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Electrochemical Reduction of CO2 Using Metal Nanoparticles

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ELECTROCHEMICAL REDUCTION OF CO$_2$ USING METAL NANOPARTICLES

A Dissertation

Submitted to the Graduate Faculty of the
Louisiana State University and
Agricultural and Mechanical College
in partial fulfillment of the
requirements for the degree of
Doctor of Philosophy

in

The Department of Chemical Engineering

by
Evan Michael Andrews
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LIST OF ABBREVIATIONS

MTG – Methanol to gasoline
RWGS – Reversible water-gas shift
DFT – Density functional theory
NMR – Nuclear magnetic resonance
FTIR – Fourier transform infrared
DRIFTS – Diffuse reflectance infrared Fourier transform
LEED – Low energy electron diffraction
UHV – Ultra high vacuum
XPS – X-ray photoelectron spectroscopy
UPS – Ultraviolet photoelectron spectroscopy
MCT – Mercury-Cadmium Telluride
GC – Gas chromatograph
TCD – Thermal conductivity detector
FID – Flame ignition detector
COMB – Charge optimized many-body
PVDF – Polyvinylidene fluoride
NMP – N-methyl-2-pyrrolidone
HER – Hydrogen evolution reaction
SBR – Styrene-butadiene rubber
TOAB – Tetraoctylammonium bromide
TEM – Transmission electron microscopy
SEM – Scanning electron microscopy
RHE – Reversible hydrogen electrode
ABSTRACT

The electrochemical reduction of CO₂ has been proposed as a method of storing electrical energy from renewable sources in the form of hydrocarbon fuels. By reverting CO₂ into high energy density fuels, a CO₂-neutral fuel cycle becomes possible while still hydrocarbon fueled engines. Cu and Au metals have been found to be particularly effective at catalyzing this reaction, yielding a majority of hydrocarbons and CO respectively. However, the CO₂ electroreduction reaction is still poorly understood and catalysts that possess both high energy efficiency and high yield are not yet developed. Nanoscale catalysts offer the ability to both increase yield and alter the selectivity of the CO₂ reduction reaction.

This dissertation investigates the use of transition metal nanoparticles as electrocatalysts and how they can be used to control the selectivity and yields of the CO₂ reduction reaction. Cu nanoparticles on ZnO, Au nanoparticles, CuAu alloy nanoparticles, Ag nanoparticles on Fe and Ni nanoparticles on Ag were all fabricated and evaluated as CO₂ reduction catalysts. The CuZnO catalysts were shown to improve selectivity to alcohols by an order of magnitude compared to Cu foils. The Au nanoparticles were supported on carbon black using polymer binders, showing that nanoparticles immobilized in a binder containing a sulfonate group has higher CO selectivity and improved onset potentials. CuAu alloys were evaluated at 2 nm and 6 nm nanoparticle sizes and as a bulk foil. The 6 nm nanoparticles were found to yield two orders of magnitude more CO than the foils and the 2 nm nanoparticles were found to yield 3x more CO, indicating strong size effects and the existence of an optimal particle size. NiAg and FeAg catalysts were fabricated via electrodeposition as in investigation into the effects of bimetallic active sites. The Ni and Fe were found to act as catalytic poisons in most situations, but the FeAg was found to produce methane, a product not seen on either pure Fe or Ag.
CHAPTER 1: INTRODUCTION

CO2 Neutral Fuels

The reduction of CO2 to hydrocarbons offers a potentially CO2-neutral method to store renewable energy generated by renewable sources as a fuel. Hydrocarbons formed via CO2 reduction can be burned with no net increase in atmospheric CO2, unlike hydrocarbons derived from fossil fuels. Photocatalysis,9, 11, 12 photosynthesis, gas phase catalysis13 and electrocatalysis14-17 all offer potential ways to reduce CO2. Photosynthesis is occurs naturally in plants, where CO2 is converted to carbohydrates via a light powered reaction cycle. The photosynthesis reaction is very selective, but the efficiency kinetics are slow, necessitating the development of other reduction methods with commercial potential.

Significant efforts have been made to replace fossil fuels with renewable energy sources such as solar, wind, hydro or geothermal. Under decades of focused research, renewable sources have made vast improvements in efficiency, but they are thus far unable to replace fossil fuels in heavy transport or as jet fuel.18 In particular, renewable sources cannot replace diesel gasoline or jet fuel’s utility as an easily stored and transportable liquid fuel. Transportation was estimated to be accountable for 27.7% of the total energy usage of the US in 2015 (Figure 1.1). Petroleum sources, including jet fuels and diesel gasoline for heavy transportation, account for >90% of that energy. Current electrical energy storage uses batteries, which in commercial vehicles only offer energy densities of ~2.6 MJ/L, while jet fuel offers 37.4 MJ/L.19 As proposed by Nobel laureate George Olah,20 an alternative solution to using batteries is the renewable energy driven synthesis of light hydrocarbons, such as CH3OH (15.6 MJ/L),21 which can be further refined to gasoline in
a CH$_3$OH to gasoline (MTG) process.\textsuperscript{22} Other CO$_2$ reduction products include CO, CH$_4$, and CH$_3$CH$_2$OH.\textsuperscript{23}

One desire to replace fossil fuels with renewable energy sources stems in part from the steady increase in atmospheric CO$_2$ concentration over the last 50 years. Atmospheric CO$_2$ reached over 400ppm in 2013, exceeding all previous historical concentrations (Figure 1.2). This increase in CO$_2$ is directly due to the global scale utilization of fossil fuels. In 2009 alone, 30.8 billion tons of CO$_2$ were released into the atmosphere, 8 billion of which is from fossil fuels.\textsuperscript{24} The amount of CO$_2$ released annually is projected to increase to 40.3 billion tons by 2050.\textsuperscript{25} If the current energy usage continues, CO$_2$ levels will only continue to rise.
Overview

This dissertation is focused on the electrochemical reduction of CO$_2$ using nanoparticle catalysts with the aim of further understanding the role of nanoscale effects and their importance in designing a viable catalyst. In this manuscript, Cu nanoparticles on ZnO, Au nanoparticles, CuAu alloy nanoparticles, Ag nanoparticles on Fe and Ni nanoparticles on Ag are all fabricated and evaluated as CO$_2$ reduction catalysts. Chapters 3 and 4 originate from publications.

Chapter 2 introduces the field of CO$_2$ reduction with a literature review covering the gas phase, photocatalytic, and electrochemical catalytic reductions of CO$_2$. The results of
experimental and computational methods are reviewed, particularly those relating to Cu and Au, which feature prominently in this work.

Chapter 3 focuses on the experimental details of CO$_2$ reduction on CuZnO. The results of product quantification and in-situ FTIR are shown. Product analysis shows that CuZnO produces CH$_3$OH and other products at significantly higher Faradaic efficiencies, but at much lower yields. In-situ FTIR reveals the presence of several theorized intermediates. Understanding the mechanisms that determine selectivity and which intermediates are involved in the reaction pathway are important for catalyst design.

Chapter 4 details the experimental evaluation of 25-atom and 5 nm Au nanoparticles and the effects of the surrounding polymer binder ink on onset potentials and product yields. This chapter establishes the importance of near-surface chemistry, and that the surrounding environment should not be discounted in catalyst design.

Experimental results for Cu-based alloys and alloy nanoclusters are discussed in chapter 5. CuCo and CuAu alloy nanoparticles are evaluated in terms of product yield and onset potentials. The effect of molar ratios and size on CuAu catalysts is explored.

Chapter 6 discusses experimental details for NiAg and FeAg catalysts. Metal nanoparticles are electrodeposited on supporting foils and their product yields analyzed.
CHAPTER 2: LITERATURE REVIEW

**CO₂ Reduction Reaction**

As the reduction of CO₂ to CH₄, CH₃OH, etc. is an endothermic reaction, a thermodynamic driving force is required, alongside a catalyst to reduce the required activation energy. There are three prominent areas or research aimed at studying these requirements: gas phase catalysis,¹³ electrocatalysis,¹⁴-¹⁷ and photocatalysis.⁹,¹¹,¹²

**Gas Phase**

The gas phase reduction of CO₂ is very similar to the well-known Fischer-Tropsch process. The Fischer-Tropsch process was developed in 1920 by Franz Fischer and Hans Tropsch as a method of producing hydrocarbon alkanes from CO and H₂ gas feedstocks.²⁶ The mixture of CO, H₂, and a small amount of CO₂ is traditionally known as syngas. The Fischer-Tropsch process produces long, waxy alkanes that are further treated to form transportable fuels. There are multiple metals that will catalyze the Fischer-Tropsch process, such as Co, Fe, Ru and Ni, though Ni favors CH₄ over long alkanes.¹³,²⁷,²⁸ CO₂ reduction begins with the reversible formation of CO and H₂O from CO₂ and H₂, known as the reverse water-gas shift reaction (RWGS). The CO produced by the RWGS is further reduced via a modified Fischer-Tropsch process using the same catalyst. For CO₂ reduction, Cu-Ni/Al₂O₃ catalysts are used for the RWGS and Fischer-Tropsch to synthesize CO and CH₄.²⁹ The catalyst is more selective to CH₄ at higher Ni content, while lower Ni content is selective to CO.¹³ Similarly, CH₃OH focused catalysts use Cu/ZnO and CuZn/Al₂O₃ to reduce CO₂ directly to CH₃OH at a high selectivity.³⁰ Despite the high selectivity afforded by gas phase CO₂ reduction, the high temperatures and pressure required makes it a relatively energy expensive method.³¹,³²
Photocatalysis

Photocatalytic conversions of CO₂, also known as artificial photosynthesis reactions, use semiconductors such as TiO₂, ZnO, GaP and CdS to directly reduce CO₂. Similar to gas synthesis, there are branching reduction pathways, resulting in multiple products such as CO, CHOO⁻, CH₃OH, CH₃CH₂OH, CH₄ and formaldehyde. The reduction is driven by the generation of electron-hole pairs by photon absorption. When an electron in the valence band is excited by a photon, it will move to a higher energy state in the conduction band, leaving a positively charged vacancy (hole) in the valence band. The electron is then donated to the adsorbed intermediate either via the semiconductor or via a co-catalyst on the surface (Figure 2.1). The hole is consumed by a water oxidation reaction, balancing the reduction. Co-catalysts are non-semiconductor metals or metal oxide nanoparticles scattered on the surface. Common co-catalysts include Pt, Pd, Cu, Ni, NiO, etc. The metal co-catalysts are more catalytically active than the semiconductors, but cannot generate electrons via photon excitation. Instead, the semiconductor’s conduction band electrons are donated to the metal if the Fermi level is below
the conduction band. Unfortunately, CO₂ photocatalysts are limited by low reaction yields (<10umol/g/h), low photonic efficiencies (<1%), and/or reliance on expensive, rare metal catalysts.⁹

Electrocatalysis

The electrocatalytic reduction of CO₂ is driven by the potential between two electrodes in a CO₂ saturated electrolyte, and balanced by oxygen evolution from water at the anode. The reduction can be carried out at room temperature and atmospheric pressure using an aqueous electrolyte, making the reaction very feasible to perform. A wide range of catalysts have been studied in CO₂ electroreduction, with the earliest work focusing on the production of formic acid from zinc electrodes,³⁶ or Cu plated with zinc.³⁷ Transition metals and noble metals in particular have received intense study.

Table 2.1: The standard potentials for CO₂ reduction half-reactions at the cathode.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>E₀</th>
</tr>
</thead>
<tbody>
<tr>
<td>2H⁺ + 2e⁻ → H₂</td>
<td>E₀ = -0.41 V vs. NHE</td>
</tr>
<tr>
<td>CO₂ + 8H⁺ + 8e⁻ → CH₄ + 2H₂O</td>
<td>E₀ = 0.24 V vs. NHE</td>
</tr>
<tr>
<td>CO₂ + 6H⁺ + 6e⁻ → CH₃OH + H₂O</td>
<td>E₀ = 0.38 V vs. NHE</td>
</tr>
<tr>
<td>CO₂ + 2H⁺ + 2e⁻ → CO + H₂O</td>
<td>E₀ = -0.53 V vs. NHE</td>
</tr>
<tr>
<td>CO₂ + H⁺ + 2e⁻ → CHOO⁻</td>
<td>E₀ = -0.61 V vs. NHE</td>
</tr>
</tbody>
</table>

The standard potentials for CO₂ reduction at pH 7 are listed in Table 2.1. The standard potentials for CH₃OH and CH₄ formation are very close to that of H₂ evolution, an undesirable side reaction. By using a metal catalyst with a high HER overpotential, such as Pb or Hg, thus shifting the HER away from its thermodynamic standard potential, can suppress H₂ evolution.
The standard potentials are also dependent on the solution pH. A Pourbaix diagram (Figure 2.2) shows the standard potential at pH between 0 and 14.\footnote{1}

The CO\textsubscript{2} reduction reaction is composed of a series of reduction steps at the catalyst surface. After the adsorption of CO\textsubscript{2} and breaking the first C=O bond, there are multiple branching pathways that ultimately lead to a wide variety of hydrocarbon products, such as those seen in Table 2.1. The selectivity between pathways is determined by a combination of formal
potentials, overpotentials, kinetic rates and mass transfer rates. Figure 2.3 shows a theoretical pathway proposed by Nie et al., based on the kinetics of elementary steps.²

The largest thermodynamic barrier is the initial reduction of CO₂ to CO₂•⁻, breaking a C=O bond by adding a single electron. As the ultimate product of combustion, CO₂ is extremely stable, requiring a large amount of energy to break the C=O double bonds. The estimated standard potential for the first electron is -1.9V vs SHE, far more cathodic than the standard potentials of the completed reaction.³⁸ It is important to ensure that the catalyst does not carry a larger cathodic overpotential for this reduction. The initial step is the most thermodynamically intensive, and the kinetics of the following steps determine which product is formed.

Figure 2.3: CO₂ reaction path on Cu(111) proposed by Nie et al. (Reprinted with permission from (Nie et al., 2013).² Copyright 2013 Angewandte Chemie)
Research groups utilizing density functional theory calculations (DFT) have recently shown that proton-transfer kinetic barriers are of significant import to CO₂ reduction. Proton-transfer to CO₂ can occur via surface protons (Langmuir-Hinshelwood), or by proton channeling from solution (Eley-Rideal).

The hydrogenation of CO is a particularly important kinetically limited intermediate step, as it determines whether or not a hydrocarbon product will be formed. Forming a hydrocarbon requires that adsorbed CO must be protonated to *COH or *CHO before the CO desorbs as a final product. This step is strongly influenced by the CO₂ reduction catalyst’s ability to bond CO. A catalyst that binds CO weakly will allow it to desorb before being hydrogenated, while a catalyst that binds CO too strongly can potentially be poisoned. Finding a catalyst that strikes an optimal balance between the thermodynamic requirements and the kinetic requirements has remained a challenge throughout the history of the field.

**CO₂ Electroreduction Literature Review**

The electrochemical reduction of CO₂ has been studied for over a century, with early work by Coehn et al. noting the production of formic acid at Zn, amalgamated Zn and Zn-plated Cu cathodes. This was followed in 1914 by Fischer et al., who used amalgamated Zn-plated Cu alongside high CO₂ pressures to reduce CO₂ to formic acid at high Faradaic efficiencies.

As the CO₂ reduction reaction was seen to compete with H₂ evolution, metals with high HER overpotentials were selected as candidates for further research. In 1954, Teeter et al. used Hg cathodes to reduce CO₂ to formic acid at near 100% efficiency in KCl, NH₄Cl, NaHCO₃ and...
N(CH$_3$)$_4$Br electrolytes.$^{39}$ Paik et al. also used Hg cathodes for CO$_2$ reduction in acidic and neutral electrolytes. Acidic electrolytes were found to produce H$_2$ in addition to formic acid while neutral electrolytes produced 100% formic acid.$^{40}$ Additional electrolytes of NaHCO$_3$, NaH$_2$PO$_4$/Na$_2$HPO$_4$, NaCl, NaClO$_4$, Na$_2$SO$_4$, LiHCO$_3$, and KHCO$_3$ were tested by Hori in 1982, displaying a more anodic CO$_2$ reduction overpotential as the electrolyte cation increases in size.$^{41}$

In 1977, Russel et al. attempted to directly reduce formic acid and formaldehyde to CH$_3$OH using Hg electrodes in neutral electrolytes. The formic acid did not reduce further on Hg, but formaldehyde was reduced to CH$_3$OH at over 90% Faradaic efficiency.$^{42}$

In the 1980s, research into the electroreduction of CO$_2$ intensified greatly. Canfield et al. displayed the reduction of CO$_2$ to CH$_3$OH, formaldehyde, and CH$_4$ in CO$_2$ saturated Na$_2$SO$_4$ electrolyte on semiconductor materials such as n-GaAs, p-GaAs and p-InP, but only at low current densities (<0.4mA/cm$^2$).$^{43}$ In 1985, Frese at al. produced similar results using Ru catalysts, producing CH$_3$OH, CH$_4$ and CO at partial current densities of 0.3 mA/cm$^2$.$^{44}$ Mo catalysts in CO$_2$ saturated 0.05M H$_2$SO$_4$ were used in 1986 by Summers et al. and yielded CH$_3$OH as a main product at >50% Faradaic efficiency as well as trace amounts of CO and CH$_4$.$^{45}$ The most impactful work however, was in 1985 by Hori, who used Au, Ag, Cu, Ni and Fe metal foils alongside Zn, Cd, Sn, Pb and In buttons to reduce CO$_2$ in aqueous bicarbonate electrolyte.$^{46}$ Cd, Sn, Pb and In were found to produce CHOO$^{-}$ as the majority product, while Zn produced a mix of CHOO$^{-}$ and CO. Ni and Fe produced mostly H$_2$ while Au and Ag produced CO at >90% efficiency. However, Cu metal was found to produce CH$_4$ at 40% Faradaic efficiency as well as 15% CHOO$^{-}$ and 3% CO at 5 mA/cm$^2$, making Cu the most interesting metal catalyst as it was able to hydrogenate CO$_2$ beyond CO and at high current densities.
Gas-diffusion electrodes were employed to improve the transportation of CO$_2$, increasing the current density of the CO$_2$ reduction reaction. In 1987, Mahmood et al. employed gas diffusion electrodes impregnated with Pb, In and Sn in CO$_2$ saturated H$_2$SO$_4$/Na$_2$SO$_4$ solution to produce CHOO$. Pb$ impregnated electrodes gave 100% formic acid yields and were able to run at 100 mA/cm$^2$, several times the current density seen on foils.$^{47}$ Furuya et al. also utilized gas-diffusion electrodes for the CO$_2$ reduction reaction, publishing several papers over 1987 to 1997.$^{48-51}$ The gas diffusion electrodes used by Furuya et al. contain metallophthalocyanine catalysts, where a metal atom is surrounded by a nitrogen heavy macrocyclic molecule. The surrounding nitrogen atoms influence the energy levels of the metal, causing changes to product distribution from unmodified metals.

In 1990, Azuma et al. investigated CO$_2$ reduction on 32 metal electrodes in aqueous KHCO$_3$ electrolyte (Figure 2.4).$^{52}$ By comparing the product yields with the metals’ position on the periodic table (Figure 2.6), a systematic rule for describing electrochemical reduction of CO$_2$ was suggested. With the exception of Ti, light transition metals (IVA, VA, VIA VIIA and part of VIII groups) are not effective for CO$_2$ reduction, producing H$_2$ at >95% Faradaic efficiency. Heavy metals in the IIB, IIIB and IVB groups reduce CO$_2$ into CHOO$, while light metals in the IIIB and IVB groups were ineffective. The IB and part of VIII groups were effective at producing CO, and Cu alone was effective at producing hydrocarbons at high Faradaic efficiencies. As a result, Cu based catalysts have been the frontal focus of CO$_2$ reduction research.

The position of a metal in the periodic table is also an indicator of the CO chemisorption ability, as shown by Brodén in 1976.$^{53}$ The metals in groups IVA through VIIA all have high CO bond strength, while groups IIIB and IVB have low CO bond strength. The bond strength of
CO and other intermediates is critical to the product distribution and kinetics of the reaction. As mentioned in a previous section, desorption or hydrogenation of CO is the limiting step for hydrocarbon production.

Recently, Peterson and Nørskov used DFT to predict the bond energies of intermediates on Ni, Cu, Pd, Ag, Pt and Au, finding that all CO$_2$ reduction intermediates follow linear scaling relationships.\(^\text{54}\) As the bond energy of the CO intermediate increases, the energies of COOH, HCOOH, and CH$_4$ decrease linearly, while the energies of CO$_2$, COH and CH$_2$ increase linearly, consistent with well-established linear scaling relationships. These results suggest that DFT can be used to efficiently predict the energetics and selectivity of CO$_2$ reduction over a range of metal electrodes.

**Table II. Typical current efficiencies (%) for CO$_2$ reduction products at −2.2 V vs. SCE (193°C) in a CO$_2$ saturated 0.05M KHCO$_3$ aqueous solution at about 0°C**

<table>
<thead>
<tr>
<th>Metal</th>
<th>( T ) (^{\circ})</th>
<th>CH$_4$</th>
<th>CO</th>
<th>CH$_4$</th>
<th>CH$_2$H$_4$</th>
<th>HCOOH</th>
<th>H$_2$</th>
<th>Sum</th>
</tr>
</thead>
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<tr>
<td>Cd$^+$</td>
<td>0</td>
<td>0.015</td>
<td>3.7</td>
<td>0.002</td>
<td>0.00056</td>
<td>55.9</td>
<td>35.7</td>
<td>95</td>
</tr>
<tr>
<td>Co$^+$</td>
<td>20</td>
<td>0.0073</td>
<td>1.8</td>
<td>0.001</td>
<td>0.00049</td>
<td>35.5</td>
<td>63.2</td>
<td>100</td>
</tr>
<tr>
<td>In$^+$</td>
<td>0</td>
<td>0.001</td>
<td>3.0</td>
<td>0.00035</td>
<td>0.0006</td>
<td>70.0</td>
<td>25.0</td>
<td>98</td>
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<td>Mn$^{2+}$</td>
<td>20</td>
<td>0.0061</td>
<td>14.7</td>
<td>0.0046</td>
<td>0.00087</td>
<td>33.3</td>
<td>56.5</td>
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<td>Sn$^+$</td>
<td>0</td>
<td>0.065</td>
<td>1.4</td>
<td>0.068</td>
<td>0.44</td>
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<td>0.10</td>
<td>0.001</td>
<td>0.0003</td>
<td>9.9</td>
<td>93.3</td>
<td>103</td>
</tr>
<tr>
<td>Zn$^{2+}$</td>
<td>0</td>
<td>0.23</td>
<td>9.8</td>
<td>t</td>
<td>t</td>
<td>19.5</td>
<td>68.1</td>
<td>96</td>
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<tr>
<td>Pd$^+$</td>
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<td>0.083</td>
<td>11.6</td>
<td>0.011</td>
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<td>3.2</td>
<td>0.061</td>
<td>0.078</td>
<td>8.6</td>
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<td>103</td>
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<tr>
<td>Ti$^+$</td>
<td>0</td>
<td>t</td>
<td>13.5</td>
<td>t</td>
<td>t</td>
<td>90.2</td>
<td>9.8</td>
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<td>1.4</td>
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<td>0.0002</td>
<td>0.013</td>
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<td>0</td>
<td>0.74</td>
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<td>0.080</td>
<td>0.18</td>
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<td>Mn$^{2+}$</td>
<td>0</td>
<td>2.5</td>
<td>0.94</td>
<td>t</td>
<td>t</td>
<td>1.6</td>
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<tr>
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<td>t</td>
<td>1.1</td>
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<td>93</td>
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<tr>
<td>Cu$^{2+}$</td>
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<td>0.13</td>
<td>0.47</td>
<td>0.057</td>
<td>0.032</td>
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<td>94</td>
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<td>Co$^{2+}$</td>
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<td>0.42</td>
<td>0.023</td>
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<td>0.10</td>
<td>0.67</td>
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<td>0.015</td>
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<td>100</td>
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<td>0.96</td>
<td>0.00100</td>
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<td>0.0005</td>
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<td>100</td>
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<td>Ir$^{7+}$</td>
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<td>100</td>
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<td>0.085</td>
<td>0.15</td>
<td>0.0057</td>
<td>0.015</td>
<td>0.58</td>
<td>100.3</td>
<td>101</td>
</tr>
</tbody>
</table>

\(^{\text{54}}\) At −2.0V vs. SCE.

Figure 2.4: Faradaic efficiencies for CO$_2$ reduction on metal electrodes in bicarbonate electrolyte. (Reprinted with permission from Azuma et al., 1990. Copyright 1990 The Journal of the Electrochemical Society)
CHO and CH₂O also increase proportionally. Hansen et al. expanded on the concept, using DFT to calculate the activity of the CO₂ to CO reaction as a function of *COOH and *CO adsorption energies. A volcano plot was created and the individual transition metals plotted on it (Figure 2.5). Unfortunately, the trendline created by the transition metals does not pass over the peak of the volcano, though Cu, Au and Ag come closest. However, the DFT by Hansen et al. also
includes calculations for the ChCODH enzyme which contains Ni and Au and departs from the trendline, showing that modified metals can break the linear scaling.

**CO₂ Reduction on Cu**

Cu has proven to be a unique catalyst for the electrochemical reduction of CO₂, capable of producing hydrocarbons at significant current densities, with its high hydrocarbon yields first discovered by Hori in 1985.⁴⁶ Hori et al.‘s results led to a second publication in 1986, which showed a temperature dependence for the selectivity between CH₄ and C₂H₄ in KHCO₃.
electrolyte. At lower temperature (0°C), CH$_4$ is heavily preferred with 65% Faradaic efficiency, but at higher temperature (40°C), CH$_4$ is only produced in trace amounts, while C$_2$H$_4$ and H$_2$ both see >20% increases in selectivity. In 1989, Hori also reduced CO$_2$ on Cu in different electrolyte solutions, reporting that CH$_4$ is favored in concentrated HCO$_3^-$ and KH$_2$PO$_4$\text{/}K$_2$HPO$_4$ solutions, while C$_2$H$_4$ and alcohols are favored in KCl, K$_2$SO$_4$, KClO$_4$ and dilute HCO$_3^-$.56

The penchant of Cu for yielding hydrocarbons inspired many works after Hori’s initial publications. In 1987, Cook et al. simultaneously electroplated Cu onto glassy carbon surfaces as a catalyst in order to constantly renew the Cu surface, negating impurities and Cu degradation. The electroplated Cu was found to produce CH$_4$ at 73% Faradaic efficiency and C$_2$H$_4$ at 25% Faradaic efficiency at a current density of 8.3 mA/cm$^2$. Later, Kim et al. reduced CO$_2$ and CO on high purity Cu foils with different pretreatments. From the results, CO was determined to be a precursor to CH$_4$ and C$_2$H$_4$ and CO dissociation, with CO formation being the rate limiting step on Cu. Aqueous 10% HCl pretreatments gave the highest CH$_4$ yields as they removed oxide films more cleanly than other acids. In 1989, Noda et al. reduced CO$_2$ on Cu foil in 0.1 M KHCO$_3$ electrolyte and measured the liquid products with high performance liquid chromatography, detecting CH$_3$CH$_2$OH, propanol, acetone and acetaldehyde in addition to the gaseous products reported by earlier publications.59

Recently, the products of Cu foil were refined even further by Kuhl et al., who used nuclear magnetic resonance spectroscopy (NMR) to detect low concentration liquid products. In addition to the CH$_3$CH$_2$OH, propanol, acetone and aldehyde discovered earlier, CH$_3$OH, allyl alcohol, glycoaldehyde, acetylaldehyde, ethylene glycol, propionaldehyde, and hydroxyacetone were detected.23
With polycrystalline Cu foil identified as an effective hydrocarbon catalyst, other forms of Cu catalysts were investigated. Cu oxides, single crystals and nanoparticles have all been studied previously.

Cu Single Crystals

Cu single crystals were evaluated experimentally by the group of Hori. In 1995, Hori et al. reduced CO$_2$ on Cu(100), Cu(110) and Cu(111) crystals in 0.1 M KHCO$_3$ electrolyte. The product selectivity was dependent on the exposed crystal facet. The Cu(100) facet shows a reduction in CH$_4$, CHOO$^-$ and CO selectivity while C$_2$H$_4$ and CH$_3$CH$_2$OH selectivity increases compared to polycrystalline foil. Meanwhile, the Cu(110) facet increases CH$_4$ and decreases C$_2$H$_4$, CHOO$^-$ and CO, while the Cu(111) facet increases CH$_4$ and H$_2$, but decreases C$_2$H$_4$, CHOO$^-$, CO and CH$_3$CH$_2$OH selectivity. Fourier transform infrared spectroscopy (FTIR) was used to observe the presence of CO on the surface of Cu(111) and Cu(100) single crystals. CO was found to give a double peak on Cu(111) at -0.55V vs SHE while only a single peak on Cu(100) was present at -0.85V vs SHE, indicating different CO adsorption modes are responsible for the differences in product distribution. In 2002, Hori et al. continued his single crystal work by investigating facets between Cu(111) and Cu(100); namely Cu(311), Cu(511), Cu(711), Cu(911) and Cu(11 1 1). The product Faradaic efficiencies were recorded. Cu(111) was found to have the highest CH$_4$ Faradaic efficiency at 50.5%, and as the facets were stepped from Cu(111) to Cu(100), the CH$_4$ efficiency decreases, reaching a minimum of 3.8% at Cu(711). However, the opposite trend was observed for C$_2$H$_4$ selectivity, where a maximum of 58.5% was reached at Cu(711) while Cu(111) was the least selective towards C$_2$H$_4$. Hori et al. attributed the dramatic shift in selectivity to the bond strength of CO on the facets and reports Cu(111) to bind CO the weakest. Step edges were considered to be the strongest binding sites for CO, allowing
adsorbed CO to form C-C bonds before dissociating from the surface, resulting in greater C$_2$H$_4$ yields.

Later computational work supports the theory of lower coordinated facets possessing stronger CO$_2$ reduction intermediate bond energies. In 2011, Durand et al. used density functional theory (DFT) to calculate the adsorption energies of COOH, CO and OCHO on Cu(111), Cu(100) and Cu(211) planes, finding that Cu(211) displayed the strongest adsorption while Cu(111) was weakest for all intermediates. The free energy of the reaction pathway to CH$_4$ was also calculated, and was also in agreement with the trend, with Cu(111) having the highest energy requirements.

Cu Nanoparticle Electrodes

In addition to single crystal and metal foil forms of Cu, nanoscale Cu catalysts have also been developed. Cu nanoparticle catalysts offer a means of increasing the number of active low coordination sites per mass Cu. By controlling the shape and size of the nanoparticle, the ratio of edge, corner and plane sites can be controlled as well. The use of oxide supports for these nanoparticles can also alter their electronic properties and aid in the CO$_2$ reduction reaction via synergistic effects. In 2014, Reske et al. synthesized spherical Cu nanoparticles with sizes ranging from 2-15 nm using polymer micelles. At all sizes, CH$_4$ and C$_2$H$_4$ selectivities were decreased while CO and H$_2$ selectivities were increased relative to Cu foil. The altered selectivities were most pronounced at the smallest nanoparticle sizes. The changes in selectivity were attributed to the low coordinated sites not being favorable for subsequent hydrogenation steps after CO. However, this conflicted with a publication by Manthiram et al. who reported increased hydrogenation rates for CO well dispersed ~23 nm Cu nanoparticles, achieving 76% CH$_4$ Faradaic efficiency. The nanoparticles from Manthiram et al. were synthesized by
colloidal methods and dispersed on glassy carbon. The difference in performance from Cu nanoparticles studied by other groups was attributed to the high dispersion of the Cu.

Loiudice et al. also tested the size effect on Cu nanocatalysts using 24-63 nm Cu nanocubes synthesized using colloidal methods. Nanocubes displayed greater current density than similarly sized spheres. The 44 nm nanocubes displayed the highest Faradaic efficiency towards the CO₂ reduction reaction and had the highest selectivity towards hydrogenated products such as CH₄ and C₂H₄. Loiudice et al. attribute this to the ratio of edge, plane and corner sites being more favorable on cubes than on spheres; while edge sites are more favorable for CO adsorption and stabilization; planar sites are also required for increasing the formation of hydrocarbons.

One suggested method to decrease the selectivity towards H₂ on Cu nanoparticles is to place them on a N-doped support. Song et al. deposited 39 nm Cu nanoparticles on N-doped graphene spikes. At -1.2V vs RHE in 0.1 M KHCO₃, the Cu nanoparticles show 63% Faradaic efficiency towards CH₃CH₂OH. DFT suggests that the N-doped graphene possesses an increased affinity for binding oxygenated carbon compounds. Song et al. propose that the support coordinates with the Cu surface in adsorbing intermediates, particularly oxygenated C2 species, making the production of CH₃CH₂OH more feasible.

**Reaction Pathway on Cu**

Computational Estimates

The actual pathway of CO₂ reduction on Cu is not fully established due to the difficulty in experimentally detecting intermediates in aqueous environments with common techniques such as in-situ Fourier transform infrared spectroscopy (FTIR) or Raman spectroscopy. Instead,
DFT calculation has been used for the prediction of the reaction pathway on Cu single crystals using thermodynamic and kinetic principles. However, there are multiple conflicting pathways that have been proposed. Recent theoretical single carbon product pathways are displayed in Figure 2.7.
In 2010, Peterson and Nørskov used DFT paired with a computational hydrogen electron model to assemble lowest free energy pathways for H\textsubscript{2}, CHOO\textsuperscript{−}, CO and CH\textsubscript{4} on Cu(211).\textsuperscript{68} In Peterson and Nørskov’s lowest energy pathway for CH\textsubscript{4}, CO\textsubscript{2} is reduced to *COOH, *CO, *CHO, *CH\textsubscript{2}O and CH\textsubscript{3}O* sequentially, before finally being reduced to CH\textsubscript{4}. CHOO\textsuperscript{−} and CO are formed when the intermediates desorb before being further reduced. However, this pathway contradicted the experimental results by Schouten et al. in 2011, where formaldehyde and methoxy were reduced on Cu electrodes in phosphate electrolyte. Schouten et al. reported that reducing aqueous formaldehyde or methoxy on Cu resulted in CH\textsubscript{3}OH, not CH\textsubscript{4}.\textsuperscript{69} Peterson et al. later published a revised DFT.\textsuperscript{70} In the revised DFT, it was proposed that only adsorbed formaldehyde and methoxy species were reduced to CH\textsubscript{4}. Formaldehyde that desorbed into solution would react with water to form CH\textsubscript{2}(OH)\textsubscript{2}, which forms CH\textsubscript{3}OH upon being reduced, making desorption of formaldehyde the selective step between CH\textsubscript{4} and CH\textsubscript{3}OH.

Another pathway was proposed by Nie et al. who determined that accounting for reaction kinetics in addition to free energy would change the theoretical path to CH\textsubscript{4}.\textsuperscript{2} The protonation steps of the reduction were examined using both water solvated and surface shuttled protons. It was found that O protonation requires H\textsuperscript{+} shuttling through a H\textsubscript{2}O molecule, while C protonation requires an adjacent adsorbed proton, resulting in a lower activation barrier for the O protonation. Nie et al. assert that the selective step is the first protonation of *CO which will lead to *COH or *CHO, and produce CH\textsubscript{4} or CH\textsubscript{3}OH respectively. *COH formation is reported to be preferred by a selectivity factor of \textasciitilde2000, matching the experimental results on Cu. This pathway implies that formaldehyde is not an intermediate of CH\textsubscript{4}, contrasting with Nørskov’s previous DFT calculations.
In 2016, the group of Nørskov refined their pathway using proton transfer reaction barriers.\textsuperscript{4} The activation barriers for the individual protonation steps were calculated on Cu, Au and Pt surfaces using DFT with an explicit solvent model. In the new pathway, the CO protonation to $^*\text{COH}$ or $^*\text{CHO}$ was found to heavily favor $^*\text{CHO}$ by a gap of 2.0 eV. Next the O is favored to be protonated twice to form $^*\text{CHOH}$ and $^*\text{CH}$, sequentially. The $^*\text{CH}$ is then protonated to form CH$_4$. CH$_3$OH formation only occurs when $^*\text{CHOH}$ is protonated to form $^*\text{CH}_2\text{OH}$ instead of $^*\text{CH}$. The largest activation energy barrier for CO$_2$ reduction on Cu(211) is the first protonation of $^*\text{CO}$.

In-situ FTIR

As the exact CO$_2$ reduction pathway is unknown, in-situ Fourier transform infrared spectroscopy (FTIR) has been used to experimentally observe intermediates on various transition metal cathodes. In-situ FTIR is a difficult experiment to perform in aqueous conditions due to light absorption by the electrolyte.

Intermediates early in the pathway such as CO have been observed previously. In 1973, Aylmer-Kelly performed FTIR on Pb in both aqueous and carbonate electrolytes, showing peaks interpreted as CO$_2^{•}$ adsorbed on the surface.\textsuperscript{71} Pt electrodes in aqueous electrolyte were later studied by Beden et al., showing adsorbed CO.\textsuperscript{72} Hori et al. observed the presence of adsorbed CO during CO$_2$ reduction on Ni electrodes as well.\textsuperscript{73,74} Due to the high coverage of CO on the Ni surface, H$_2$ evolution was inhibited. In 1998, Hori et al. again used FTIR to show the presence of adsorbed CO on Cu(100) and Cu(111) crystals.\textsuperscript{75} Post-CO intermediates such as hydrocarbons have thus far not been detected, which is why the pathway is disputed.
CO₂ Reduction on Au

Despite being a noble metal, Au is also an effective electrocatalyst for the reduction of CO₂ to CO. Au was first identified as a CO₂ electroreduction catalyst in 1987 by Hori et al., who used an Au electrode in 0.5 M KHCO₃ electrolyte.⁷⁶ CO, H₂ and CHOO⁻ were observed as products, with Faradaic efficiencies of 92%, 9% and 1% respectively at -0.98V vs NHE. As CO₂ will not be hydrogenated beyond CO on Au, there has not been as much research focus as on Cu.

However, Au nanoparticles have recently become an area of interest. In 2012, Kauffman et al. synthesized Au₂₅ nanoparticles for use as CO₂ reduction catalysts.⁷⁷ Au₂₅ nanoparticles consist of a Au₁₃ core surrounded by a shell consisting of 12 Au atoms and 18 phenylethanethiol molecules held together by the S groups of the thiols. When used as a CO₂ reduction catalyst in 0.1 M KHCO₃, the onset potential is shifted anodically by 200-300 mV compared to bulk Au and produces CO at faradaic efficiencies of approximately 100%. These improvements are attributed to the inherent negative charge of the Au₂₅ nanoparticle and the unique structure.

The size and structural effects of Au nanoparticles on CO₂ reduction have been noted by other groups as well. Size effects from Au nanoparticles have been observed by Mistry et al.⁷⁸ and Zhu et al.,¹⁰ who observe that CO yields are increased on nanoparticles possessing more low coordination sites such as edges and corners. Having synthesized and tested 4, 6, 8 and 10 nm spherical Au nanoparticles, Zhu et al. claim a maximum in CO selectivity occurs at 8 nm due to an optimal ratio of edge and corner active sites, and that nanoparticles below 2.7 nm will begin to display finite size effects (Figure 2.8).¹⁰ The ratio of edge and corner sites was addressed again by Zhu et al. using Au nanowires.⁷⁹ By increasing the amount of reactive edge sites, the
Figure 2.8: CO partial current density (top left) and Faradaic efficiency (top right) on Au nanoparticles. Calculations assuming perfect cuboctahedra show the ratio between different active sites (bottom). (Reprinted with permission from (Zhu et al. 2013). Copyright 2013 Journal of the American Chemical Society)
nanowires were able to reduce CO$_2$ to CO at up to 95% Faradaic efficiency and at greater current densities than the previous 8 nm nanoparticle Au.

Other structural effects were noted by Chen et al. who synthesized nanostructured Au for CO$_2$ reduction. By oxidizing Au foil in H$_2$SO$_4$ using square wave voltammetry, oxidized electrodes with roughed surfaces were prepared as catalysts.\textsuperscript{80} Once under reductive potential, the oxide was quickly reduced, leaving a nanostructured Au layer. The nanostructured Au was able to produce CO at 100% Faradaic efficiency and at 200 mV lower overpotentials than Au foils. Likewise, concave rhombic dodecahedral Au catalysts synthesized by Lee et al. displayed improvements as a result of nanoparticle structure. Under a reducing potential in 0.5 M KHCO$_3$ electrolyte, concave rhombic dodecahedral catalysts reached up to 93% Faradaic efficiency to CO, and shifted the onset potential for CO$_2$ reduction by 230 mV anodically compared to polycrystalline Au foil.\textsuperscript{81} The improvements were attributed to the high index facets available on the concave rhombic dodecahedron surface.

\textbf{CO$_2$ Reduction on Alloy Catalysts}

Alloying makes it possible to select the electronic properties of the metal catalyst, offering some degree of control over the binding energies of the CO$_2$ reduction intermediates. As a result, alloys can display very different products and yields than the pure component metals. Some transition metal alloy combinations, particularly those containing Cu, have been studied previously. Ideally, the added metal will improve Cu’s ability to stabilize intermediates that lead to CH$_3$OH, such as *CHO while not effecting its ability to efficiently hydrogenate CO.

In 1991, Watanabe et al. tested CuNi, CuSn, CuPb, CuZn, CuCd and CuAg alloy electrodes in 0.05 M KHCO$_3$ as CO$_2$ reduction catalysts.\textsuperscript{82} CuPb and CuSn produced >50%
Faradaic efficiency CHOO’ and smaller amounts of CO and H₂ with enhanced reaction rates. CuAg produced >20% CO and >30% CHOO’, while CuZn gave >40% CO and >30% CHOO’. CuNi and CuCd were found to produce mostly H₂, and small amounts of CO, CH₃OH and formic acid.

In 2012, Christophe et al. used CuAu alloys to show that product selectivity and yields altered as the alloy composition changed. Foils with molar compositions of Au₁Cu₉₉, Au₁₀Cu₉₀, Au₂₀Cu₈₀ and Au₅₀Cu₅₀ were held at -1.9V vs Ag/AgCl in CO₂ saturated phosphate solution. The addition of Au to Cu, even in ratios as low as 1:99, causes a significant decrease in the amount of hydrocarbons produced. As the Au content increased, CO yield and Faradaic efficiency increased, with Au₅₀Cu₅₀ alloys producing more CO than bulk Au.

CuIn alloys have also been an active area of study recently. Rasul et al. reported that CuIn metal catalysts suppressed H₂ evolution while enhancing CO yields. CuIn electrodes were formed by oxidizing Cu metal sheets and reducing them in an InSO₄ solution. The CuIn alloy was held at potentials of -0.3V to -0.7V vs RHE in CO₂ saturated 0.1 M KHCO₃, producing 90% CO at -0.5V vs RHE.
CHAPTER 3: CuZnO AND AuTiO₂

Introduction

Photocatalytic and gas-phase CO₂ reduction catalysts often consist of metal nanoparticles deposited on semiconductor or oxide supports. In the case of CuZnO, Cu nanoparticles are scattered on a ZnO single crystal surface using thermal deposition techniques. ZnO is an excellent oxide support for both the aforementioned gas phase CH₃OH synthesis, and a semiconductor support for the photocatalytic reduction of CO₂. With CuZnO CH₃OH synthesis catalysts, the ZnO provides several beneficial, synergistic effects. In addition to dispersing Cu into nanoclusters on the surface, ZnO aids in the adsorption and reduction of CO₂, as well as allowing some mobility of the intermediates over its surface.⁸⁴ The Cu-ZnO interfaces are also important active sites.

Likewise, ZnO and TiO₂ supports are frequently paired with Au nanoclusters for CO₂ reduction⁸⁵,⁸⁶ and CO oxidation reactions⁸⁷ in gas phase catalysis. The Au-oxide interfaces are thought to be the most important active sites, as CO₂ adsorbed to the Au surface can pass its O onto the Zn, reducing to CO.⁸⁶ The existence of stable, positively charged Au states due to electronic effects from the ZnO surface has also been suggested. The positively charged Au theoretically acts as the catalyst site, attracting CO₂ via slight dipole moments, resulting in an increase in activity.⁷⁷

ZnO, TiO₂ and other oxide supports are difficult to use as cathodes, as the oxide will be reduced when sufficient cathodic potential is applied. As a result, they are often overlooked.

when considering electrocatalysts. However, in work by Le et al., CuZnO was shown to be an effective CH$_3$OH electrocatalyst and at far greater selectivity than polycrystalline Cu when operated above the reduction potential of ZnO. Le et al. also observed that the catalyst is stable when operated at the potentials more cathodic than the ZnO reduction potential.

Gas phase CuZnO has also been used in diffuse reflectance FTIR (DRIFTS) experiments which elucidate the reaction pathway of CH$_3$OH synthesis from syngas. The Cu islands dispersed on the ZnO support enhance the IR absorption, making CuZnO suitable for FTIR experiments. Aqueous phase FTIR experiments are also possible, though the strong absorptive properties of water make observing the electrode surface difficult.

Here, CuZnO electrodes are fabricated and used in an in-situ FTIR to observe CO$_2$ reduction intermediates. By observing intermediates, it is hoped that the CO$_2$ reduction pathway on Cu metals will be elucidated. The hydrocarbon yields of CuZnO are compared to Cu(111) at the same potential.

Material and Methods

CuZnO Electrode Fabrication

Electrodes were fabricated by cleaning single crystal ZnO(1010) substrates (MTI Corporation), followed by vacuum deposition of Cu. The wet cleaning sequence included rinsing in deionized water, acetone, and CH$_3$OH. Following the wet clean, ZnO single crystals were sputter-cleaned using cycles of Neon-ion bombardment (5 x 10$^{-5}$ Torr, 1.5 kV, 15 mA, 30 minutes) at room temperature and annealed up to 700ºC (P=10$^{-9}$ Torr). A well-defined low-energy electron diffraction (LEED) pattern was used to verify long-range surface structural order.
Cu (99.999%, Alfa Ltd) was thermally deposited on the clean ZnO(1010) surface at room temperature for 20s to form approximately 3 monolayers (UHV 1.0 KV, 100 mA). Ultraviolet photoelectron spectroscopy (UPS) and x-ray photoelectron spectroscopy (XPS) analyses following Cu evaporation showed no evidence of alloy formation (without annealing).

AuTiO$_2$ and AuZnO Electrode Fabrication

TiO$_2$(110) and ZnO(1010) single crystals were obtained commercially from MTI Corporation. The electrodes were fabricated by cleaning the single crystals using wet and UHV methods, followed by vacuum deposition of Au. The wet cleaning sequence included rinsing in deionized water, acetone, and CH$_3$OH. Following the wet clean, the single crystals were sputter-cleaned using cycles of Neon-ion bombardment ($5 \times 10^{-5}$ Torr, 1.5 kV, 15 mA, 30 minutes) at room temperature and annealed up to 700°C ($P=10^{-9}$ Torr). A well-defined low-energy electron
diffraction (LEED) pattern was used to verify long-range surface structural order. Au (99.999%, Alfa Ltd) was thermally deposited on the clean surfaces at room temperature for 20s to form approximately 3 monolayers (UHV 1.0 KV, 100 mA).

Electrochemical and FTIR Analysis

Electrochemical experiments were carried out in aqueous 0.1 M KHCO$_3$(Sigma Aldrich) electrolytes saturated with CO$_2$(Air Products, 99.999%) using either a single compartment PTFE cell for in-situ FTIR (Figure 3.2) or a 2-compartment (fritted) glass cell for (higher volume) product analysis. The custom three-electrode single compartment PTFE cell included an Ag/AgCl (saturated with NaCl) reference electrode and a Pt counter electrode. The single crystal cathode (with Cu nanoclusters) was located approximately 1 mm below a transparent CaF$_2$ window and infrared absorption behavior was monitored as potentials were applied to the working electrode. Infrared spectra were collected with a Nicolet 6700 FTIR with a Mercury-Cadmium-Telluride (MCT) detector cooled by liquid nitrogen. The interferograms were recorded at a resolution of 4 cm$^{-1}$ and over 16 scans. Voltammetric experiments including chronoamperometric experiments used for the in-situ FTIR analysis were conducted using a Princeton Applied Research 2273 potentiostat.

In parallel experiments to determine product yields, a 56 cm$^{3}$ three-electrode glass cell with anode and cathode compartments was used. The counter electrode was a Pt wire, and the reference was Ag/AgCl. The reactor included a persulfonate polymer (Nafion$^\text{TM}$) membrane to separate the working and counter electrodes and prevent the re-oxidation of the products. Gas phase products were detected by GC-TCD and FID (Shimadzu, GC 2014). Liquid phase products were quantified by 1D $^1$H NMR (Varian 700 MHz spectrometer). As described in studies by Kuhl et al., the product identification was carried out (using 10 mM DMSO as a reference peak)
by a 2D homonuclear correlation spectroscopy (COZY) experiment to determine which proton peaks are correlated in the $^1$H NMR spectra.

**Results and Discussion**

**AuTiO$_2$ and AuZnO**

The 3ML AuZnO was held at -1.4V vs Ag/AgCl and showed 6% Faradaic efficiency to CO with the balance H$_2$. Likewise, AuTiO$_2$ held at -1.2V vs Ag/AgCl showed only 5% Faradaic efficiency to CO with the balance hydrogen. Both of these catalysts showed less selectivity towards the CO$_2$ reduction reaction than unmodified Au. The most likely explanation is that the Au nanoparticles are unable to benefit from the synergistic effects of oxide supports, while the oxides provide a greater surface area for the HER reaction to occur on. Burch et al. describe the gas-synthesis ZnO support as a hydrogen reserve which passes protons to the metal catalyst,
usually Cu, enabling hydrogenation of the intermediates.\textsuperscript{93} However, unlike Cu, Au has a low affinity for hydrogen, which could impede the transfer of surface protons from the oxide.\textsuperscript{5}

CuZnO

Figure 3.3 shows the voltammetric behavior of the Cu/ZnO and ZnO electrodes in aqueous bicarbonate electrolytes with and without CO\textsubscript{2}. The initial cathodic scan using Cu/ZnO electrode shows a CO\textsubscript{2} reduction current density similar to Cu electrodes. The small shoulder near $-1.1\text{V}$ versus Ag/AgCl in the first scan is associated with reduction of some oxidized Cu
formed from exposure to air prior to the experiment.\textsuperscript{88} Voltammetric scans performed without CO\textsubscript{2} or using only ZnO(1010) electrodes show very low current densities; reduction current densities increase slightly with the introduction of CO\textsubscript{2} and product analysis shows H\textsubscript{2} as a primary product with minor production of CHOO\textsuperscript{-} and carbon monoxide. It is important to note that previous CO\textsubscript{2} reduction studies using polycrystalline ZnO (sintered powder) in carbonate electrolytes showed only CO and HCOO\textsuperscript{-} as products along with the partial reduction of ZnO (Zn formation) at $-1.4\text{V}$ versus Ag/AgCl,\textsuperscript{94} however no metallic zinc or voltammetric peaks were seen with the single crystal substrates considered here at potential positive of $-1.6\text{V}$ versus Ag/AgCl. The Cu nanocluster-ZnO electrodes were significantly more active toward CO\textsubscript{2} reduction showing a normalized current density of approximately 12 mA/cm\textsuperscript{2} at $-1.4\text{V}$ versus Ag/AgCl, which is similar to metallic Cu electrodes. H\textsubscript{2} evolution rates increase as the potential increases cathodically beyond $-1.2\text{V}$ and the single crystal ZnO substrate itself is reduced at potentials negative of $-1.6\text{V}$ versus Ag/AgCl. Liquid product analysis using the Cu nanocluster-ZnO electrode in 1 hour batch experiments in the glass cell, and gas product analysis with continuous CO\textsubscript{2} flow ($-1.4\text{V}$ versus Ag/AgCl) are shown in Table 3.1 along with yields from parallel experiments using single crystal Cu (111) electrodes using the same electrolyte, reactors, reaction times and potentials. In both cases, reported yield data are normalized to Cu surface areas (estimated as 0.30 mm\textsuperscript{2} based on STM analysis of the Cu/ZnO electrode).

As shown in Table 3.1, Faradaic efficiencies observed with Cu(111) electrodes at -1.4V vs. Ag/AgCl ($\sim$-0.8V versus RHE) are similar to previous reports.\textsuperscript{23,95} It is important to note that Faradaic efficiencies are potential dependent, CH\textsubscript{4} is seen as a primary product on Cu(111) at more negative potentials.\textsuperscript{95} At this potential (-1.4V versus Ag/AgCl), however, H\textsubscript{2} is the primary
product in both cases along with significant levels of CO, HCOO−, CH4 and C2H6. Remarkably, the relative selectivity of alcohols increases by at least one order of magnitude when CuZnO electrodes are used in place of Cu(111). Faradaic efficiencies are based on product analysis using both GC and NMR and their summations are slightly less than unity due to measurement limitations. Specifically, some products such as formaldehyde (easily hydrated to CH2(OH)2) cannot be easily detected by either system. To better understand the reaction pathway and intermediates, a custom cell was fabricated to allow in-situ infrared analysis during the reduction reaction. Cu nanocluster-ZnO electrodes were cathodically biased at the same potential (-1.4V versus Ag/AgCl) while simultaneously collecting infra-red spectra. In the absence of potential, the only substantial change in absorbance was associated with CO2 uptake (2380 cm⁻¹) upon carbonating the electrolyte. CO2 saturated electrolytes were used in subsequent analyzes and background spectra were acquired immediately prior to reduction experiments.

Table 3.1: Faradaic efficiencies and yields for products of CO2 reduction on 3 ML Cu/ZnO and Cu(111) electrodes in 0.1 M KHCO3 at -1.4 V versus Ag/AgCl. (Reprinted with permission (from Andrews et al., 2013). Copyright 2013 The Journal of the Electrochemical Society)
Assignments of adsorption peaks in spectra shown in Figure 3.4 were made by analogies with experimental spectra of known compounds (in the same cell) and by comparison with published literature. Initial spectra (<120 s after applied potential) appear to include adsorbed species while the mature spectra are dominated by solution species similar to those described in Table 3.1. With the exception of methoxy and CHOO⁻ species, other infra-red adsorption dynamics in the early reduction period appear to be related to rearrangement of water and carbonates near the electrode.

Figure 3.4 (a) and (b) show spectra collected in the initial period after applied potential focusing on specific peaks associated with surface species. As shown in Figure 3.4(a), two peaks near 1044 and 1029 cm⁻¹ are seen within the initial 120 s of applied potential. Literature reports
of C-O stretching from methoxy adsorbates on Cu and ZnO surfaces occurs near 1044 cm$^{-1}$\textsuperscript{199, 100} while free CH$_3$OH is observed near 1030 cm$^{-1}$\textsuperscript{100, 101}. In this case, the absorption associated with methoxy adsorbates is relatively constant, while the free CH$_3$OH peak increases over time as expected from product analysis. It is also possible the peak near 1029 cm$^{-1}$ is associated with free CH$_3$CH$_2$OH which was also determined using NMR. Further, evaporation of CH$_3$OH on the same electrode showed a strong absorbance near 1045 cm$^{-1}$, consistent with methoxy adsorbates. The O-H stretching modes from CH$_3$OH and CH$_3$CH$_2$OH also contributed to the large peak observed at $\sim$3600 cm$^{-1}$, however, this peak is also heavily influenced by the rearrangement of water near the electrode. Figure 3.4(b) shows absorption behavior associated with CHOO$^-$ in the initial reduction period. Free CHOO$^-$ is associated with the intense broad peak at 1580 cm$^{-1}$ along with two small sharp peaks at 1380 and 1350 cm$^{-1}$\textsuperscript{102}. In this case, adsorbed CHOO$^-$ is indicated by C-H stretching at 1580 cm$^{-1}$ and 1601 cm$^{-1}$ (bridging mode)\textsuperscript{103}.

Figure 3.5 shows a mature in-situ FTIR spectrum along with spectra dynamics obtained over 5 minutes at -1.4V versus Ag/AgCl. In these spectra, the relatively broad peaks near 3600 cm$^{-1}$ and 1687 cm$^{-1}$ are associated with water (OH) rearrangement in electrochemical double layer. Similarly, the peaks at 1734 cm$^{-1}$ and 1462 cm$^{-1}$ are related to rearrangement of carbonates\textsuperscript{104}. The broad peak centered near 2137 cm$^{-1}$ is due to dissolved CO and is consistent with gas phase product analysis\textsuperscript{105}. The triplet near 2900 cm$^{-1}$ is associated with the stretching of C-H bonds of multiple species. In this case, the 2958 cm$^{-1}$ peak is shared with several signals such as CH stretching of bidentate CHOO$^-$ and asymmetric CH stretching of alcohols\textsuperscript{106, 107}. Likewise, the 2864 cm$^{-1}$ peak is shared by symmetric CH stretching of alcohols and bridging
The peak at 2902 \( \text{cm}^{-1} \) is likely due to the symmetric CH\(_3\) stretching mode of free CH\(_3\)CH\(_2\)OH.\(^{108,109}\)

It is interesting to consider the product distributions and in-situ spectra observed here relative to proposed mechanisms and theoretical predictions. Remarkably, alcohol selectivities improve by at least one order of magnitude with CuZnO electrodes relative to Cu(111).
nature of this relative increase is not clear; however, there are several possible mechanisms. Previous experiments with oxidized Cu electrodes or Cu(I) films have shown CH₃OH production in short experiments prior to (or along with) reduction of oxidized Cu; however, the alcohol yields observed in this case are stable and independent of reaction times. Selectivities of alcohols and C₂-products are also known to be a function of crystal surfaces and the coordination level of surface Cu. Rough Cu surfaces, particularly electrodes formed using oxidized Cu have shown significant increases in current density and increases in alcohol yields. In this case, the normalized current densities associated with Cu nanoclusters on ZnO surfaces and Cu(111) are similar and C₂H₄ yields are also similar. One possibility is that the ZnO supports stable low-coordinated Cu sites that favor alcohols. Another possibility is the selectivity change is related to interactions between Cu nanoclusters and the semiconducting ZnO support. The role of ZnO and the active sites for reduction have been a subject of controversy in gas-phase CH₃OH catalysis for some time; however, there is a general consensus that CO and CO₂ hydrogenation reactions occur at different sites on the CuZnO surfaces. The ZnO is thought to help disperse Cu and enhances CH₃OH synthesis via a “Cu-ZnO synergy” effect. In the gas phase reaction, CO₂ hydrogenation is thought to occur at Cu₀ sites, and CO hydrogenation is thought to occur at Cu⁺ sites or Cu sites with modified electronic structures near ZnO interfaces. Although the gas phase CO₂ pathway involves CHOO⁻ and does not resemble proposed electrochemical routes (where CHOO⁻ is considered a dead end), the reduction of CO at CuZnO surfaces is thought to proceed through a series of products including CHO, CH₂O and CH₃O*. Cu⁺ sites (or Cu⁸⁺) are thought to be well suited for CO reduction to CH₃OH due to σ-donor interactions and π backbonding to increase the strength of the CO bond allowing activation of the C atom for
nucleophilic attack by hydrides.\textsuperscript{116} A similar synergistic effect may occur in the electrochemical case and may contribute to the improved selectivity.

It is also possible that Cu-Zn interfaces influence the reduction pathway. A recent model of the gas-phase synthesis reaction including DFT calculations suggest the Zn plays a more direct role and that active CH\textsubscript{3}OH sites are located near steps at Cu surfaces with Zn\textsuperscript{δ+} atoms at the stepped surfaces; these sites allow stronger binding of intermediates and results in lower energy barriers and increased activity in both CO\textsubscript{2} and CO pathways.\textsuperscript{113} While the CuZnO electrodes used here (non-annealed) showed no evidence of alloy formation, it is possible that the natural interfaces of Cu and ZnO could also lower the barriers for hydrogenation of adsorbed CO. A recent Charge Optimized Many Body (COMB) model for the CuZnO systems suggests Cu atoms near ZnO develop a positive charge when interacting with multiple oxygen atoms on ZnO surfaces.\textsuperscript{117} The magnitude of these local interactions related to the oxide support (including oxygen vacancies) under cathodic potentials are difficult to estimate, however, Cu-Zn interfaces may effect hydrogenation behavior of key intermediates such as CO* or CH\textsubscript{2}O* adsorbates.

As described in the model for the electrochemical reduction of CO\textsubscript{2} at Cu (111) electrodes by Nie et al.\textsuperscript{2} which includes the effects of water and kinetics, there are likely two primary reduction pathways. Both paths begin with the reduction of CO\textsubscript{2} to CO; however, CH\textsubscript{4} pathway proceeds via hydrogenation of the O atom of adsorbed CO* species while the CH\textsubscript{3}OH pathway proceeds via hydrogenation of the C atom. In the CH\textsubscript{4} path, the C-OH species is deoxygenated and the carbon atom is subsequently hydrogenated to form CH\textsubscript{4}. For CH\textsubscript{3}OH, a formyl (CHO*) species undergoes hydrogenation to form CH\textsubscript{2}O and CH\textsubscript{3}O* sequentially. The relative barriers determined for CO\textsubscript{2} reduction at Cu(111) electrodes favors the CH\textsubscript{4} path by a factor of approximately 2000 (-0.18 eV). In this case with CuZnO, the relative increase in selectivity
toward alcohols may be associated with an increase in formation of CHO species at the critical (selectivity controlling) CO* reduction step. As mentioned previously, increased hydrogenation of the carbon atom of adsorbed CO* may be due to the relatively stronger metal-carbon binding associated with a ZnO support or interface. Independent of the mechanism for increased hydrogenation of the carbon atom, a CHO intermediate may progress to CH₂O and CH₃O* through subsequent hydrogenation steps.

The in situ spectroscopy presented here shows CH₃O* adsorbates; however, it is difficult to associate these solely with alcohol production. Indeed it is possible that methoxy adsorbates form either CH₄ or CH₃OH (or C₂H₄ and CH₃CH₂OH). Petersen et al. suggests that the gas-phase synthesis is produces CH₃OH since surface H⁺ is limited to react with the oxygen atoms of methoxy adsorbates. In the liquid phase, it is possible methoxy adsorbates can react with either surface H⁺ or protons in solution and the same authors indicate a 0.18 eV preference for the protonation of the carbon atom. As shown in the model by Nie et al.,² kinetic models suggests the upright methoxy adsorbate will most likely form CH₃OH. This model appears consistent with the experimental results shown here as we would expect to increased methoxy adsorbates consistent with increased alcohol production. Of course, there is a need for greater experimental resolution of intermediates; however many have relatively low kinetic barriers and therefore are likely to have relatively short lifetimes and limits the usefulness of traditional FTIR. Formaldehyde, in particular, is a considered a key intermediate in several pathways, but has not been experimentally verified.², ⁶⁸ Other aldehydes such as acetylaldheyde and propionaldehyde have been experimentally identified as minor reduction products at Cu electrodes; however, formaldehyde is difficult to detect since it is quickly hydrated to CH₂(OH)₂ (t₁/₂ <100 ms)⁹⁶, ⁹⁷ which cannot be easily detected in gas chromatography⁹⁸ or H NMR due to interferences with
water. While these results suggest methoxy adsorbates lead primarily to CH$_3$OH, it would be interesting to leverage other in-situ analysis methods (e.g. ultrafast sum-frequency spectroscopy) to follow intermediates (such as formaldehyde) and their behaviors including the role of water. Ultimately the combination of in-situ tools with simulation may provide the insights needed to further tune CO$_2$ reduction selectivity toward alcohols.

**Conclusion**

CO$_2$ reduction on Cu single crystal and CuZnO electrodes showed CO, H$_2$, CH$_4$, CH$_3$OH, CH$_3$CH$_2$OH, CHO$	ext{O}^-$ and C$_2$H$_4$ as products at -1.4V vs Ag/AgCl. The Cu nanoparticles supported on ZnO offer lower yields than Cu foils, but increase the selectivity towards CH$_3$OH and CH$_3$CH$_2$OH by over an order of magnitude. The exact mechanism behind the change in selectivity is likely due to the existence of Cu-Zn interface active sites, or charge transfer effects from the ZnO interface strengthening the Cu-CO bond via π backbonding and making hydrogenation more favorable. However, as yields were extremely low, other nanoparticle catalysts were used for future experiments.

The in-situ FTIR spectroscopy showed peaks corresponding to adsorbed and solution forms of CHO$	ext{O}^-$ as well as adsorbed methoxy and CH$_3$OH. Dissolved CO was also observed. The difficulties of performing in-situ FTIR analysis in an aqueous environment precluded the observation of the other CO$_2$ reduction intermediates.
CHAPTER 4: SURFACE CHEMISTRY EFFECTS ON Au$_{25}$ NANOPARTICLE CATALYSTS

Introduction

Au metal is a stable catalyst that can reduce CO$_2$ to CO at large current densities and >90% Faradaic efficiency.$^{76}$ The CO yields and onset potentials can be improved further by utilizing Au nanoscale catalysts such as thiolated nanoclusters,$^{77}$ nanowires,$^{79}$ and colloidal nanoparticles.$^{10, 78}$ The nanoscale Au catalysts are synthesized, characterized, and immobilized on a supporting substrate for use as electrocatalysts. However, despite the nanocatalysts being well characterized upon synthesis, it is possible that the surfaces are restructured during the electrode preparation procedure. In particular, this is a risk for electrodes using polymer binder inks. Ideally, binders should be inert polymer matrices that immobilize the nanoparticles in a conductive matrix while allowing transport of reactants and products. Nafion$^{\text{TM}}$ and polyvinylidene fluoride (PVDF) are two commonly used fluoropolymer binders. Though similar, Nafion$^{\text{TM}}$ contains a sulfonate group which conducts protons along the polymer matrix, while PVDF lacks such a functional group. While Nafion$^{\text{TM}}$ binder is not expected to interfere with nanoparticles, sulfonate can chemisorb to Au surfaces, possibly displacing the current ligands.$^{118}$

For Au$_{25}$ nanoclusters, phenylethane thiol is used as the stabilizing ligand and forms an integral part of the overall nanoparticle structure. Au$_{25}$ nanoclusters consist of a Au$_{13}$ core surrounded by a shell of 12 Au atoms held in place by bidentate thiol bonds. These bidentate bonds are what give Au$_{25}$ its well-known stability, and desorption would fundamentally change

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Figure 4.1: Structure of thiol-protected Au$_{25}$ nanoclusters. The structure consists of an icosahedral 13 Au atom core and a 12 Au atom outer shell. (Reprinted with permission (from Andrews et al., 2015). Copyright 2015 The Journal of the Electrochemical Society)

the structure of the nanoparticle surface. Larger nanoparticles are not as structurally dependent on their ligands, but surfaces can be restructured by adsorbates.$^{119}$

Thiolated Au$_{25}$ nanoclusters and thiolated or citrate protected 5 nm Au nanoparticles were synthesized and use as CO$_2$ reduction catalysts in Nafion™ and PVDF binders. The gas and liquid products were measured as a function of nanoparticle size, surface chemistry and binder. Onset potentials were characterized by voltammetry and XPS was used to study the effects of different binders on the Au charge.
Experimental

Synthesis

Au25 nanoclusters were prepared using established methods and integrated into conductive inks for subsequent use as electrodes. In the synthesis process, phenyl thiol-stabilized [Au25(SCH2CH3Ph)18]− clusters were made by solvating tetrachloroaurate(III)trihydrate (0.4 mmol HAuCl4•3H2O) in ultra-pure DI water and phase-transferring to toluene with tetraoctylammonium bromide (0.47 mmol TOAB). The aqueous layer was then decanted and the toluene solution containing the Au salt was purged with N2 and cooled to 0°C. Phenylethylthiol (0.17 mL PhCH2CH2SH) was added as a capping agent. The reduction was performed at 0°C by adding sodium borohydride (4 mmol NaBH4) in ultra-pure water at 0°C. The aqueous layer was decanted and the toluene solution was dried. CH3CH2OH was added to separate Au25 clusters from TOAB and other side products. The Au25 clusters were collected after removing the supernatant and purified by extracting twice with acetonitrile.

The 5 nm thiol-capped Au nanoclusters were made using other established methods and also integrated into conductive inks. In this synthesis procedure, HAuCl4•3H2O (0.25 mmol) was solvated in DI water and phase transferred into toluene via TOAB. The aqueous layer was then decanted and dodecanethiol added as a capping agent. The reduction was performed at 55°C using a tert butyl-amine borane complex (Sigma Aldrich). The toluene solution was evaporated and CH3CH2OH added to separate the 5 nm Au clusters from TOAB and other side products. The remaining nanoparticles were again dispersed in acetone. Other 5 nm Au nanoparticles with citrate termination were obtained commercially from BBInternational for use in spectroscopy studies.
Nanoparticle electrodes were made by depositing composite inks onto glassy carbon electrodes. The Au$_{25}$/Nafion™ and Au 5 nm/Nafion™ inks were prepared by mixing Vulcan XC-72R carbon black (100 mg), 5% Nafion™ (1.2 mL) (Sigma Aldrich), and ~10 mg of Au nanoparticles solvated in acetone (1 mL). Likewise, Au$_{25}$/PVDF and Au 5 nm/PVDF inks were prepared by mixing Vulcan XC-72R carbon black (100 mg), 5% PVDF solvated in N-methylpyrrolidone (1.2 mL) (Sigma Aldrich), and ~10 mg of Au nanoparticles solvated in acetone (1 mL). In this case, electrodes were synthesized using approximately 5 mL of citrate colloid solution (0.316 mg Au) mixed with 0.5 mL Nafion™ and 40 mg of carbon black. All ink mixtures were sonicated for 30 minutes before application to electrode surfaces. Inks were applied to 5 mm diameter glassy carbon electrodes in a Teflon sheath (Pine Instruments) using a brush and allowed to dry at room temperature for approximately 24 hours.

Characterization

Nanoparticles surfaces and solutions of nanoparticles were examined using XPS and UV-visible spectroscopy. Substrates specifically intended for XPS analyses were prepared in the same fashion using 1 cm$^2$ polished glassy carbon (STI) or Ag(111) single crystals. Au$_{25}$ samples including: Au$_{25}$ in toluene, Au$_{25}$ in acetone with 0.05% by weight Nafion™ and Au$_{25}$ in acetone with 0.05%wt PVDF before and after use in CO2 reduction reactions were deposited dropwise onto the surface and allowed to dry. Citrate-terminated Au colloid samples including 5 nm Au in water and 5 nm Au in water with 0.05%wt Nafion™ were prepared similarly. The samples were mounted onto Ta sample holders using graphite tape for transfer into the XPS system. All XPS experiments were performed in an ultra-high vacuum chamber with base pressure of 1 × 10−10 Torr. Measurements were performed using an Omicron XM1000 source providing monochromatic Al Kα$_1$ radiation ($h\nu = 1486.6$ eV) and a Specs PHOIBOS 150 hemispherical
analyzer. High-resolution spectra of the Au 4f region were recorded using 20 eV pass energy. Sample charging was not observed in any XPS spectra, as verified using the C 1s line from the glassy carbon substrate. Spectra were de-convoluted using the fitting routines available in CasaXPS.

UV-visible absorption characteristics of nanoparticle solutions were obtained using a Hitachi U-2001 NIR-UV-VIS Spectrophotometer in acetone (including solvent spectra subtraction). The Au$_{25}$ nanoclusters samples were freshly synthesized followed by the addition of 0.5%wt Nafion™ or 0.5%wt PVDF in n-methyl pyrrolidone (NMP). The same samples without Au$_{25}$ were also prepared to ensure other solvents or binders did not interfere with the Au$_{25}$ absorption peaks. Absorption spectra were recorded between 300 and 900 nm wavelengths.

Electrochemical Analysis

Aqueous electrochemical experiments were conducted in a two compartment cell with a Nafion™ membrane. The working and reference electrodes were in one compartment with a fitted tube for gas dispersion, and the reference electrode was in the second compartment. The catholyte was continuously bubbled with CO$_2$, and the vent led directly to a GC auto-injection port. A Pt wire was used as the counter electrode in the anolyte with an Ag/AgCl reference electrode. The saturated CO$_2$ solution included 0.1M KHCO$_3$ (Sigma Aldrich) and was operated at room temperature (22°C). The pH of carbonate electrolyte was measured at 6.8 when saturated with CO$_2$, and 8.9 when purged with N$_2$. These values were used when converting to the RHE scale. Voltammetry was conducted at a scan rate of 10 mV/s. Reaction yields were determined using potentiostatic experiments using gas chromatography (GC) (TCD & FID) or nuclear magnetic resonance spectroscopy (NMR) to analyze gas and liquid products (with a reaction time of at least 1h). Liquid samples were taken before and after each reaction and analyzed using
NMR spectroscopy (Varian System 700, 5 mm HCN probe) using methods reported by Kuhl et al..

Onset potentials were calculated by plotting the natural log of the current density against the potential, and then denoting when the line departed from linear behavior (Figure 4.2). The departures indicate an increase in electron transfer due to the CO\textsubscript{2} reaction taking place.

**Results**

Linear sweep voltammetry was used to study the current density and onset potentials of the CO\textsubscript{2} reduction reaction at several electrodes: Au foil, 5 nm Au nanocluster and Au\textsubscript{25} nanoclusters in both Nafion\textsuperscript{TM} and PVDF binders. As shown in Figure 4.3 and Figure 4.4, the

Figure 4.2: Natural log of current density of Au\textsubscript{25} in Nafion\textsuperscript{TM}. Dotted lines show the linear regions. The departure from linear behavior shows the onset of CO\textsubscript{2} reduction.
onset potentials for CO₂ reduction is dependent on both the size of the nanocluster and binder. At Au₂₅/PVDF electrodes, the CO₂ reduction onset is shifted anodically by 70 mV relative to Au foil while the onset potential with Au₂₅/ Nafion™ electrodes is shifted anodically by 190 mV relative to Au foil. Likewise, on 5 nm Au/PVDF electrodes the onset is shifted anodically by 60 mV relative to Au foil, while on 5 nm Au/Nafion™ electrodes the onset is shifted anodically by 140 mV relative to Au foil (Figure 4.4). Onset potentials for CO₂ reduction at Au foil (near -0.44V versus the RHE) and the shift observed with Au/Nafion™ electrodes are consistent with previous works; however, the effect of the binder (Nafion™ versus PVDF) is striking. Reduction current-potential behavior and current densities are similar in each case; note the current associated with composite electrodes is normalized by the exposed area based on electrode loading and specific area of the nanoparticles (~1.3 m²/gink for Au₂₅ and ~0.31 m²/gink for 5 nm Au).

The onset potential of the hydrogen evolution reaction (HER) in the absence of CO₂ was also studied using linear sweep voltammetry. As shown in Figure 4.5, the HER onset potential is shifted cathodically for both Au₂₅ (300 mV in Nafion™, 280 mV in PVDF) and 5 nm Au nanoparticles (250 mV in Nafion™, 210 mV in PVDF) relative to Au foil.

The combination of the anodic shifts for CO₂ reduction and cathodic shifts for the HER is extremely beneficial for the production of CO in terms of both selectivity and yield. Even relatively small shifts separating the onset potentials for CO reduction and HER can result in profound improvements on the practical ability to generate fuels due to the exponential current-overpotential relationship. This effect can be seen in the improved Faradaic efficiencies for CO production at lower overpotentials and relatively high current densities. As shown in Figure 4.6, the primary products of the reduction reaction were determined to be CO and H₂ along with trace...
Figure 4.3: Linear voltammograms of Au foil, Au<sub>25</sub>/Nafion<sup>TM</sup> and Au<sub>25</sub>/PVDF in CO<sub>2</sub> saturated 0.1M KHCO<sub>3</sub>. (Reprinted with permission (from Andrews et al., 2015). Copyright 2015 The Journal of the Electrochemical Society)

Figure 4.4: Linear voltammograms of Au foil, 5 nm Au/Nafion<sup>TM</sup> and 5 nm Au/PVDF in CO<sub>2</sub> saturated 0.1M KHCO<sub>3</sub>. (Reprinted with permission (from Andrews et al., 2015). Copyright 2015 The Journal of the Electrochemical Society)
Figure 4.5: Linear voltammograms of Au foil, Au$_{25}$/Nafion$^\text{TM}$, Au$_{25}$/PVDF, 5 nm Au/Nafion$^\text{TM}$ and 5 nm Au/PVDF in N$_2$ purged 0.1M KHCO$_3$. (Reprinted with permission (from Andrews et al., 2015). Copyright 2015 The Journal of the Electrochemical Society)

Figure 4.6: Faradaic efficiency plot for CO production of Au$_{25}$/Nafion$^\text{TM}$, Au$_{25}$/PVDF, 5 nm Au/Nafion$^\text{TM}$ and 5 nm Au/PVDF catalyst inks. (Reprinted with permission (from Andrews et al., 2015). Copyright 2015 The Journal of the Electrochemical Society)
amounts of CHOO⁻ (<1% Faradaic efficiency). The Faradaic efficiency of CO for Au_{25} clusters in the Nafion™ binder increased with cathodic potential, up to ~90% Faradaic efficiency at -0.8V versus RHE. At the same potential, Au_{25} clusters in PVDF binder reached CO Faradaic efficiencies near 55% while the larger 5 nm Au nanoparticles electrodes reached a maximum near 41% when using a Nafion™ binder. For comparison, these Faradaic efficiencies are significantly greater than those than for bulk Au at similar potentials (FE ~4.6% at -0.8V^{77}).

A key question centers on the nature of the improvement to the CO₂ reduction and HER onset potentials. Previous studies suggest that the improvement is due to the contributions of both the reduction site and surface chemistry of the nanoclusters. The anodic shift of CO₂ reduction is may be due to reduced CO binding energy at the low-coordinated active sites on the Au nanoclusters, as suggested by Peterson and Nørskov.\textsuperscript{124-127} In fact, a recent work by Peterson et al.\textsuperscript{79} demonstrates that CO generation is favored at the edge sites of Au nanowires while the HER is favored at corner sites, so nanowires with relatively high edge to corner ratios improve CO₂ reduction and suppress the HER. On the other hand, another work by Peterson et al. suggests that local environment (particularly oxides at Cu surfaces) can also influence CO₂ reduction selectivity.\textsuperscript{128} In the case of Au with thiolated surfaces, work by Jin et al. considers the unique interactions between CO₂ and Au_{25} (weakly bound) due to charge redistributions in the thiolated-Au_{25} clusters as the key mechanism responsible for improved CO₂ reduction behavior. In addition to promoting CO₂ reduction, it is also possible that the interfacial chemistry may interfere with H₂ formation. Adsorbed thiols are known to result in cathodic shifts in the onset potential for the HER on Au surfaces \textsuperscript{129} and the results from this study (Figure 4.5) also show cathodic shifts in HER onset potentials for all thiolated nanoparticle electrodes relative to Au foil.
In this case, the most dramatic differences in reduction behavior are the anodic shifts in CO$_2$ reduction associated with the binder (viz. Nafion$^{\text{TM}}$).

The voltammetry and Faradaic efficiencies obtained using either Au$_{25}$ or 5 nm Au nanoparticles suggest that the sulfonate moieties of Nafion$^{\text{TM}}$ provide a significant contribution for the observed shifts in onset potentials. In the case for Au$_{25}$ nanoparticles, the differences in onset potentials between the CO$_2$ reduction and HER were ~340 mV with Nafion$^{\text{TM}}$ versus ~220 mV with PVDF. The larger window (between CO$_2$ onset and HER onset) associated with Nafion$^{\text{TM}}$ could be related to reactions between the thiolated Au$_{25}$ nanoparticles and sulfonate

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Figure 4.7: Au4f XPS spectra. On the left, from bottom to top, Au$_{25}$ nanoparticles in toluene deposited on an Ag single-crystal substrate, an Au/ Nafion$^{\text{TM}}$ sample on glassy carbon prior to reaction, and an Au/ Nafion$^{\text{TM}}$ sample on glassy carbon after reaction. On the right, from bottom to top, Au$_{25}$ nanoparticles in toluene deposited on an Ag single-crystal substrate, an Au/PVDF sample on glassy carbon prior to reaction, and an Au/PVDF sample on glassy carbon after reaction. The vertical dotted lines indicate the binding energy of bulk Au. (Reprinted with permission (from Andrews et al., 2015). Copyright 2015 The Journal of the Electrochemical Society)
groups of the Nafion™ binder. Previous work by Negishi et al. suggests that sulfates can oxidize Au25, causing the formation of stable [Au25(SCH2CH2Ph)18]⁺ species;¹³⁰ however, these species should be easily reduced at the potentials used for CO₂ reduction. It is also possible that the equilibrium associated with the bidentate thiols is shifted by the relatively high concentration of sulfonates, leading to exchanging thiolates for sulfonates.

XPS was used to study the oxidation state of the Au in the nanoparticles. Figure 4.7 shows XPS spectra from three Au25 samples: 1. “as prepared” (bottom), 2. mixed with binders before the reaction (middle), and 3. the same electrodes after their use in CO₂ reduction for 15 minutes at -1.4V vs Ag/AgCl (top). The Au 4f peaks show the expected 3.7 eV split due to spin-orbit interactions, but both are shifted approximately 0.8 eV to higher binding energy compared to bulk Au. This shift is comparable to results previously found for Au25 nanoparticles synthesized through different methods, and has been attributed to initial-state effects due to the small particle size.¹³¹ The Au 4f peaks for the Au25/Nafion™ ink electrode (left side of Figure 4.7) shows the same set of peaks as the Au25 reference, but also shows two new shoulders with higher binding energies, including a smaller spin-orbit split (3.5 eV vs. 3.7 eV for the reference spectrum) associated with partially oxidized Au25 clusters. The majority of the spectra remains identical to those fit to the Au25 reference sample and suggests that core Au atoms may remain intact. These results suggest the equilibrium associated with high concentrations of sulfonates in the Au25/Nafion™ system may lead to sulfonated Au-binder interfaces. After the CO₂ reduction reaction, the shoulders remain; suggesting the new Au25 species in the Nafion™ binder may be relatively stable or is easily re-formed after the reduction reaction. The small peak shift observed between 0.2-0.7 eV after the reaction may be associated with partial desorption at cathodic potentials; however, this is not considered significant. As shown in Figure 4.8, another XPS
analysis using 5 nm Au nanoparticles made with either citrate or thiolate capping ligands show the same secondary peaks associated with sulfonated Au species arising when combined with Nafion™. In the case with the larger 5 nm Au nanoparticles, the relative area of the secondary peaks is somewhat smaller, consistent with the lower surface-to-volume ratio of the larger nanoparticles. Here it is important to note that ligand exchange (sulfonate for thiolate) in itself does not necessarily change the oxidation state of the Au;¹³² however, it may be possible that

Figure 4.8: Au 4f XPS spectra. The top spectra shows 5 nm citrate protected Au colloid sample on glassy carbon. The bottom spectra shows a 5 nm citrate protected Au colloid sample with a dilute Nafion™ binder on glassy carbon. (Reprinted with permission (from Andrews et al., 2015). Copyright 2015 The Journal of the Electrochemical Society)
sulfonates destabilize the initial bridge sulfur atom in the outer shell of Au$_{25}$ resulting in a oxide-like shell. This may result in relatively lower CO binding energies or it is also possible that the surfaces of the nanoparticles are reconstructed into relatively more active sites for CO$_2$ reduction.

UV-visible spectroscopy was used to evaluate to the structure of Au nanoparticles, shown in Figure 4.9. In the spectra for Au$_{25}$ nanoclusters (in acetone), there are absorption peaks at

Figure 4.9: UV-visible data showing the spectra for freshly synthesized Au$_{25}$ nanoclusters in acetone, Au$_{25}$ in acetone with dilute PVDF dissolved in NMP and Au$_{25}$ in acetone with dilute Nafion™ as well as control spectra for Nafion™, NMP and PVDF in acetone. Peaks at ~400, 450, and 670 indicate thiol bridged Au$_{25}$ clusters and are visible in the PVDF and fresh Au$_{25}$ samples, but not in the dilute Nafion™ sample. (Reprinted with permission (from Andrews et al., 2015).) Copyright 2015 The Journal of the Electrochemical Society)
~400, 450, and 670 nm which are indicative of the Au$_{25}$ structure, detailed in previous reports.\textsuperscript{133, 134} A second spectra taken after the addition of PVDF to the Au$_{25}$ solution indicates Au$_{25}$ nanoclusters retain a similar structure even after exposure to PVDF. The peak strength is lower due to dilution, but the peak locations are otherwise unchanged. In contrast, after the addition of Nafion\textsuperscript{TM} to the Au$_{25}$ solution, the peaks at 400 and 670 nm are lost, and the peak at 450nm is shifted to a higher wavelength suggesting either an agglomeration or alteration of the nanoparticle. While it is possible that some Au$_{25}$ particles may agglomerate in the liquid phase used for UV-visible spectroscopy, the Au$_{25}$ spectra in PVDF and the spectra in Nafion\textsuperscript{TM} remained constant over several hours and did not resemble the spectra associated with the larger 5 nm Au particles. This behavior along with the voltammetry, yields and XPS analyses suggests that the particles likely remain as 25 atom clusters albeit with an altered structure.

As noted previously, the sulfonate interaction is somewhat unexpected, since the thiolates are generally considered to be relatively stable, especially on magic-number nanoclusters.\textsuperscript{130, 135, 136} However, it is possible the relatively high concentrations of sulfonate moieties shift the equilibrium to favor sulfonated Au$_{25}$ interfaces, resulting in a beneficial condition for CO$_2$ reduction. The enhanced CO$_2$ reduction observed with Nafion\textsuperscript{TM} binders was observed using both 5 nm Au and Au$_{25}$ nanoparticles suggesting that the primary origin of the decreased CO$_2$ onset potentials may be associated with sulfonate interactions rather than the anionic charge associated with Au$_{25}$. While the surface chemistry and preferential reduction sites remain unknown under reduction conditions, it is possible that the Au-sulfonate interface remains intact during the reduction and induces changes in the binding strength of adsorbed CO$_2$, CO or other intermediates similar to the role of Cu oxides as described by Peterson et al.\textsuperscript{128} It is also possible that the sulfonates contribute to a reconstruction of the Au surface generating sites that are
relatively more active to CO$_2$ reduction (similar to the oxygen-induced restructuring of Au surfaces observed by Friend et al.$^{137}$). In either case, there is considerable evidence that surface chemistry of the electrocatalyst plays a strong role in CO$_2$ reduction behavior and that these interface effects may be leveraged to improve selectivities and/or Faradaic efficiencies.

**Conclusion**

The close proximity of the formal potentials for the electrochemical generation of CO and H$_2$ form a fundamental barrier to realizing the efficient production of fuels from CO$_2$. Here, we demonstrate nanoscale Au electrocatalysts and interfaces that are particularly useful in promoting CO$_2$ reduction while preventing the HER. As shown in linear sweep voltammetry and Faradaic efficiencies, Au nanoclusters immobilized in Nafion$^\text{TM}$ are significantly more active at reducing CO$_2$ to CO than the same Au nanoclusters immobilized in PVDF binders. The sulfonate environment appears to provide a $\sim$170 mV anodic shift in the onset for CO$_2$ reduction with Au$_{25}$ nanoparticles and a $\sim$140 mV shift in the onset with 5 nm Au nanoparticles versus Au foil, whereas are the shifts are only 70 mV and 60 mV (respectively) for the same nanoparticles in PVDF binders. The results indicate that surface chemistry plays a substantial (perhaps dominant) role in determining selectivity relative to the size or initial charge of the nanoparticles. Based on the XPS results, the underlying mechanism for the improved Faradaic efficiencies for CO production may be attributed changes in the binding energies of CO$_2$, CO or other intermediates induced by the Au-sulfonate surface or favorable reconstructions in the presence of sulfonates (or a combination of these effects). In either case, the results demonstrate the pronounced influence of surface chemistry in designing and controlling selectivity of CO$_2$ reduction reactions.
CHAPTER 5: ALLOY NANOPARTICLES

Introduction

Nanoparticle alloys are promising potential catalysts for the electroreduction of CO\textsubscript{2} to hydrocarbons due to their high amount of low coordination active sites and their controllable intermediate binding energies. Alloy catalysts such as CuAu\textsuperscript{138, 139} and CuIn\textsuperscript{83} have been experimentally shown to be capable of improving CO\textsubscript{2} reduction activity compared to bulk foils and at decreased overpotentials. Likewise, catalysts such as Au nanoclusters\textsuperscript{77} and Cu nanoparticles\textsuperscript{140} have displayed activity over twice that of foils. As seen from the CuZnO samples detailed earlier, they can also alter the selectivity towards alcohols given the right support.

Density functional theory calculations have also shown that alloys can potentially outperform their component transition metals, which are thermodynamically limited. Hansen et al. show that the binding energies of the *CO and *COOH intermediates adsorbed on transition metal surfaces follow linear scaling relationships.\textsuperscript{5, 54} On all transition metals, the adsorption energies of the *CO, *COOH and *CHO intermediates are proportional in such a way that the reaction energetics and pathways are not altered by the electronic properties of the catalyst.\textsuperscript{54} This limitation suggests that the optimal pathways for CO\textsubscript{2} reduction to hydrocarbons cannot be obtained using transition metal electrodes, although Cu is nearest to the optimal spot.\textsuperscript{5}

Regarding alloys, Hirunsit et al. has shown using DFT calculations that alloys offer alternate pathways to desired products such as CH\textsubscript{4} and CH\textsubscript{3}OH. The DFT claims Cu\textsubscript{3}Au, Cu\textsubscript{3}Ag, Cu\textsubscript{3}Ir, Cu\textsubscript{3}Co, Cu\textsubscript{3}Ru and Cu\textsubscript{3}Ni should all have pathways to CH\textsubscript{4} from *CHO and *COH, while Cu\textsubscript{3}Pt and Cu\textsubscript{3}Pd should possess a path to CH\textsubscript{3}OH.
Here, CuCo and CuAu nanoparticles are evaluated as CO\textsubscript{2} reduction catalysts. Cu microparticles were used to verify the experimental procedure in multiple conductive binder inks. CuCo supported on silica has previously been verified as an CH\textsubscript{3}CH\textsubscript{2}OH catalyst in gas phase synthesis, making it a possible candidate for CO hydrogenation in the liquid phase.\textsuperscript{141}

\textbf{Materials and Methods}

\textbf{Cu Microparticles}

Spherical Cu microparticles with diameters of \textasciitilde10 \textmu m were purchased commercially from Sigma Aldrich. The microparticles were immobilized into Nafion\textsuperscript{TM}, polyvinylidene fluoride (PVDF) and styrene-butadiene rubber (SBR) binder inks. The inks were made from either 10 mg or 40 mg of Cu microparticles, 100 mg carbon black and 50 mg binder dissolved in 2 mL of appropriate solvent. The ink was sonicated and applied by brush to a glassy carbon substrate in a Teflon\textsuperscript{TM} holder.

\textbf{CuCo Nanoparticles Supported on MoO\textsubscript{3}}

CuCo nanoparticles supported on MoO\textsubscript{3} were synthesized in a dry procedure by Prof. Petra Dejonhg’s group from Utrecht University. The nanoparticles were immobilized in a Nafion\textsuperscript{TM} binder ink. The ink was made by mixing 40 mg of nanoparticles, 100 mg carbon black, 1.3 mL Nafion\textsuperscript{TM} 5\% resin (Sigma Aldrich) and 1 mL acetone. The ink was sonicated and applied by brush to a glassy carbon substrate in a Teflon\textsuperscript{TM} holder.

\textbf{CuAu Nanoparticles}

The 2 nm nanoclusters were synthesized using the following procedure modified from Hostetler et al. and Yin et al.\textsuperscript{142,143} HAuCl\textsubscript{4} \textsubscript{xH\textsubscript{2}O and CuCl\textsubscript{2} were dissolved in DI water along with KBr. Cu/Au molar ratios were altered to match desired alloy. Tetraoctylammonium bromide
(TOAB) was dissolved in toluene. The solutions were stirred together until the aqueous solution was clear, indicating the phase transfer of the ions. Dodecanethiol (600 µL) was added and the solution was stirred for until the toluene phase became clear. 0.5 g of NaBH₄ in DI water was slowly added to the solution, resulting in a brown color. The solution was stirred for 3 hours and the aqueous phase removed by pipette. The toluene solvent was evaporated under vacuum and the nanoparticles washed and filtered with CH₃CH₂OH.

The 6 nm nanoclusters were synthesized using a modified procedure based on literature.²⁴³,²⁴⁴ 2 nm nanoparticles were synthesized following the previous procedure, but after removing the aqueous phase, the toluene was evaporated to give a nanoparticle solution of ~15x concentration. The resulting solution was sealed in glass reactor and heated at 150°C for 2 hours. The remaining toluene was evaporated under vacuum and the nanoparticles washed and filtered with CH₃CH₂OH.

Electrodes were prepared by mixing the nanoparticles with carbon black inks using Nafion™ as a conductive polymer binder. 100 mg carbon black was mixed with 50 mg of Nafion™ resin and 10 mg of nanoparticles in 2 mL acetone then sonicated for 30 minutes to ensure even dispersion. Ink was applied to a glassy carbon electrode in a Teflon™ holder by paintbrush, giving a nanoparticle loading of 0.06 mg/cm².

CuAu Bulk Foils

Bulk CuAu foils were obtained commercially from ESPI metals. The alloys were 10%, 25% and 50% Au by weight, corresponding to molar ratios of Cu₇₅.₆Au₂₄.₄, Cu₉₀.₃Au₉.₇ and Cu₉₆.₆Au₃.₄ respectively. Several 1 cm² squares were cut from the foils and used as working electrodes for electrolysis.
TEM

Transmission electron microscopy (TEM) samples were prepared by dispersing dilute samples in toluene onto Cu mesh grids.

XPS

X-ray photoelectron spectroscopy (XPS) was used to determine the Cu:Au ratios of the nanoparticles after synthesis.

Electrochemical Analysis

Electrochemical experiments were performed in a two-compartment cell with a Nafion™ membrane as described in a previous work. 0.1M KHCO₃ was used as the electrolyte. The catholyte in the working compartment was continuously bubbled with CO₂ which was vented to a gas chromatograph injection port (Shimadzu GC-2014). The reference electrode was Ag/AgCl, and the counter electrode was a Pt wire. The pH of carbonate electrolyte was measured at 6.8 when saturated with CO₂, and 8.9 when purged with N₂, and used for converting to the RHE scale. Voltammetry was conducted at a scan rate of 10 mV/s. Onset potentials were calculated by plotting the natural log of current against voltage and determining where the curve departed from linear behavior. Reaction yields were determined using potentiostatic experiments using gas chromatography (TCD & FID).

The yield data was normalized using the surface area of the nanoparticles in order to compare nano and bulk scale catalysts. Surface area normalization was also necessary to compare nanoparticles of the same size, as the density of the alloy changes with composition.
Results and Discussion

Cu Microparticles

The 15µm Cu microparticles were tested in Nafion™, SBR and PVDF binders in order to verify the experimental procedure. Gas chromatography on the Cu microparticles found H₂ to be the major product, and CH₄ and CO as notable minor products. The different binders were evaluated by the amount of CH₄ produced. Both Nafion™ and PVDF were found to give similar yields of CH₄ at appropriate nanoparticle concentrations, though SBR was a poor binder for this procedure. CH₄ was produced at up to 25% Faradaic efficiency, less than reported on Cu foils, but as expected of low coordination Cu.⁶²,¹⁴⁰ As Nafion™ and PVDF gave similar results, it was decided to use Nafion™ for the remainder of the procedures.

CuCo Nanoparticles

Cyclic voltammetry on the CuCo nanoparticles showed a small anodic shift in onset potential for the Cu₁Co₁ nanoparticles compared to Cu₃Co₁. However, the Cu₃Co₁ nanoparticles were found to produce more CH₄ and CO at similar potentials. At -1.4V vs RHE, the CH₄ Faradaic efficiencies were 2.7% for Cu₃Co₁ and 0.6% for Cu₁Co₁ while the CO Faradaic efficiencies were 9% and 2% respectively. Liquid analysis showed trace amounts of propanol and CHOO⁻ for both CuCo compositions.

CuCo produces hydrocarbons at a lower selectivity compared to bulk Cu or the Cu microparticles. This is likely caused by the addition of Co. Co has an overly strong CO bond strength, similar to Fe and Ni, and as a pure foil, produces >99% hydrogen.⁴⁶,¹⁴⁵ In Fischer-Tropsch reactions on CuCo, Co provides an adsorption site for CO, resulting in the formation of C₂ compounds, while Cu produces CH₃OH. However, in electrochemical reduction at the
Cu$_1$Co$_1$ and Cu$_3$Co$_1$ compositions, the CO adsorbs on Co so strongly as to act as a poison, resulting in the lowered selectivity towards hydrocarbons. The relatively higher CO and CH$_4$ selectivity of the Cu$_3$Co$_1$ nanoparticles suggests that Co is not beneficial to the CO$_2$ reduction reaction in this system. Interestingly, on Cu$_3$Co$_1$, the selectivity towards CO was increased despite the decreased hydrocarbon efficiency, which implies that the hydrogenation of CO was decreased despite the improved CO bond strength. This may be due to the nanoparticle size effect similar as noted by Reske et al. on Cu nanoparticles, where small diameter nanoparticles displayed lowered hydrogenation due to the immobility of CO and H$^+$ on the surface.$^{64}$

Figure 5.1: Faradaic efficiency of CH$_4$ using Cu microparticles immobilized in Nafion$^\text{TM}$, PVDF and SBR at concentrations of 10 mg Cu/50 mg binder and 40 mg Cu/50 mg binder.
Figure 5.2: On the top is the Faradaic efficiency for the gas products of CO$_2$ reduction on Cu microparticles immobilized in a Nafion$^{\text{TM}}$ binder. On the bottom are the yields for the gas products, normalized to the geometric area of the electrode.
While a metal with high CO affinity such as Co did not improve the formation of hydrocarbon products due to its overly strong bond energy, a low CO affinity metal could give the CO and adsorbed protons more surface mobility on nanoscale catalysts, allowing for hydrogenation to occur via surface hydrogen. As a result, CuAu was chosen as the next nanoparticle alloy to be evaluated as its bulk form has been shown to enhance CO$_2$ reduction yields compared to plain Au and Cu.

CuAu Nanoparticles

Following synthesis, the CuAu nanoparticles were characterized and integrated into electrodes for use in CO$_2$ reduction experiments. TEM was used to verify the size of the synthesized nanoparticles (Figure 5.5). The 2 nm nanoparticles were a uniform size. The heat
Figure 5.4: The gas product yields of CO$_2$ reduction, normalized to the geometric electrode area. On the top is Cu$_1$Co$_1$. On the bottom is Cu$_3$Co$_1$. 
Figure 5.5: TEM scans of Cu$_{68}$Au$_{32}$ 2 nm nanoparticles (left) and Cu$_{38}$Au$_{62}$ 6 nm nanoparticles (right).
treated 6 nm nanoparticles showed slightly more variance as well as a few 2 nm nanoparticles that did not aggregate, but were considered acceptable for the purposes of this experiment.

The molar composition was evaluated by comparing the relative areas of the Cu 2p and Au 4f peaks. The Cu 2p peaks are at 932 eV and the Au 4f peaks are at 84 eV, which is consistent with metallic nanoparticle Cu and Au. Remarkably, the molar ratio of the nanoparticles was different before and after the heat treatment, with the nanoparticles apparently

Figure 5.6: XPS scans of the 6 nm Cu 2p (top left) and Au 4f (bottom left) peaks and 2 nm Cu 2p (top right) and Au 4f (bottom right) peaks.
becoming more Au rich. This may be due to the movement of Au to the outside of the nanoparticle during heating due to its lower surface energy, causing slight segregation.\textsuperscript{146}

Foil alloys were used to set a baseline for comparison with the nanoparticles alloy electrodes. Figure 5.7 shows the CO yields of the bulk alloy foils as well as individual Cu and Au foils. All alloy foils show higher CO yields compared to individual Cu and Au foils, with the Cu\textsubscript{75}Au\textsubscript{25} foil yielding the most. At -1.0 V vs RHE, Cu\textsubscript{75}Au\textsubscript{25} foils yield 3.4 times more CO than bulk Au foil and 22.3 times more than bulk Cu foil. However, Au foil showed a higher Faradaic efficiency than Cu\textsubscript{90}Au\textsubscript{10} and Cu\textsubscript{96}Au\textsubscript{4} alloys at lower overpotentials, likely due to the increased H\textsuperscript{+} affinity of Cu (Figure 5.8). This is consistent with the results published previously by Christophe et al.\textsuperscript{139}

The 2 nm alloy nanoparticles’ CO yields and Faradaic efficiencies are shown in Figure 5.9 and Figure 5.10 respectively. The Cu\textsubscript{25}Au\textsubscript{75} alloy gave the highest CO yield, peaking at 1.47 mmol/cm\textsuperscript{2}/h and producing ~9 times the CO yield as 2 nm Cu\textsubscript{70}Au\textsubscript{30} at -1.1 V vs RHE. Cu\textsubscript{25}Au\textsubscript{75} also had the greatest peak CO Faradaic efficiency of 37%, while Cu\textsubscript{70}Au\textsubscript{30} possessed only 22% Faradaic efficiency towards CO. Cu\textsubscript{68}Au\textsubscript{32} showed a maximum yield of 0.65 mmol/cm\textsuperscript{2}/h and a Faradaic efficiency of 28%.

The 6 nm alloy nanoparticles’ CO yields and Faradaic efficiencies are shown in Figure 5.11 and Figure 5.12 respectively. Cu\textsubscript{38}Au\textsubscript{62} gave the highest CO yield, peaking at 8.8 mmol/cm\textsuperscript{2}/h with a Faradaic efficiency of 50%. Despite having a lower relative yield of 5.7 mmol/m\textsuperscript{2}/h, Cu\textsubscript{9}Au\textsubscript{91} possessed the greatest Faradaic efficiency towards CO with a maximum of 73%. Cu\textsubscript{59}Au\textsubscript{41} showed a maximum yield and Faradaic efficiency of 1.25 mmol/cm\textsuperscript{2}/h and 18% respectively.
Figure 5.7: CO yield on bulk CuAu, pure Au and pure Cu foils. Yields are normalized to foil surface area.

Figure 5.8: Faradaic efficiency of CO on bulk CuAu, Au and Cu foils.
Figure 5.9: CO yield on 2 nm CuAu nanoparticle catalysts. Yields are normalized to the surface areas of the nanoparticles.

Figure 5.10: Faradaic efficiency of 2 nm CuAu nanoparticle catalysts.
The onset potentials for CO$_2$ reduction are shown in Table 5.1. The onset potential is not heavily dependent on alloy composition, with catalysts of the same size having potentials within 50 mV windows. However, the size of the catalyst has a significant effect on the onset potential. The 6 nm nanoparticle electrodes show at least a 200 mV anodic shift compared to bulk alloys, and the 2 nm nanoparticles show at least a 150 mV anodic shift. The onset potentials for the HER are given in Table 5.2. While there was some cathodic shift in HER onset, it was not significant relative to that observed with CO$_2$ reduction.

Comparing the foils, 2 nm nanoparticles and 6 nm nanoparticles, a clear size effect is observed, with the 2 nm and 6 nm nanoparticles producing one and two orders of magnitude more CO than foils respectively. At their maximums, the 6 nm nanoparticles (Figure 5.11) yield 8.8 mmol/cm$^2$/h of CO, the 2 nm nanoparticles (Figure 5.9) yield 1.47 mmol/cm$^2$/h and the foils (Figure 5.7) yield only 0.175 mmol/cm$^2$/h. The relatively high activity of the 6 nm nanoparticles compared to the 2 nm nanoparticles is somewhat surprising. The difference may be due to the size effects observed on small nanoparticles where there are optimal particle sizes for reaction activity. For example, Pt nanoparticles used for oxygen reduction lose activity at sizes smaller than 2 nm.\textsuperscript{147, 148} The electrode morphology and binder may also play a role in the activity of small particle electrodes; smaller nanoparticles are more likely to be trapped in internal pores, limiting their access to CO$_2$.\textsuperscript{149} However, the most likely explanation is that the CO$_2$ reduction active sites on a 6 nm are denser than on a 2 nm nanoparticle. The edge site to corner site ratio is higher on a larger diameter spherical nanoparticle,\textsuperscript{150} and as shown by Zhu et al., metal catalysts with high edge to corner ratios such as Au nanowires are very active for CO$_2$ reduction.\textsuperscript{79} Mistry et al. show that Au nanoparticles in the 2-8 nm size range have significant size effects, where H$_2$ selectivity increases as the particle size decreases, a result attributed to the higher ratio of corner
Figure 5.11: CO yield on 6 nm CuAu nanoparticle catalysts. Yields are normalized to the surface areas of the nanoparticles.

Figure 5.12: Faradaic efficiency of CO on 6 nm CuAu nanoparticle catalysts.
Table 5.1: CO$_2$ reduction onset potentials in CO$_2$ saturated 0.1M KHCO$_3$

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<td>Cu$<em>{70}$Au$</em>{30}$ -0.26</td>
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Table 5.2: HER formation onset potentials in N$_2$ purged 0.1M KHCO$_3$

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sites where H₂ evolution is preferred. The relatively low CO Faradaic efficiency of the 2 nm CuAu nanoparticles compared to CuAu foils matches this observation. Despite the improved yields, the overall selectivity shifts towards hydrogen.

More importantly, when comparing alloy nanoparticles to pure bulk foils, we observe a two order of magnitude increase in CO yields. At -1.1 V vs RHE, 6 nm Cu₃₈Au₆₂ produces CO at ~50 times the yield of bulk Cu₇₅Au₂₅, and at ~175 times the yield of bulk Au. Previous reports involving CO₂ reduction on 1.9 nm and 4.8 nm Cu nanoparticles and 2 nm and 6 nm Au nanoparticles have described single order of magnitude, increases (9x and 40x for Au 6 nm and 2 nm nanoparticles respectively at -1.2 V vs RHE). Moreover, the increase in CO yields for the nanoparticle electrocatalysts is accompanied by a shift in onset potentials unlike the foil electrocatalysts.

Alloy composition effects were readily observed in both the foil and the 2 nm and 6 nm nanoparticle electrodes, with a larger Au ratio in the alloy generally correlating to a greater CO yield. At -1.0 V vs RHE, the Cu₇₅Au₂₅ alloy foil yields ~1.2 times more CO than the Cu₉₀Au₁₀ and Cu₉₆Au₄ foils. Similarly, at -1.1 V vs RHE, the 2 nm Cu₂₅Au₇₅ produces ~9 times the CO yield as the 2 nm Cu₇₀Au₃₀ and the 6 nm Cu₃₈Au₆₂ produces ~11 times the CO yield as the Cu₅₉Au₄₁. However, the 6 nm Cu₉Au₉₁ nanoparticles yield ~50% less CO than the 6 nm Cu₃₈Au₆₂ nanoparticles, despite having a Faradaic efficiency of 77% towards CO. An excess of Au content may result in higher Faradaic efficiency, up to the >95% seen from the pure Au nanoparticles from Kauffman et al., but decrease the net catalytic activity. There may be an optimum CuAu alloy ratio for CO yield between the Cu₃₈Au₆₂ and Cu₉Au₉₁ compositions.
The increased yields have been attributed to improved CO desorption on alloys due to weakened CO bond energy on Cu.\textsuperscript{139} Alloying the metals results in a change in electronegativity, showing a shift in electron charge of ~0.2 eV towards Au.\textsuperscript{151} This results in improved Au binding sites for CO, which is an electron acceptor, primarily bonding to the surface via pi orbitals, and prefers to bind at metal sites with electron rich d orbitals.\textsuperscript{152} Likewise, *COOH is expected to be stabilized on CuAu alloy corner sites.\textsuperscript{153} As such, *CO and *COOH bonded to CuAu will be less stable relative to Cu surfaces, but more stable than Au.

There are several explanations for the underlying nature of the dramatic improvements in CO yield observed with nanoparticle CuAu alloys. Christophe et al. proposed that electronic effects can alter the bond strength of CO, causing an increase in kinetics.\textsuperscript{139} Hirunsit et al. have used DFT calculations to reach a similar conclusion, showing that the adsorption energy of *CO is 0.19 eV weaker on Cu\textsubscript{75}Au\textsubscript{25} than on Cu and that the change in bond energy plays a role on several alloys.\textsuperscript{154,155} The most significant yield increases are associated with nanoparticle alloys. Kim et al. proposed that the presence of Cu adjacent to Au surface atoms also increases the stability of the *COOH intermediate by allowing a single *COOH to bond to both Au and Cu atoms.\textsuperscript{138} The Cu atom is the more oxyphilic of the two metals, so the C atom bonds to the Au, and an O to the Cu. As the alloys increase in Au content, the number of Cu sites with neighboring Au atoms increases, which contributes towards the increase in CO yield. The aforementioned reactions are most likely to occur at low-coordinated sites and thus the alloy effect is more pronounced at the nanoscale. Other groups utilizing alloys such as CuIn,\textsuperscript{83} Cu\textsubscript{3}Ni,\textsuperscript{156} and AuCd\textsuperscript{157} have also proposed bimetallic active sites as the key part of the electrocatalysts; however, DFT calculations of CuAu alloy nanoclusters performed by Lysgaard et al. suggest no O-Cu bonds were formed by *COOH in their simulation, although Au edge and
apex sites adjacent to Cu were still preferred for reactivity. Other works propose the metal with lower surface energy (Au in this case) is observed to migrate to the surface, causing the alloy to act similarly to the segregated surface metal. Likewise, works considering intentionally segregated electrocatalysts such as core-shell nanoparticles and thin overlayers have noted the lattice strain as another factor affecting the reaction. In all cases, edge sites and other low coordination sites such as grain boundaries are identified as the key active sites for CO$_2$ reduction.

The results from this work suggest that the dramatic yield increases originate from both improved deoxygenation of CO$_2$ at Cu and the reduced adsorption energy of CO at Au. Likewise, the remarkable increases in yield associated with nanoscale CuAu alloys suggest that the relative impact of these effects are significantly greater at low-coordinated Cu-Au interfaces, as the 6 nm nanoparticles which have the highest ratio of edge sites give the greatest CO yield. It was also found that the nanoparticles with higher Au ratios were more favorable for CO formation which is in agreement with DFT by Lysgaard et al.. The DFT suggests that Au heavy surfaces with Cu cores are the most stable structurally and have similar adsorption strength to pure Au nanoparticles, though CuAu bimetallic sites are the most preferred for CO adsorption.

**Conclusion**

Cu microparticles showed that the effects of the binder were less pronounced on microscale particles than on nanoparticles. However, the microparticles produced far less CH$_4$ than foil Cu due to size effects.

The Cu$_5$Co$_1$ supported on MoO$_3$ showed H$_2$ at up to 69% Faradaic efficiency as a majority product, as well as 2.7% CO and 0.6% CH$_4$. While the selectivity towards CO and CH$_4$
were higher on the alloy nanoparticle than on Co foil, both had lower selectivity than would have been expected from a pure Cu nanoparticle of similar size, indicating that Cu alloyed with a high CO affinity metal would not improve CO hydrogenation or CO$_2$ reduction, contrary to expectations.

CO yields from CuAu alloy electrodes are significantly greater than either pure Au or Cu electrocatalysts. While the alloy effect leads to a ~3x increase in CO yields at foil electrodes, CO yields increase by more than 175x with the use of CuAu nanoparticles. In addition to the increased yields, voltammetry shows reduction CO$_2$ reduction onset potentials are shifted anodically by >150 mV for 2 nm alloys and >200 mV for 6 nm alloy electrodes. Likewise the increased yields and anodically shifted onset potentials are associated with an increase in edge sites and the synergistic electronic effects of CuAu alloys on the nanoparticle alloy electrodes. These results suggest CuAu alloys, particularly low-coordinated interfaces thereof, improve both the deoxygenation CO$_2$ and desorption of CO.
CHAPTER 6: NiAg AND FeAg

Introduction

As the bimetallic sites on previously examined CuAu nanoparticles were found to be extremely beneficial, other methods of combining metals were attempted. Similar to the metal-oxide interfaces of CuZnO, depositing nanoparticles on a transition metal substrate can provide metal-metal interfacial sites. By combining metals with high hydrogen affinity that would normally be poisoned by CO with metals that have low CO affinity, one could theoretically create a catalyst able to readily hydrogenate CO and desorb the product at the bimetallic active sites.

Ni and Fe metals have overly strong CO bond strengths, making them poor CO₂ reduction catalysts. Unmodified, Fe produces >94% H₂ and no hydrocarbon products while Ni produces >90% H₂ and 2% CH₄. Meanwhile, low CO bond strength Ag foils produce 82% CO, 12% H₂ and 0.8% CHOO⁻. Literature DFT calculations show that the bond strengths of Ni and Fe can be tempered by the addition of other metals, such as Ag, Au or Cu.

Unfortunately, Ni and Fe are thermodynamically insoluble with Ag, making NiAg or FeAg alloys impossible to create using traditional metallurgical methods. In order to create the desired bimetallic active sites, alternative fabrication methods must be considered. Metal nanoparticles can be deposited on a conductive substrate using electrochemical deposition. For example, depositing Ag nanoparticles on a Ni substrate will result in a catalyst possessing Ag-Ni interfacial sites. Simultaneous deposition can also create a surface with bimetallic interfaces. By simultaneously depositing two normally immiscible metals, a metastable alloy can be created.
However, segregation can still occur under experimental conditions, with Ni preferring to migrate to the surface. Here, Ni/Ag and Ag/Fe supported nanoparticle catalysts are created by electrodeposition and the products of CO₂ electroreduction measured. A metastable NiAg alloy was created using simultaneous electrodeposition and used as a CO₂ electroreduction catalyst.

**Experimental**

**Ag/Fe**

A Fe foil was cleaned via exposure to HCl and dried with a stream of N₂ gas. The Fe foil was immersed in a 5mmol AgNO₃ solution, and a current of 1 μA was applied for 300 s.

**Ni/Ag**

A Ag foil was cleaned via exposure to HCl and dried with a stream of N₂ gas. The Ag foil was immersed in a Ni plating solution (NiCl₂, NiSO₄, H₃BO₃) and a current of 1μA was applied for 300 s.

**NiAg Codeposition**

A graphite rod was immersed into a Ni-Ag plating solution (Citrate, NiSO₄, AgNO₃) and held at a current of 1 mA for 900 s as described in literature.

**Electrochemical Analysis**

Electrochemical experiments were performed in a two-compartment cell with a Nafion™ membrane as described in a previous work. 0.1M KHCO₃ was used as the electrolyte. The catholyte in the working compartment was continuously bubbled with CO₂ which was vented to a gas chromatograph injection port (Shimadzu GC-2014). The reference electrode was
Ag/AgCl, and the counter electrode was a Pt wire. The pH of carbonate electrolyte was measured at 6.8 when saturated with CO$_2$, and 8.9 when purged with N$_2$, and used for converting to the RHE scale. Voltammetry was conducted at a scan rate of 10 mV/s. Reaction yields were determined in potentiostatic experiments combined with gas chromatography (TCD & FID).

**Results and Discussion**

**Characterization**

Metal supported nanoparticle samples were characterized by scanning electron microscopy (SEM). Ag/Fe electrodes showed Ag deposited on the Fe, but with a wide size variance and low surface coverage. The individual particles were separated. Ni/Ag electrodes showed Ni to have a low surface coverage, and that the Ni formed in clusters rather than individual particles.

**CO$_2$ reduction**

CO$_2$ was reduced on Ag/Fe electrodes after deposition and the gas phase products measured using GC. H$_2$, CO and CH$_4$ were the observed products, as seen below in Figure 6.3. The presence of CH$_4$, even at Faradaic efficiencies as low as 0.5%, is remarkable, as CH$_4$ is not observed on pure Fe or Ag catalysts. However, H$_2$ is still the majority product at near 100% efficiency. This is likely due to the extremely low surface coverage of Ag leading to very few Ag-Fe interfacial sites, and thus few places for CH$_4$ to form. As most of the catalyst surface is Fe, it is inactive for CO$_2$ reduction, producing only H$_2$. However, it is unlikely that simply increasing the nanoparticle surface coverage will provide the necessary amount of interfacial sites to produce CH$_4$ at a desirable selectivity. For the Ni/Ag catalysts, the Ag was used as the supporting metal, as Ni sites lacking Ag interfaces will get poisoned by CO.
Figure 6.1: SEM images of Ag nanoparticles electrodeposited on Fe foil.
Figure 6.2: SEM images of Ni nanoparticles electrodeposited on Ag foil.
The Ni/Ag electrodes were used as CO\(_2\) reduction catalysts, producing H\(_2\), CO and CH\(_4\) (Figure 6.4). At -1.12V, faradaic efficiencies of 36% H\(_2\), 32% CO and 0.5% CH\(_4\) was observed. Compared to bulk Ag electrodes found in literature, which produce ~80% Faradaic efficiency CO at the same potential, the CO selectivity is low\(^{171}\). However, CH\(_4\) is not normally produced by Ag electrodes at that potential and is likely due to the Ni nanoparticles on the surface. Ni foil produces CH\(_4\) at a Faradaic efficiency of 2%, although the Ni will simultaneously be poisoned by CO\(^{95}\). Similar to Ag/Fe, Ni/Ag interfacial sites change the product distribution of CO\(_2\) reduction, but unmodified sites still behave as the regular metals, which at low surface coverage levels

Figure 6.3: Gas product yields of CO\(_2\) reduction on Ag/Fe in 0.1 M KHCO\(_3\).
means only minor changes in product distribution. In order to achieve significant CH$_4$ yields and Faradaic efficiencies, a more homogenous mixing of the two metals is required.

As NiAg alloys are immiscible through metallurgical mean simultaneous deposition was used to process NiAg electrodes.\textsuperscript{172} As seen in Figure 6.5, simultaneously deposited NiAg alloy yielded H$_2$, CO and CH$_4$ as products. At -1.10V, CH$_4$ was observed at a Faradaic efficiency of ~2%, CO at 0.5% and H$_2$ at 99%, similar to Ni foil except for the trace amount of CO. A poisoning effect was observed, where there Ni surface turned dark as the reaction proceeded, indicating the buildup of carbon.\textsuperscript{173}
The data point at -1.03V was repeated with a simultaneous deposition NiAg alloy with a greater Ag content, giving Faradaic efficiencies of 95% $\text{H}_2$, 1.5% CO and 2% $\text{CH}_4$. The increase in CO is likely due to the slight increase in Ag content. The same discoloration from CO poisoning was also observed.

The bimetallic catalysts all displayed small changes to the expected product yields or Faradaic efficiencies of $\text{CO}_2$ reduction, but did not deviate far from the majority metal. Ag/Fe performed similarly to bulk Fe, Ni/Ag behaved most like bulk Ag, and simultaneous deposition NiAg performed almost identically to bulk Ni. On the electrodeposited nanoparticle catalysts, the low surface coverage of nanoparticles was thought to be responsible, as most active sites did not
benefit from the bimetallic nature of the catalyst. The NiAg simultaneous deposition process was chosen in order to create an alloy surface consisting mainly of bimetallic sites. Another expected benefit of alloying Ni and Ag was the reduction of intermediate adsorption energies.\textsuperscript{165} However, the CO bond strength of Ni is such that it was poisoned despite the electronic effects of adjacent Ag atoms.

**Conclusion**

The Ag/Fe electrodes only produced CO\textsubscript{2} reduction products at extremely low Faradaic efficiencies, with 99\% of the current being directed towards H\textsubscript{2} evolution. CH\textsubscript{4} was present, which is unexpected for both Ag and Fe, but only at <1\% Faradaic efficiency. Ni/Ag electrodes produced CO at comparable Faradaic efficiencies to H\textsubscript{2}, 32\% and 30\% respectively, alongside CH\textsubscript{4} at <1\%. NiAg simultaneously deposited alloy produced 95\% H\textsubscript{2}, with 2\% CH\textsubscript{4} and 1.5\% CO, similar to Ni foil, but with a minor increase in CO, attributed to the Ag content. The use of high CO affinity metal containing alloys does not result in improvements to the CO\textsubscript{2} reduction reaction when paired with a relatively low CO affinity metal such as Ag.
CHAPTER 7: CONCLUSIONS

The ultimate aim of CO₂ reduction is to create a commercially viable process for storing electrical energy generated by renewable sources as a combustible chemical. In order for electrochemical reduction of CO₂ to be viable, the overall process needs to be highly energy efficient (>80%) with a current density of ~1 A/cm² and long term stability. Kenis et al. have compiled graphs (Figure 7.1) showing the Faradaic efficiency and energy efficiency of various CO₂ catalysts from literature plotted against their respective current densities.⁸ There are many catalysts that are highly selective towards CO or HCOO⁻, but only at low current densities.¹⁰ Higher value products such as CH₃OH and CH₃CH₂OH are only produced at extremely low selectivity or extremely low current density. While HCOO⁻ and CO can potentially be further processed to higher energy density chemicals using processes such as Fischer-Tropsch, the low current density remains a problem. In order to create a commercially viable catalyst, it is necessary to obtain an understanding of all the factors influencing the CO₂ reduction reaction so as to create catalysts that are capable of breaking the trend suggested by current literature.

Natural photosynthesis makes use of bimetallic, nanoscale and enzyme chemistry. The effects seen in photosynthesis have been the basis for much of the previous research in this field. Groups studying the electrochemical reduction of CO₂, such as those of Nørskov, Jaramillo, Kenis and Kauffman, have looked at computational results⁵⁴ as well as bimetallic,¹⁵⁷, ¹⁷⁴ nanoscale,⁷⁷ and chemical⁵ experimental approaches for the electroreduction of CO₂.
Figure 7.1: Summary of electrochemical performance for CO₂ conversion from literature. Faradaic efficiencies (a) and energetic efficiencies (b) plotted against current density. (Reprinted with permission from (Jhong et al., 2013). Copyright 2013 Current Opinion in Chemical Engineering)
The chapters of this dissertation discuss the use of various nanoparticle-based electrodes as CO₂ electroreduction catalysts. CuZnO, Au₂₅, CuAu, CuCo, NiAg and FeAg nanoparticles are all experimentally investigated as means to observe the effect of various metals and conditions on CO₂ reduction. The Cu nanoparticles with a ZnO support displayed an order of magnitude increase in alcohol selectivity, with the oxide aiding in the transport and binding of CO to the Cu catalyst as well as hydrogenation. Likewise, the beneficial effect of near-surface chemistry due to sulfonates on Au₂₅ and 5 nm Au nanoparticle catalysts is shown in the CO₂ reduction onset potentials and CO Faradaic efficiency. The Nafion™ binder’s sulfonate alters the charge of the Au surface and the resulting CO binding energy, yielding a ~170mV anodic shift in the onset for CO₂ reduction with Au₂₅ nanoparticles and a ~140mV shift in the onset for 5 nm Au nanoparticles versus Au foil.

Alloy effects from both CuCo and CuAu nanoparticles showed both beneficial and detrimental effects on the CO₂ reduction reaction. Compared to the pure Cu equivalents in literature, CuCo showed a reduced selectivity towards CO₂ reduction, while CuAu nanoparticles showed increased selectivity as well as increased CO yields. Compared to Au foil, CuAu yielded one order of magnitude greater as a 2 nm nanoparticle, and two orders of magnitude greater as a 6 nm nanoparticle. Meanwhile, CuCo reduced the selectivity towards CO₂ reduction, with H₂ being produced at ~70% Faradaic efficiency. The effect of using multi-transition metal catalysts was also observed using NiAg and FeAg. The Ni nanoparticles on Ag foil, the Ag nanoparticles on Fe foil and the simultaneously electrodeposited NiAg catalyst all showed large selectivity towards H₂, regardless of Ag content. However, the FeAg was observed to produce small amounts of CH₄, something not observed on either pure Fe or pure Ag,
indicating that the combination of metals can lead to new products, not just shifts in selectivity and onset potential.

While current implementations of CO₂ reduction are far from the required efficiency and current densities, some method of creating liquid fuels will inevitably be required to offset the depleting reserves of fossil fuels. Other means of electrochemically converting renewable energy to fuel, such as ammonia production or hydrogen evolution for fuels cells, struggle with low performance or other physical limitations, such as hydrogen storage.¹⁷⁵

CO₂ reduction offers the most promising method for securing fuels for the future, though it will take a great deal more research to fully master the CO₂ reduction reaction.

To create a CO₂ reduction catalyst capable of selectively producing desirable hydrocarbon products, it will ultimately be necessary to utilize many different beneficial effects. The first step in future research should be to find stable alloy combinations that will make CO₂ reduction more thermodynamically favorable. A partnership of both computational techniques and experimental verification will be required to identify potential alloys, as experimentally evaluating every possible alloy is a daunting task. Near surface chemical modification using functional groups such as sulfonates, amines, or pyridines should be used to tune the selectivity of the reaction on the most promising alloys. Finally, nanoscale features should be considered to increase the catalytic mass activity as well as to take advantage of beneficial low-coordination effects observed on nanowires and CuAu catalysts. Surface-modified nanoclusters, nanowires, bulk materials with nanoscale surface features and individual-atom metal catalysts, such as porphyrins, are all potential directions for future CO₂ catalysts.
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Publication: Journal of Physical Chemistry Letters

Publisher: American Chemical Society

Date: Feb 1, 2013

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Evan Andrews was born in 1989 in Louisiana. While most of his time was spent in Louisiana, Evan also spent several years residing in the United Kingdom and later New Zealand. He obtained a Bachelors of Science in chemical engineering at Case Western Reserve University where he became interested in research electrochemistry, and went on to become a Doctor of Philosophy in chemical engineering at Louisiana State University.