au, Pt, Ag, Zn, Fe, Al, Ti & Ni plus carbon. (b) Faradaic Efficiency for CO₂ versus Potential for all metals tested plus carbon. (c) Zoom-in of (b)](image)

**Table I.** Products of CO₂ reduction on metals tested.

<table>
<thead>
<tr>
<th>Metal</th>
<th>Major Products</th>
<th>Minor Products</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>CO, H₂</td>
<td>CO, H₂, HCOO⁻, CH₃OH, CH₄, C₂H₆, C₆H₆</td>
</tr>
<tr>
<td>Pt</td>
<td>CO, H₂</td>
<td>CO, H₂, HCOO⁻, CH₃OH, CH₄, C₂H₆, C₆H₆</td>
</tr>
<tr>
<td>Au</td>
<td>CO, H₂</td>
<td>CO, H₂, HCOO⁻, CH₃OH, CH₄, C₂H₆, C₆H₆</td>
</tr>
<tr>
<td>Ag</td>
<td>CO, H₂</td>
<td>CO, H₂, HCOO⁻, CH₃OH, CH₄, C₂H₆, C₆H₆</td>
</tr>
<tr>
<td>Zn</td>
<td>CO, H₂</td>
<td>CO, H₂, HCOO⁻, CH₃OH, CH₄, C₂H₆, C₆H₆</td>
</tr>
<tr>
<td>Fe</td>
<td>CO, H₂</td>
<td>CO, H₂, HCOO⁻, CH₃OH, CH₄, C₂H₆, C₆H₆</td>
</tr>
<tr>
<td>Ti</td>
<td>CO, H₂</td>
<td>CO, H₂, HCOO⁻, CH₃OH, CH₄, C₂H₆, C₆H₆</td>
</tr>
<tr>
<td>Al</td>
<td>CO, H₂</td>
<td>CO, H₂, HCOO⁻, CH₃OH, CH₄, C₂H₆, C₆H₆</td>
</tr>
<tr>
<td>C</td>
<td>CO, H₂</td>
<td>CO, H₂, HCOO⁻, CH₃OH, CH₄, C₂H₆, C₆H₆</td>
</tr>
</tbody>
</table>

The sensitivity of our experimental setup allowed us to detect minor products on a number of metals for the first time. Figure 10 shows the mechanism of methane formation on a Cu electrode calculated by DFT.¹ A key intermediate along the pathway is the methoxy intermediate present in step 5. On Cu, it is believed that the majority of this methoxy intermediate is converted to methane with the next proton transfer in step 6, leaving behind an oxygen on the surface which is eventually reduced to water. However, a small amount of methanol is also produced, suggesting that in some cases the reaction proceeds by protonation of the oxygen of the methoxy group. Assuming a similar mechanism on other transition metals, Table I shows that Au, the least oxophilic metal studied, produces methanol but no methane. This can be explained by unfavorability of step 6 in Figure 10, which would leave a single oxygen atom bound to the Au surface. In contrast, Zn, Fe, and Ti, all oxophilic metals, produce methane and no methanol, presumably due to the favorability of the surface oxygen in step 6.

¹
Studies of Electrochemical Reduction of CO₂ on Pt metal and Polyaniline-Pt

While pure metals can produce a variety of CO₂ reduction products, the overpotential required is larger than desired. Selectivity is also a major concern as a wide variety of CO₂ reduction products are made, in addition to (or instead of) the desirable hydrocarbons or liquid fuels that could coexist with our existing infrastructure. In an effort to understand how to impact catalyst activity and selectivity on metal surfaces, we have begun exploring metal alloys as well as chemically modified surfaces. In one particular study, we are investigating the impact of polyaniline (PANi) on Pt.

As an aqueous CO₂ reduction catalyst, Pt is reported to produce primarily H₂ with 0.1% faradaic efficiency for formate at 5mA/cm², though one study does show methanol, formaldehyde, trace amounts of methane as well. Using our recently developed experimental methods with improved sensitivity limits, we detect and quantify efficiencies for H₂, formate, CO, methanol, and trace amounts of methane on Pt metal in 0.1 M KHCO₃ at current densities explored up to 10mA/cm² as seen in Figure 11.

To investigate effects of polyaniline at the Pt-liquid interface, approximately 10nm of polyaniline was electrochemically deposited on Pt metal foils using cyclic voltammetry, and these PANi-Pt films were tested using the same CO₂ reduction procedures. While H₂ was still the dominant species produced, the product distribution of among the minor species was significantly altered. The most noticeable changes are an increase in the production of formate to F.E.’s up to 1.5% vs. 0.3% for pure Pt, and a reduction in methanol production as seen in Figure 11. The CO production also appears to increase at higher overpotentials. CO₂ experiments confirmed that the increased formate was not attributable to degradation of the PANi film. As formate and CO are 2e⁻ products with the same proposed rate-limiting step, and methanol has a different proposed rate-limiting step, it is possible that the amine groups of PANi are stabilizing the intermediate for the 2e⁻ products and destabilizing methanol intermediates. These effects are critical in impacting the CO₂ reduction selectivity, and ongoing efforts are aimed at understanding how and why the polyaniline can produce such differences.

Figure 10: Calculated free energy diagram for electro-catalytic CO₂ reduction to CH₄ on copper. The black path represents the free energy at U = 0 V. The free energy at the limiting potential of U = -0.74 V is shown in red.
A working device for the reduction of CO\(_2\) requires a source of protons and electrons; employing water oxidation, i.e. the oxygen evolution reaction (OER), could serve as the other half-reaction for this purpose. Through this GCEP-funded effort, we aimed to develop MnO\(_x\) catalysts for OER catalysis using two approaches. The first project involved developing a new and efficient method for synthesizing active supported MnO\(_x\) catalysts. This work was based off of work done by Gorlin et al.\(^{20}\) who had managed to synthesize a highly active thin film of MnO\(_x\) via anodic electrodeposition onto a glassy carbon (GC) disk substrate followed by calcination. The ORR and OER activity of this thin film MnO\(_x\) is superior to that of the best MnO\(_x\) catalysts reported in literature and is comparable to that of the best known precious metal catalysts. However, the synthesis process is slow, small-scale, and substrate-selective; hence this procedure is not amenable for commercial use. To overcome the limitations involved yet retain the excellent ORR activity, we designed a new and efficient synthesis procedure which incorporated MnO\(_x\) onto GC particles via a classic impregnation technique. This is followed by a high-temperature calcination process that generated a nanostructured morphology for the catalyst. The MnO\(_x\)-GC particles synthesized displayed comparable ORR and OER activity with the MnO\(_x\) thin films as seen in Figure 12(a) and can be easily loaded onto carbon paper substrate for use in fuel cells and electrolyzers.

The second project involved synthesizing Co-MnO\(_x\) thin films for OER. MnO\(_x\) can be synthesized via cathodic electrodeposition followed by high temperature calcination to produce an active OER catalyst. To further improve the OER activity, we added a Co precursor into the deposition solution to synthesize Mn-Co mixed oxides. SEM revealed that the Mn-Co mixed oxides have a hollow rod-like morphology which is different from that of the pure Mn oxides and Co oxides. Electrochemical testing showed that the Mn-
Co mixed oxides are more active than the pure Mn and Co oxides as seen in Figure 12(b). The most active mixed oxide is that with a Co/Mn ratio of 2.2, which corresponds to MnCo₂O₄ based on XPS and XRD data. MnCo₂O₄ requires 470 mV of overpotential to reach 10 mA/cm², and stability testing showed that it was still active after 1000 cycles.

![Figure 12.](image)

**Figure 12.** (a) Rotating disk voltammograms displaying oxygen electrode activities of MnOₓ-GC particles and MnOₓ thin film. The inset shows an SEM image of MnOₓ-GC particles which display a nanostructured morphology. (b) Cyclic voltammograms showing oxygen evolution activities of Mn₂O₃, Co₃O₄, and Co-MnOₓ thin films. The inset on the left displays the overpotential required to reach 10 mA/cm² for the various catalysts, while the inset on the right shows an SEM image of the Co-MnOₓ catalyst (Co/Mn = 2.2) which has a hollow rod-like morphology.

**Progress**

We have developed methods for testing the activity of catalysts for CO₂ reduction. Using these methods, a detailed study of Cu catalysis was undertaken and several new products detected. Based on the product distribution we can hypothesize about likely reaction pathways and provide insight into reaction mechanisms. On sulfide materials we detected hydrogen as the major product and found that the some materials studied were
unstable at the negative potential required to reduce CO₂. Theoretical efforts have been instrumental in guiding us toward more promising avenues with sulfides. By understanding how biological catalysts can effectively catalyze CO₂ reduction or ammonia synthesis, we believe that we can utilize those principles to design solid-state surfaces with similar functionality.

We have also carefully investigated numerous other transition metals. We have detected a number of new minor products on the transition metals tested so far and can identify trends in the product distribution based on oxophilicity. Beyond pure metals, we modified the activity of platinum to produce more formate by the addition of a conducting polymer to the surface. And towards developing a non-precious metal OER catalyst, we have worked out new synthesis methods for MnOₓ catalysts that are suited to scale-up and explored the addition of Co to improve the water oxidation activity of MnOₓ.

**Future Plans**

Our next steps will focus on furthering our mechanistic understanding of CO₂ reduction on Cu and examining the catalytic activity and selectivity of more pure metals and alloys. Our ultimate goal is to uncover the factors that govern catalytic activity and selectivity for this reaction, aiming to engineer the surface chemistry appropriately. Bimetallic surfaces and polymer/metal interactions are promising means to achieve these goals. In addition to pursuing metallic systems, we will focus on furthering our mechanistic understanding of CO₂ reduction on the nitrogenase and CODH enzymes and their cubane counterparts. There is much to be learned from the biological catalysts. We will further characterize the activity and selectivity in terms of adsorbate binding energies and geometries, looking for favorable deviations from the scaling relations exhibited by transition metal surfaces. We will also continue studies of the ligand environments in the real enzymes for inspiration in designing optimal ligand networks that may promote catalytic activity or selectivity. When coupled with microkinetic modeling, this will give insight into the design of optimal catalysts.

**Publications & Presentations**


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