MICROFLUIDIC PLATFORM FOR STUDYING THE ELECTROCHEMICAL REDUCTION OF CARBON DIOXIDE

BY

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DISSERTATION

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Abstract

Diminishing supplies of conventional energy sources and growing concern over greenhouse gas emissions present significant challenges to supplying the world’s rapidly increasing demand for energy. The electrochemical reduction of carbon dioxide has the potential to address many of these issues by providing a means of storing electricity in chemical form. Storing electrical energy as chemicals is beneficial for leveling the output of clean, but intermittent renewable energy sources such as wind and solar. Electrical energy stored as chemicals can also be used as carbon neutral fuels for portable applications allowing petroleum derived fuels in the transportation sector to be replaced by more environmentally friendly energy sources.

However, to be a viable technology, the electrochemical reduction of carbon dioxide needs to have both high current densities and energetic efficiencies (Chapter 1). Although many researchers have studied the electrochemical reduction of CO₂ including parameters such as catalysts, electrolytes and temperature, further investigation is needed to improve the understanding of this process and optimize the performance (Chapter 2). This dissertation reports the development and validation of a microfluidic reactor for the electrochemical reduction of CO₂ (Chapter 3). The design uses a flowing liquid electrolyte instead of the typical polymer electrolyte membrane. In addition to other benefits, this flowing electrolyte gives the reactor great flexibility, allowing independent analysis of each electrode and the testing of a wide variety of conditions. In this work, the microfluidic reactor has been used in the following areas:

- Comparison of different metal catalysts for the reduction of CO₂ to formic acid and carbon monoxide (Chapter 4).
• Investigation of the effects of the electrolyte pH on the reduction of CO₂ to formic acid and carbon monoxide (Chapter 5).

• Study of amine based electrolytes for lowering the overpotentials for CO₂ reduction and suppressing undesirable hydrogen evolution (Chapter 6).

• Investigation of the effects of reaction temperature on the Faradaic efficiency and current density for CO₂ reduction on several catalysts (Chapter 7).

These studies demonstrate the utility of this flexible reactor design and provide increased understanding of the electrochemical reduction of CO₂ and the critical parameters for optimization of this process.
To Heather
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Chapter 1

Introduction*

1.1 Challenges in Energy and Climate Change

One of the world’s greatest challenges today is supplying clean, affordable and reliable energy to meet the increasing demand from the world’s population. As shown in Figure 1.1, the global energy demand is expected to continue to increase dramatically over the next few decades.\(^1\) Much of this increased demand is due to large and growing populations in developing countries whose demand for energy is rising sharply as their economies become more developed. The result is that energy demand is expected to increase by nearly 50% from 2007 to 2035.

\[\text{Figure 1.1: Historical and projected energy demand by region. Source: U.S. Energy Information Agency’s International Energy Outlook (July 2010).}\]

Increasing the world’s energy output to meet this large growth is a significant challenge by itself, without considering the limiting factors associated with the world’s energy supply sources.

In addition to rapidly increasing demand, another complicating factor in the world’s energy situation is the finite supply and uneven distribution of conventional energy sources, particularly petroleum. While it is anticipated that the global supply of natural gas and oil will be sufficient to meet demand at least until 2030, an increasing amount of oil and gas will have to come from “unconventional” sources, such as oil sands, which have added risks and costs. Furthermore, the conventional oil and natural gas resources are increasingly concentrated in a few countries, and about half of the inter-regional petroleum shipping goes through a few potential “choke points” such as the Suez canal. The non-uniform distribution of oil resources is shown in Figure 1.2, which shows the net oil imports by region for the year 2005 and the projections for 2030. The concentration of oil resources in a few areas and the reliance of many

Figure 1.2: Net regional oil imports and exports. © National Petroleum Council 2007, reprinted with permission from Hard truths: Facing the Hard Truths About Energy: A Comprehensive View to 2030 of Global Oil and Natural Gas.
countries, such as the United States, on imports threatens the energy security of those countries relying on imports from other regions because their supply is susceptible to interruptions due to political instability, leveraging by producers, and disruptions in shipping.\(^2\)

Also adding to the challenges of supplying the increasing demand for energy is the concern over the accumulation of greenhouse gases (GHG) in the atmosphere. Measurements have shown that the levels of key greenhouse gases in the atmosphere have increased dramatically over the past two centuries since the industrial revolution (Figure 1.3).\(^3\) Furthermore, measurements of the average air and ocean temperatures, melting snow and ice, and average sea level show that the global climate is warming (Figure 1.4).\(^3\) The Intergovernmental Panel on Climate Change (IPCC) has recently concluded that most of the observed warming is “very likely” due to the increased anthropogenic emissions of GHGs.\(^3\) The main contributor to global warming is carbon dioxide for which the main source of emissions is

---

**Figure 1.3:** Atmospheric concentrations of CO\(_2\), CH\(_4\) and N\(_2\)O over the last 10,000 years (large panels) and since 1750 (inset panels). Measurements are shown from ice cores (symbols with different colors for different studies) and atmospheric samples (red lines). The corresponding radiative forcings relative to 1750 are shown on the right hand axes of the large panels. © IPCC, 2008. Reprinted with permission from “Climate Change 2007: Synthesis Report”, in Fourth Assessment Report (AR4).\(^3\)
the consumption of fossil fuels as seen in Figure 1.5.\(^3\) These facts have caused increased pressure to decrease carbon emissions, particularly emissions from energy production, which creates additional challenges in trying to meet the growing demand for energy. As a result, finding ways to supply the rapidly increasing demand for energy while also limiting or decreasing carbon emissions is a critical challenge facing the world today.

1.2 Approaches and Technologies to Address Challenges in Energy and Climate Change

In response to the need to increase energy supply and energy security while decreasing GHG emissions, a variety of technologies are being investigated and proposed. Carbon capture and sequestration (CCS) at large emission sources, such as power plants, has been proposed as a strategy to decrease the accumulation of CO\(_2\) in the atmosphere. Proposed sequestration methods include geological or deep sea storage, and mineralization. To reduce our dependency on imported petroleum, the development and expansion of natural gas to liquid (GTL) and coal to liquid (CTL) technology has been proposed. GTL and CTL yield syngas, a mixture of hydrogen and carbon monoxide, which is then converted into liquid fuels via the

![Figure 1.4: Observed changes in (a) global average surface temperature; (b) global average sea level from tide gauge (blue) and satellite (red) data; and (c) Northern Hemisphere snow cover for March-April. All differences are relative to corresponding averages for the period 1961-1990. Smoothed curves represent decadal averaged values while circles show yearly values. The shaded areas are the uncertainty intervals estimated from a comprehensive analysis of known uncertainties (a and b) and from the time series (c). © IPCC, 2008. Reprinted with permission from “Climate Change 2007: Synthesis Report”, in Fourth Assessment Report (AR4).\(^3\)](image)
Fischer-Tropsch process,\textsuperscript{4, 5} and are well developed technologies.\textsuperscript{6-9} While the implementation of CSS will decrease emissions and CTL and GTL would allow the use of relatively abundant coal and natural gas to decrease our dependence on imported oil for transportation fuels, such a solution does not address the non-renewable nature of fossil fuels or the need to reduce GHG emissions. Because of this issue, CCS and GTL/CTL will likely serve as bridging technologies to a more sustainable energy supply needed for the long term.\textsuperscript{9}

Several other potentially more sustainable alternatives to fossil fuels are being researched. For example, significant progress is being made in the production of biofuels from algae and woody biomass.\textsuperscript{10, 11} These are promising technologies that could potentially supply carbon neutral fuels while minimizing competition with the food supply. Wind, solar, and tidal power are also very popular and expanding rapidly along with increased interest in expanding nuclear energy.\textsuperscript{12-14} Another attractive alternative to CO\textsubscript{2} sequestration is the use of captured carbon as a reagent for producing useful chemicals either through chemical or electrochemical means. Carbon dioxide is already used in the production of chemicals such as urea, salicylic acid, and polycarbonates,\textsuperscript{15, 16} however, the demand for these products is very small compared to the amount of CO\textsubscript{2} produced from the consumption of fossil fuels for energy, and thus unlikely to make a significant impact on emissions. Carbon dioxide can also be reacted with hydrogen to
yield a mixture of water and carbon monoxide via the reverse water gas shift reaction (RWGS) (Eq. 1.1) or to directly produce water and methanol (Eq. 1.2):  
\[
\text{CO}_2 + \text{H}_2 \rightleftharpoons \text{CO} + \text{H}_2\text{O} \quad (1.1)
\]
\[
\text{CO}_2 + 3\text{H}_2 \rightleftharpoons \text{CH}_3\text{OH} + \text{H}_2\text{O} \quad (1.2)
\]
While the RWGS process is difficult to drive to completion, pilot plants producing methanol have already been built. Methanol production is particularly attractive if the hydrogen comes from renewable sources. We refer the reader to a number of good reviews for a more detailed account of the various options for carbon sequestration and CO\(_2\) utilization. At this point it is unclear which of these strategies are technologically feasible and make economic and practical sense, be it in distributed fashion or on a large scale. Furthermore, important research is advancing in the related areas of photochemical, biochemical, and mediated electrochemical conversion of CO\(_2\) using homogeneous catalysts.  

This dissertation focuses on the investigation of CO\(_2\) utilization via electrochemical reduction at electrodes with heterogeneous catalysts.

The electrochemical reduction of carbon dioxide involves reducing CO\(_2\) to organic compounds using electrical potential (instead of temperature or chemical reducing agents) as the driving force for the uphill reactions. The process is essentially running a fuel cell in reverse. To illustrate the similarities, Figure 1.6 compares a direct formic acid fuel cell to an electrochemical cell for reducing CO\(_2\) to formic acid. In the fuel cell, the formic acid is oxidized on the anode to produce CO\(_2\), protons and electrons. The protons travel through an ion conducting electrolyte while the electrons travel through an external electrical circuit providing electrical power. The protons and electrons recombine on the cathode with oxygen, which is reduced to water. In contrast, in the CO\(_2\) reduction cell, water is oxidized on the anode forming oxygen, protons and
The protons travel through the electrolyte and the electrons through the external circuit. However, since the electrons are travelling uphill, \( i.e. \), to the cathode at a more negative potential, electrical power is required to drive this flow. The protons and electrons then combine on the cathode to reduce \( \text{CO}_2 \) to formic acid. Thus, the cathode reaction for the \( \text{CO}_2 \) reduction cell is the reverse of the anode reaction in the fuel cell, and the anode reaction for the \( \text{CO}_2 \) cell is the reverse of the cathode reaction in the fuel cell.

### 1.3 Potential Role of the Electrochemical Reduction of \( \text{CO}_2 \)

Research on the direct electrochemical reduction of \( \text{CO}_2 \) has already shown that several products can be produced including formic acid,^{41-46} carbon monoxide,^{32, 33, 43, 47, 48} methane,^{43, 49, 50} ethylene,^{43, 51} and methanol.^{52-54} These products can be used as commodity chemicals as well.
as fuels, thus allowing CO$_2$ to be recycled into compounds that can act as energy carriers. The key requirement, of course, is that the electricity used to convert the CO$_2$ must be renewable, or at least from a carbon neutral source such as nuclear, otherwise more CO$_2$ would be emitted in producing the electricity than would be reduced in the process. Also, using renewable electricity to replace electricity produced by carbon intensive energy sources, e.g. coal, would likely result in a greater reduction in emissions than using that electricity to convert CO$_2$ into liquid fuels.

Still, the electrochemical conversion of CO$_2$ has great potential to help overcome several of the challenges facing the implementation of carbon neutral energy sources because it provides a means of storing renewable electricity in a convenient, high energy density form. Particularly exciting is the ability to produce methane and ethylene directly on copper catalysts and the possibility of producing even longer hydrocarbons from syngas. The storage of electrical energy in chemical form is potentially useful in two key areas: (1) leveling the output from intermittent electricity sources such as wind and solar and (2) enable the production of liquid fuels for the transportation sector with renewable electricity. In comparison, the electrolysis of water, which is a mature technology, also allows storage of electricity in chemical form (hydrogen), however, hydrogen does not fit into the existing infrastructure as well as liquid fuels, has a lower volumetric energy density and requires compression or liquefaction for storage.

Many studies have shown that drastic reductions in CO$_2$ emissions are needed to limit the potential effects of climate change. The fact that fossil fuel consumption accounts for the majority of CO$_2$ emissions, and the need to reduce dependence on imported fossil fuels indicate that significant reductions in fossil fuel use will be necessary in the future even as energy demand continues to rise. Figure 1.7 highlights some of the challenges that such changes would present and the role that the electrochemical conversion of CO$_2$ could play by comparing our
current energy consumption with a hypothetical situation in which fossil fuel use is significantly reduced as part of efforts to reduce CO$_2$ emissions and dependence on imported energy.

The left-hand side of Figure 1.7 shows the primary energy consumption by source and sector in the U.S. for 2008$^{60,61}$, which is also representative for the rest of the developed world although the exact percentages vary (e.g. the fraction of nuclear energy is 13% in Europe$^{62}$). This information points out several key aspects of our current energy use in relation to its sources. The most dramatic is the almost complete dependence of the transportation sector on petroleum derived liquid fuels. Also noteworthy is that the vast majority of carbon neutral energy (renewable and nuclear) produces electricity, effectively limiting utilization of these desirable energy sources to the electrical grid. Furthermore, many popular and fast growing renewable sources, such as wind and solar, are intermittent and to varying degrees unpredictable. The fluctuating nature of these sources limits them to no more than 15-20% of the total.

![Figure 1.7: Primary U.S. energy consumption by source and sector for 2008$^{60}$ (left) with a hypothetical scenario in which emissions are reduced by significantly reducing fossil fuel consumption (right). Key enabling technologies in the future scenario: (1) Gas to liquid conversion, (2) Coal to liquid conversion, (3) Biofuels and electrochemical conversion of CO$_2$ to liquid fuels using renewable electricity, e.g., wind and solar, (4) Electrochemical conversion of CO$_2$ to liquid fuels using nuclear power supplied electricity, (5) Wind, solar, and tidal power with storage via electrochemical conversion of CO$_2$ or other methods such as pumped hydro, compressed air, and flow batteries.$^{64}$ © ACS Reprinted with permission from Whipple and Kenis$^{61}$](image-url)
electricity demand unless non-trivial large scale electricity storage is used to level output and prevent instability in the system.  

The right side of Figure 1.7 shows a hypothetical, qualitative distribution of energy sources that accomplishes a reduction of CO$_2$ emissions through significant reduction of fossil fuel consumption while increasing carbon-neutral sources. While the total energy demand is expected to continue to increase substantially, the relative demand of each energy-consuming sector is not predicted to change significantly. Thus, the future scenario uses the same breakdown. This hypothetical scenario is not intended to be a quantitative prediction of the only or even the most probable conditions in the future. Certainly, these reductions could be achieved in several different ways, and which technologies are most feasible and end up being implemented at a meaningful scale will depend on factors such as local environment and political and economic conditions, factors that go well beyond the technical merit of each of these technologies. Similarly, given the immature technical status of the electrochemical conversion of CO$_2$ as well as the issues just mentioned, predicting the time frame or scale at which the electrochemical reduction of CO$_2$ could be implemented is impossible at this time. The purpose of the hypothetical scenario is to highlight some of the challenges that will be faced in meeting energy demand as concerns over climate change and a scarce supply of fossil fuels, particularly petroleum, cause a shift away from a fossil fuel-dominated energy portfolio and the possible role that the electrochemical conversion of CO$_2$ could play (as one of many options being investigated) in overcoming these challenges.

While the exact makeup of future energy supply sources may not be certain, undoubtedly, we will face a number of challenges as we move away from fossil fuels. The first and foremost challenge will be to continue to supply energy to the transportation sector while fossil fuel use is
being decreased. Unless a complete overhaul to hydrogen fuel cell or battery powered vehicles is made, liquid fuels will continue to play a major role. Some of these liquid fuels could be supplied by GTL and CTL technology (arrows 1 and 2 in Figure 1.7), and still more could come from biofuels and fuels produced from the electrochemical reduction of CO₂ using electricity from renewable and nuclear sources (arrows 3 and 4 in Figure 1.7). A second key challenge will be to significantly increase the supply of electricity from carbon-neutral sources, that is, nuclear and renewables. For nuclear, this is fairly straightforward because we are already very familiar with this process and it provides a steady predictable supply. Increases in the use of renewable, but intermittent, sources such as wind and solar, however, would require leveling through an energy storage process, for example, through the electrochemical conversion of CO₂ (arrow 5). While many methods for massive electricity storage, such as pumped hydro, compressed air, and batteries,⁶⁴ are being proposed, storage in a chemical form via the electrochemical reduction of CO₂ gives added versatility as the products can be used as sources for electricity production, transportation fuels, or chemical feedstocks. These two challenges of the need to continue to provide energy to the transportation sector and the need to increase electricity production from carbon neutral sources highlight the value of a process that could convert and thus store electrical energy in a chemical form, particularly as a liquid, both for facilitating the penetration of renewable energy into sectors such as transportation and for storing excess electricity from intermittent sources.

1.4 Current Status of Electrochemical CO₂ Conversion

While the electrochemical conversion of CO₂ has great potential, significant advances are still needed for this process to be viable. Much of the early work in this area has focused on exploring different catalysts and the products that can be produced. Also, several investigations
have elucidated how parameters such as electrolyte and temperature favor certain products over others.\textsuperscript{50, 65, 66} More recently, several researchers have also proposed various reactor designs for the electrochemical reduction of CO\textsubscript{2} to either formic acid or syngas.\textsuperscript{48, 67-71} \textbf{However, to be feasible the electrochemical conversion of CO\textsubscript{2} needs to meet two criteria: (i) high energy efficiency and (ii) high reaction rates.} While it is not often discussed in literature, the energetic efficiency is a critical parameter since it specifies the recoverable energy contained in the product; in other words, it defines the energy cost of producing the product. High energetic efficiency is achieved through a combination of high selectivity (Faradaic or current efficiency) and low overpotentials (Figure 1.8).

While researchers have reported high Faradaic efficiency for many products (typically >90\% for formic acid and carbon monoxide, 65-70\% for methane and ethylene), high overpotentials are a major hindrance to improving energy efficiency. The reaction rate, as measured by the current density is also an important parameter as it determines the reactor size and thus capital cost of the process. To date, researchers have reported moderate to high current

\begin{align*}
\varepsilon_{\text{Faradaic}} &= \frac{n \cdot F \cdot n}{Q} \\
\varepsilon_{\text{energetic}} &= \frac{E^0}{E^0 + \eta} \times \varepsilon_{\text{Faradaic}} \\
\text{where} \quad \varepsilon_{\text{energetic}} &= \text{energetic efficiency} \\
\varepsilon_{\text{Faradaic}} &= \text{Faradiac efficiency} \\
n &= \text{number of electrons} \\
F &= \text{Faraday’s constant} \\
n &= \text{number of moles of product} \\
Q &= \text{charge passed} \\
E^0 &= \text{standard potential} \\
\eta &= \text{overpotential}
\end{align*}

\textbf{Figure 1.8:} Qualitative reaction scheme for CO\textsubscript{2} conversion. Catalysts and electrolytes acting as co-catalysts can lower the energy of the intermediate and improve energetic efficiency. We use $\varepsilon$ as the symbol for the Faradaic and energetic efficiencies to avoid confusion with the $\eta$ symbol for the overpotential. \textsuperscript{©ACS Reprinted with permission from Whipple and Kenis}.\textsuperscript{61}
densities (200-600 mA/cm²) using gas diffusion electrodes (GDE) similar to those in fuel cells.

As mentioned above, despite the challenges of hydrogen storage and transport, water electrolysis is an attractive option for electricity storage, and thus the efficiency and current density of a viable CO₂ reduction process should be close to those for water electrolyzers. Figure 1.9 shows the efficiencies and current densities for CO₂ reduction from data in the literature⁴², 43, 45, 47-51, 68, 69, 72-77 compared to the typical values for water electrolyzers.⁵⁶-⁵⁸, ⁷⁸-⁸⁰

Typical efficiencies for commercial water electrolyzers are in the 56-73% range with alkaline electrolyzers running at 100-300 mA/cm² and PEM electrolyzers running at much higher current densities (800-1600 mA/cm²).⁵⁸, ⁷⁸, ⁸⁰ The efficiencies for the electrolyzers are total system efficiencies (including losses from system peripherals), but since no complete systems for CO₂ reduction are available at this time, the efficiencies plotted only include losses on the cathode and ignores anode and system losses. Also, the current densities plotted are the partial current densities (only that current producing the desired product) rather than the total current density because it provides a more accurate measure of product formation. The direct electrochemical reduction to hydrocarbons (methane and ethylene) is particularly interesting; however this approach typically has the lowest energy efficiency due to exceptionally high overpotentials. In contrast, the

Figure 1.9: Comparison of the energy efficiencies and partial current densities for CO₂ reduction to formic acid,⁴²,43,45,47,69,74-77 syngas,⁴³,47,48,68,73,76 and hydrocarbons (methane and ethylene)⁴³,47,49-51,75 reported in literature with those of water electrolyzers.⁵⁶-⁵⁸,⁷⁸-⁸⁰ Efficiencies of electrolyzers are total system efficiencies, while the CO₂ conversion efficiencies only include cathode losses and neglect anode and system losses. (Adapted from Whipple and Kenis 2010)
electrochemical reduction to carbon monoxide has some of the highest energy efficiencies since
the main side product, hydrogen, is included in the syngas product. However, since hydrogen
evolution has a higher (less negative) theoretical reduction potential than carbon monoxide it will
likely be more efficient to optimize the electrolysis cell for CO production and supply the
hydrogen from a different renewable source such as electrolysis, biomass, or water gas shift.\textsuperscript{58}
Detailed system analysis of each of the options is required to identify the most effective method.
In summary, Figure 1.9 shows that current research efforts in the electrochemical conversion of
\text{CO}_2 have achieved moderate efficiencies and reasonably high current densities, although not at
the same time. This data, as well as the fact that additional losses have yet to be accounted for
(system, anode), indicates that further work is needed to significantly improve the energetic
efficiency and current densities for \text{CO}_2 reduction. A thorough review of the literature on the
electrochemical reduction of carbon dioxide is provided in Chapter 2 of this dissertation.

1.5 Remaining Challenges and Opportunities

The main challenge for advancing \text{CO}_2 reduction is increasing the energy efficiency,
which is primarily hindered by high overpotentials for \text{CO}_2 reduction. The limiting step in the
reduction of \text{CO}_2 is the formation of a \text{CO}^2^- radical anion intermediate. This step has a standard
potential of -1.9V vs. SHE and is the reason for the high overpotentials.\textsuperscript{81, 82} This potential can
be improved by stabilizing the intermediate, which is one of the main functions of catalysts.
Research has shown that the potential to form this radical anion can be improved by 0.3V by
adsorbing it on a catalyst surface.\textsuperscript{81} Further improvements could be possible through
optimization of the catalyst. The Principle of Sabatier predicts that the best catalysts have
intermediate adsorbate-surface bond strengths.\textsuperscript{83} This principle leads to the volcano curves seen
in Sachtler-Fahrenfort and Tanaka-Tamaru plots. However, in an electrochemical reaction, the
presence of an electrolyte, which can also act as a co-catalyst, adds complexity to the system. The added stabilizing effect of the electrolyte could result in shifting the volcano peak, thus opening the possibility to use other catalysts that may be more attractive for reasons such as price, availability, or stability. The complexity of the catalyst, electrolyte (co-catalyst) and intermediate interactions makes understanding the transition state in the reaction particularly difficult and is an important area of future research. Furthermore, the main competing reaction to CO₂ reduction is hydrogen evolution. Consequently, metals with high hydrogen overpotentials typically give the highest Faradaic efficiencies. However, higher energy efficiency could potentially be achieved using catalysts with low hydrogen overpotentials in combination with electrolytes and reactor conditions that minimize hydrogen evolution. Thus, as research continues to improve our understanding of CO₂ reduction reaction intermediates, it will lead to more effective combinations of catalysts and electrolytes.

As shown in Figure 1.9, efforts to increase the current densities for CO₂ reduction have been fairly successful, with partial current densities reaching approximately 400 mA/cm². These higher current densities have been achieved using catalysts deposited on gas diffusion electrodes (GDE) as is done in fuel cells.⁴⁹,⁵¹,⁸⁴ While these results are very encouraging, significant improvements still need to be made. Improvements in the reactor design, particularly the electrode, and optimization of the reaction conditions will enable further increases in current densities. One of the key limiting factors in CO₂ conversion is mass transfer of CO₂ to the cathode surface, especially given the low solubility of CO₂ in many electrolytes. As mentioned earlier, mass transfer limitations have largely been overcome using GDEs, which create a 3-phase interface between the gaseous reactants, the solid catalyst, and the electrolyte. Thus, optimizing the electrode and reactor will be key to improving current densities. The extensive
work on GDE and reactor flow field optimization for fuel cells over the past decades will greatly accelerate progress in this area. Furthermore, as seen in fuel cell work, temperature is key to improving performance of fuel cells, indicating that optimizing the reaction temperature will yield significant improvements for CO$_2$ reduction.$^{85,86}$ Also, work with solid oxide electrolyzers based on solid oxide fuel cells has already given promising results for high temperature CO$_2$ reduction.$^{87-90}$

In summary, recent work on the electrochemical reduction of CO$_2$ has shown the possibility of storing electricity as chemicals. The prospect of producing hydrocarbon fuels from CO$_2$ and renewable electricity is particularly interesting for addressing several intertwined energy and climate change issues; however, significant improvements are still needed. **The purpose of this dissertation is to develop and validate a microfluidic reactor that has the flexibility to aid in gaining the understanding necessary to achieve these improvements.**

The following chapter (Chapter 2) provides a summary of the studies on the electrochemical reduction of carbon dioxide reported in the literature. Chapter 3 details the design of the reactor and the electrodes developed in this work. The subsequent chapters present studies investigating the effects of catalysts (Chapter 4), electrolyte pH (Chapter 5), amine based electrolytes (Chapter 6), and temperature (Chapter 7) on the electrochemical reduction of CO$_2$. Finally, Chapter 8 summarizes the key findings and conclusions obtained from this work.

### 1.6 References


Chapter 2

Literature Overview

2.1 Introduction

The possibility of producing organic molecules via the electrochemical reduction of carbon dioxide has been known for over 100 years\(^2\) and has been studied extensively for the past few decades with several good reviews written on the subject.\(^5\)-\(^9\) Extensive research has been done investigating different products that can be formed using various catalysts with the majority of the work being done on metal electrodes in either aqueous\(^11\)-\(^14\) or organic media.\(^10\),\(^15\)-\(^17\) In aqueous electrolytes, most metal catalysts fall into four main groups: (1) metals forming mainly formic acid (Pb, Hg, In, Sn, Cd, Tl), (2) metals forming mainly CO (Au, Ag, Zn, Pd, Ga), (3) metals which form significant amounts of hydrocarbons, usually methane and ethylene (Cu), and (4) metals producing mainly hydrogen.\(^13\) Other products that have been reported include some alcohols (methanol, ethanol, propanol)\(^6\) and oxalic acid\(^14\),\(^18\),\(^19\) (typically seen only in organic electrolytes).

Since hydrogen evolution is the main competing reaction to CO\(_2\) reduction, metals with high overpotential for hydrogen evolution, such as Hg, In, Pb, Cd, have higher efficiencies for CO\(_2\) reduction. Table 2.1 shows

<table>
<thead>
<tr>
<th>Reaction</th>
<th>(E^0) (V vs. SHE)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(2\text{CO}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2\text{C}_2\text{O}_4)</td>
<td>-0.475</td>
</tr>
<tr>
<td>(\text{CO}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{HCOOH})</td>
<td>-0.199</td>
</tr>
<tr>
<td>(\text{CO}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{CO} + \text{H}_2\text{O})</td>
<td>-0.109</td>
</tr>
<tr>
<td>(\text{CO}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow \text{HCHO} + \text{H}_2\text{O})</td>
<td>-0.071</td>
</tr>
<tr>
<td>(\text{CO}_2 + 6\text{H}^+ + 6\text{e}^- \rightarrow \text{CH}_3\text{OH} + \text{H}_2\text{O})</td>
<td>+0.030</td>
</tr>
<tr>
<td>(\text{CO}_2 + 8\text{H}^+ + 8\text{e}^- \rightarrow \text{CH}_4 + 2\text{H}_2\text{O})</td>
<td>+0.169</td>
</tr>
<tr>
<td>(2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2)</td>
<td>0.0</td>
</tr>
</tbody>
</table>

**Table 2.1:** Reduction potentials for reactions relevant to CO\(_2\) reduction at 298K and pH = 0.\(^4\)
standard potentials that are more negative than hydrogen evolution showing the need to suppress hydrogen evolution either through catalysts or reaction conditions (such as aprotic electrolytes) in order to achieve high Faradaic efficiency. The following sections will summarize the results in the literature for various CO$_2$ reduction products, literature studies investigating how reaction conditions affect the reduction reaction and the various reactor designs that have been reported.

### 2.2 Formic Acid

The production of formic acid on mercury electrodes were some of the earliest reports of electrochemical reducing of carbon dioxide. Formic acid has been shown to be produced with very high Faradaic efficiencies (>90%) on mercury, amalgams and several other metal catalysts.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Electrolyte</th>
<th>Eff (%)</th>
<th>Potential (V NHE)</th>
<th>Current Density (mA/cm$^2$)</th>
<th>CO$_2$ Pressure (atm)</th>
<th>T (ºC)</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb (GDE)</td>
<td>50g/L NaSO$_4$</td>
<td>100</td>
<td>-2.0</td>
<td>45</td>
<td>1</td>
<td>20</td>
<td>3</td>
</tr>
<tr>
<td>Pb (GDE)</td>
<td>50g/L NaSO$_4$</td>
<td>100</td>
<td>-2.4</td>
<td>115</td>
<td>1</td>
<td>20</td>
<td>3</td>
</tr>
<tr>
<td>Hg</td>
<td>0.1 M KHCO$_3$</td>
<td>99.5</td>
<td>-1.51</td>
<td>0.5</td>
<td>1</td>
<td>18.5</td>
<td>13</td>
</tr>
<tr>
<td>Pb</td>
<td>0.1 M KHCO$_3$</td>
<td>97.4</td>
<td>-1.63</td>
<td>5.0</td>
<td>1</td>
<td>18.5</td>
<td>13</td>
</tr>
<tr>
<td>TI</td>
<td>0.1 M KHCO$_3$</td>
<td>95.1</td>
<td>-1.6</td>
<td>5.0</td>
<td>1</td>
<td>18.5</td>
<td>13</td>
</tr>
<tr>
<td>In</td>
<td>0.1 M KHCO$_3$</td>
<td>94.9</td>
<td>-1.6</td>
<td>5.0</td>
<td>1</td>
<td>18.5</td>
<td>13</td>
</tr>
<tr>
<td>Hg</td>
<td>0.05 M KHCO$_3$</td>
<td>90.2</td>
<td>-2.0</td>
<td>1</td>
<td>0</td>
<td></td>
<td>11</td>
</tr>
<tr>
<td>Ru-Pd (GDE)</td>
<td>0.5 M KHCO$_3$</td>
<td>90</td>
<td>-1.1</td>
<td>80</td>
<td>1</td>
<td>25</td>
<td>23</td>
</tr>
<tr>
<td>Pb (GDE)</td>
<td>50g/L NaSO$_4$</td>
<td>89</td>
<td>-1.6</td>
<td>56</td>
<td>1</td>
<td>20</td>
<td>3</td>
</tr>
<tr>
<td>Sn</td>
<td>0.1 M KHCO$_3$</td>
<td>88.4</td>
<td>-1.5</td>
<td>5.0</td>
<td>1</td>
<td>18.5</td>
<td>13</td>
</tr>
<tr>
<td>Hg</td>
<td>0.05 M KHCO$_3$</td>
<td>87.6</td>
<td>-2.0</td>
<td>1</td>
<td>20</td>
<td></td>
<td>11</td>
</tr>
<tr>
<td>In</td>
<td>0.1 M TEAP/H$_2$O</td>
<td>87.6</td>
<td>-2.0</td>
<td>1</td>
<td>1</td>
<td></td>
<td>14</td>
</tr>
<tr>
<td>In (GDE)</td>
<td>50g/L NaSO$_4$</td>
<td>87</td>
<td>-2.3</td>
<td>100</td>
<td>1</td>
<td>20</td>
<td>3</td>
</tr>
<tr>
<td>In</td>
<td>0.1 M TEAP/H$_2$O</td>
<td>83.2</td>
<td>-2.4</td>
<td>1</td>
<td>1</td>
<td></td>
<td>14</td>
</tr>
<tr>
<td>Cu(Hg)</td>
<td>10% NaSO$_4$ sat w NaHCO$_3$</td>
<td>81.5</td>
<td>3.5*</td>
<td>1</td>
<td>1</td>
<td></td>
<td>24</td>
</tr>
<tr>
<td>Pb (GDE)</td>
<td>0.5 M KHCO$_3$ + 0.02 M KNO$_4$</td>
<td>80</td>
<td>-1.9</td>
<td>1</td>
<td>25</td>
<td></td>
<td>29</td>
</tr>
<tr>
<td>Pb</td>
<td>0.1 M TEAP/H$_2$O</td>
<td>78.9</td>
<td>-2.4</td>
<td>1</td>
<td>1</td>
<td></td>
<td>14</td>
</tr>
<tr>
<td>Cd</td>
<td>0.1 M KHCO$_3$</td>
<td>78.4</td>
<td>-1.6</td>
<td>5.0</td>
<td>1</td>
<td>18.5</td>
<td>13</td>
</tr>
<tr>
<td>Pb</td>
<td>0.3M KOH in MeOH</td>
<td>77</td>
<td>-2.0</td>
<td>~5</td>
<td>1</td>
<td>15</td>
<td>15</td>
</tr>
<tr>
<td>Cd (GDE)</td>
<td>0.5 M KHCO$_3$ + 0.02 M KNO$_2$</td>
<td>75</td>
<td>-2.9</td>
<td>1</td>
<td>25</td>
<td></td>
<td>29</td>
</tr>
</tbody>
</table>

**Table 2.2:** Summary of literature results for electrochemical reduction of CO$_2$ to formic acid.
Formic acid is used as a preservative and antibacterial agent for livestock feed, and in leather tanning. Furthermore, researchers have shown direct formic acid fuel cells to be a promising technology, which makes formic acid an attractive option for recycling CO₂ for energy storage. The results for formic acid production from several groups are summarized in Table 2.2. As seen in the table, high efficiencies have been obtained repeatedly on Hg, Pb, In, and Sn electrodes. Particularly interesting is the work of Mahmood et al.³ who achieved 100% efficiency on Pb GDEs with high current density (115 mA/cm²) as well as that of Furuya et al.²³ who achieved 90% Faradaic efficiency at a low potential of -1.1V vs. NHE and 80 mA/cm². This potential is about 500 mV lower than the potentials of other electrodes with high Faradaic efficiencies, which is important when considering the overall energetic efficiency of the process.

2.3 CO and Syngas

Carbon monoxide is another product that has been produced with high efficiency by reducing CO₂ at various electrodes.¹,¹³ Carbon monoxide is useful as a reactant with H₂ in Fischer-Tropsch reactions to produce liquid fuels. As mentioned before, hydrogen evolution is the main competing reaction with carbon dioxide reduction. Instead of trying to suppress hydrogen evolution, another approach used by some researchers is to control the relative rates of CO and H₂ production to make syngas of the correct composition for production of other products, e.g., 1:1 for dimethyl ether or 1:2 for methanol.²⁵,²⁶ However, given the fact that the theoretical potential for CO₂ reduction to CO is more negative than the potential for hydrogen evolution, there will be a higher overpotential for hydrogen than for CO, and other options for producing hydrogen will likely be more energy efficient. The relevant literature data for CO and syngas production is summarized in Table 2.3. High Faradaic efficiencies (80-90%) for CO have been achieved on several metals including Au, Ag, and Zn. However, the highest reported
Faradaic efficiencies for CO (up to ~100%) were achieved by Furuya et al. using metal phthalocyanines on GDEs.\(^1\)\(^{,27}\) Zhao et al. have also done work reducing supercritical CO\(_2\) in ionic liquids. The main products were CO and H\(_2\) with the Faradaic efficiencies ranging from 25%-50% and 40%-65% respectively.\(^30\) Also, the high temperature electrolysis of carbon dioxide using solid oxide cells produces syngas exclusively.\(^32\)\(^{,33}\)

### 2.4 Hydrocarbons

Copper is unique in its ability to reduce CO\(_2\) to hydrocarbons at ambient temperature and pressure and as a result has been studied extensively. However, one of the main challenges with copper is that it lacks selectivity for one product. Cu alloys have also been investigated, but the main products obtained were CO, HCOOH and MeOH, not hydrocarbons, and high selectivity could not be obtained.\(^34\)\(^{-36}\) While copper is the only metal that produces methane and ethylene at atmospheric pressure, significant amounts of hydrocarbons have also been produced on Pt GDEs at elevated pressures.\(^20\) Thus, there is the potential that other catalysts could produce hydrocarbons if tested at similarly high pressures. Significant results in reducing CO\(_2\) to
hydrocarbons are shown in Table 2.4. One particularly interesting result is the work by Cook et al. with copper catalyst on GDE based electrodes. In their work they obtained ethylene as the major product, while in most other literature reports, methane was the dominant hydrocarbon product. This indicates that mass transfer of CO\(_2\) to the catalyst, which is significantly improved with GDEs, can play an important role in determining the reduction product distributions.

Despite the extensive work that has been done on producing hydrocarbons, high efficiencies (>75%) have yet to be obtained. Furthermore, the highest Faradaic efficiencies reported also have had very high overpotentials, resulting in lower energetic efficiencies.

As mentioned earlier, copper’s ability to produce hydrocarbons has caused it to receive a lot of attention and much of the studies investigating other parameters have used Cu as the catalysts. Most of the work looking at alloys has focused on Cu alloys. Similarly, the most extensive studies looking at the effect of the supporting electrolyte on the selectivity of CO\(_2\) reduction have used copper electrodes.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Electrolyte</th>
<th>Efficiency (%)</th>
<th>CH(_4)</th>
<th>C(_2)H(_4)</th>
<th>Potential (V NHE)</th>
<th>Current Density (mA/cm(^2))</th>
<th>CO(_2) Pressure (atm)</th>
<th>T (°C)</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>0.5M LiClO(_4) in MeOH</td>
<td>71.8</td>
<td>1.6</td>
<td>-2.78</td>
<td>27</td>
<td>1</td>
<td>-30</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>Cu</td>
<td>0.25M NaClO(_4) in MeOH</td>
<td>70.5</td>
<td>3.1</td>
<td>-2.78</td>
<td>22.7</td>
<td>1</td>
<td>-30</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>Cu</td>
<td>0.5M LiCl in MeOH</td>
<td>68.4</td>
<td>4</td>
<td>-2.78</td>
<td>16.4</td>
<td>1</td>
<td>-30</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>Pt (GDE)</td>
<td>0.5 M KHCO(_3)</td>
<td>38.8</td>
<td>-1.73</td>
<td>600</td>
<td>20</td>
<td>25</td>
<td>20</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pt (GDE)</td>
<td>0.5 M KHCO(_3)</td>
<td>36.3</td>
<td>-1.7</td>
<td>600</td>
<td>10</td>
<td>25</td>
<td>20</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pt (GDE)</td>
<td>0.5 M KHCO(_3)</td>
<td>33.4</td>
<td>-1.73</td>
<td>600</td>
<td>30</td>
<td>25</td>
<td>20</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu</td>
<td>0.1 M KHCO(_3)</td>
<td>33.3</td>
<td>25.5</td>
<td>-1.44</td>
<td>5.0</td>
<td>1</td>
<td>18.5</td>
<td>13</td>
<td></td>
</tr>
<tr>
<td>Pt (GDE)</td>
<td>0.5 M KHCO(_3)</td>
<td>31.2</td>
<td>-1.69</td>
<td>600</td>
<td>5</td>
<td>25</td>
<td>20</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ru</td>
<td>0.2M Na(_2)SO(_4)</td>
<td>30</td>
<td>-0.31</td>
<td>&lt;0.3</td>
<td>1</td>
<td>61</td>
<td>10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu (GDE)</td>
<td>1M KOH</td>
<td>9.1</td>
<td>69</td>
<td>-2.788</td>
<td>400</td>
<td>1</td>
<td>2</td>
<td>28</td>
<td></td>
</tr>
<tr>
<td>Cu (GDE)</td>
<td>1M KOH</td>
<td>6.7</td>
<td>65</td>
<td>-3.238</td>
<td>467</td>
<td>1</td>
<td>2</td>
<td>28</td>
<td></td>
</tr>
<tr>
<td>Cu (GDE)</td>
<td>1M KOH</td>
<td>6.3</td>
<td>65</td>
<td>-3.668</td>
<td>533</td>
<td>1</td>
<td>2</td>
<td>28</td>
<td></td>
</tr>
<tr>
<td>Cu (GDE)</td>
<td>1M KOH</td>
<td>7.4</td>
<td>60</td>
<td>-4.318</td>
<td>600</td>
<td>1</td>
<td>2</td>
<td>28</td>
<td></td>
</tr>
<tr>
<td>Cu (GDE)</td>
<td>1M KOH</td>
<td>7.5</td>
<td>53</td>
<td>-4.528</td>
<td>667</td>
<td>1</td>
<td>2</td>
<td>28</td>
<td></td>
</tr>
</tbody>
</table>

Table 2.4: Summary of literature results for electrochemical reduction of CO\(_2\) to hydrocarbons
2.5 Alcohols

Methanol is a very desirable product due to its utility as a fuel and as an intermediate in the production of many commodity chemicals. However, unlike formic acid and other products, relatively little work has been directed at the electrochemical reduction of CO$_2$ to methanol, and only a few have reported high current efficiencies.$^{31, 38-40}$ Those that have reported high current efficiency have either had very low current densities or not reported them. Some researchers have also reported the production of other alcohols including, ethanol and propanol, from the electrochemical reduction of CO$_2$, however these were produced with Faradaic efficiencies much less than those for methanol.$^{13, 20, 41}$ A summary of the results in the literature for the electrochemical reduction of carbon dioxide to alcohols is shown in Table 2.5. Another approach that is more common than direct electrochemical reduction of CO$_2$ to methanol is to take H$_2$ from the electrolysis of water and react it with CO$_2$ to form methanol.$^{42-45}$ CO$_2$ can also

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Electrolyte</th>
<th>Efficiency (%)</th>
<th>Potential (V NHE)</th>
<th>Current Density (mA/cm$^2$)</th>
<th>CO$_2$ Pressure (atm)</th>
<th>T (ºC)</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ru-GCE</td>
<td>0.2M Na$_2$SO$_4$</td>
<td>100</td>
<td>-0.5</td>
<td>0.2</td>
<td>1</td>
<td>1</td>
<td>38</td>
</tr>
<tr>
<td>Mo</td>
<td>0.2M Na$_2$SO$_4$</td>
<td>84</td>
<td>-0.6</td>
<td>0.12</td>
<td>1</td>
<td>2</td>
<td>40</td>
</tr>
<tr>
<td>Ru</td>
<td>0.2M Na$_2$SO$_4$</td>
<td>42</td>
<td>-0.3</td>
<td>&lt;0.3</td>
<td>1</td>
<td>60</td>
<td>31</td>
</tr>
<tr>
<td>Ru</td>
<td>0.2M Na$_2$SO$_4$</td>
<td>25</td>
<td>-0.31</td>
<td>&lt;0.3</td>
<td>1</td>
<td>61</td>
<td>31</td>
</tr>
<tr>
<td>RuO$_2$/TiO$_2$ NT</td>
<td>0.5 M NaHCO$_3$</td>
<td>60.5</td>
<td>-0.56</td>
<td>1</td>
<td>25</td>
<td>39</td>
<td></td>
</tr>
<tr>
<td>RuO$_2$/TiO$_2$ NP</td>
<td>0.5 M NaHCO$_3$</td>
<td>40.2</td>
<td>-0.56</td>
<td>1</td>
<td>25</td>
<td>39</td>
<td></td>
</tr>
<tr>
<td>Cu/Ni</td>
<td>0.05 M KHCO$_3$</td>
<td>10</td>
<td>-0.65</td>
<td>1</td>
<td>2</td>
<td>36</td>
<td></td>
</tr>
<tr>
<td>La$<em>1$xSr$</em>{0.2}$CuO$_4$</td>
<td>0.5 KOH</td>
<td>1</td>
<td>30.7</td>
<td>180</td>
<td>1</td>
<td>25</td>
<td>41</td>
</tr>
<tr>
<td>Cu</td>
<td>0.1 M KHCO$_3$</td>
<td>5.7</td>
<td>-1.44</td>
<td>5.0</td>
<td>1</td>
<td>18.5</td>
<td>13</td>
</tr>
<tr>
<td>Pt(GDE)</td>
<td>0.5 M KHCO$_3$</td>
<td>2.9</td>
<td>-1.69</td>
<td>600</td>
<td>5</td>
<td>25</td>
<td>20</td>
</tr>
<tr>
<td>Pt(GDE)</td>
<td>0.5 M KHCO$_3$</td>
<td>2.8</td>
<td>-1.7</td>
<td>600</td>
<td>10</td>
<td>25</td>
<td>20</td>
</tr>
<tr>
<td>Pt(GDE)</td>
<td>0.5 M KHCO$_3$</td>
<td>2.6</td>
<td>-1.73</td>
<td>600</td>
<td>20</td>
<td>25</td>
<td>20</td>
</tr>
<tr>
<td>Pt(GDE)</td>
<td>0.5 M KHCO$_3$</td>
<td>2.3</td>
<td>-1.73</td>
<td>600</td>
<td>30</td>
<td>25</td>
<td>20</td>
</tr>
<tr>
<td>Pt(GDE)</td>
<td>0.5 M KHCO$_3$</td>
<td>1.9</td>
<td>-1.62</td>
<td>500</td>
<td>30</td>
<td>25</td>
<td>20</td>
</tr>
</tbody>
</table>

Table 2.5: Summary of literature results for electrochemical reduction of CO$_2$ to methanol and other alcohols
be electrochemically reduced to CO to yield synthesis gas (CO and H₂), which can then be used to make methanol or hydrocarbons via Fischer-Tropsch synthesis.

2.6 Oxalic Acid

While less common than other products, multiple researchers have reported the production of oxalic acid from the electrochemical reduction of carbon dioxide. In each case an organic electrolyte was needed to see significant amounts. Ikeda et al. observed significant amounts of oxalic acid on several metal catalysts including Cr, Mo, Fe, Cd, Hg, Tl, and Pb using propylene carbonate electrolyte with 0.1M TEAP. Pb was the most selective towards oxalic acid with a Faradaic efficiency of 77%. They also observed that oxalic acid production dropped sharply with the addition of small amounts of water. Abbott et al. also measured up to 41% Faradaic efficiency on Pt and Pb electrodes in super critical HFC 134a. Finally, Tomita et al. compared different acetonitrile-water mixtures with 0.1M TEAP and observed over 70% Faradaic efficiency for oxalic acid on a Pt electrode. As also observed by Ikeda et al., increasing the water concentration (>4 mM) quickly suppressed oxalic acid production.

2.7 Reaction Conditions

2.7.1 Electrolytes

Researchers have used various electrolytes both aqueous and organic for the electrochemical reduction of CO₂, however studies systematically comparing different electrolytes are rare and limited to Cu as the catalyst. Kaneco et al. did an extensive comparison of methanol based catholytes with various supporting salts on a Cu electrode. Their results showed several trends in product distribution: (1) methane formation increased with decreasing cation size (Cs⁺, Ru⁺, K⁺, Na⁺, Li⁺), (2) ethylene formation is highest with OH⁻ and K⁺ ions, (3) in halide and thiocyanide electrolytes CO efficiency increased with increasing cation
size, with Cs$^+$ giving the highest efficiencies, and (4) Faradaic efficiency for HCOOH tends to be highest with Cs$^+$ and K$^+$ cations. One limitation to this study is that the efficiency for each electrolyte was reported at one potential and not always the same potential for each electrolyte. This can complicate the comparison since the product distribution is strongly dependent on the potential.

Hori et al. compared a number of salts in aqueous electrolytes for their effect on CO$_2$ reduction on Cu.$^6,^{37,46}$ They compared potassium salts with several different anions. KCl, KClO$_4$, and K$_2$SO$_4$ favored methane and alcohols compared to KHCO$_3$, which favored methane. K$_2$HPO$_4$ favored hydrogen evolution with very little CO$_2$ reduction products, which they attributed to the buffering action of the anions. They also compared different cations with a bicarbonate anion, which showed that the ratio of CH$_4$ to C$_2$H$_4$ decreased with increasing cation size. Li and Oloman$^{47}$ also compared K$^+$ with Na$^+$ cations and Cl$^-$ with CO$_3^{2-}$ anions. They observed potassium cations and carbonate anions gave higher Faradaic efficiency for formic acid on a Sn catalyst. Schwartz et al.$^{41}$ studied the effects of various hydroxide salts on the performance of a perovskite-type catalyst. They showed that the Faradaic efficiency for alcohols increase with increasing cation size (Cs>Rb>K>Na>Li).

Finally, Tomita et al.$^{19}$ studied CO$_2$ reduction on a Pt electrode in acetonitrile-water mixtures with tetraethylammonium perchlorate. At low water concentrations (<10mM) oxalic acid is the major product. As the water concentration increases, formic acid becomes the major product but when the water concentration increases to ~1M (~ 1:1 molecular ratio CO$_2$:H$_2$O) hydrogen evolution dominates. These results demonstrate that the aqueous-organic nature of the solvent can significantly affect the product distribution for CO$_2$ reduction and that hydrogen
evolution on metals with low hydrogen overpotentials can be suppressed with organic electrolytes, thus allowing CO₂ reduction to occur.

2.7.2 Electrolyte pH

While, as with fuel cells, the pH of the electrolyte should have a large effect on the electrochemical reduction of carbon dioxide, studies investigating the effect of pH have been limited. In many of the studies where the pH of the electrolyte was investigated, there was also variation in the electrolyte species making it difficult to separate out the effects. Mahmood et al.³ studied the performance of lead impregnated GDEs in Na₂SO₄ adjusted to various pH values and found that between a pH of 5 and 2, there was little effect on the Faradaic efficiency or current density, but efficiency significantly dropped for pH of 1.5 and 1. The limited work done investigating the effects of pH on CO₂ reduction makes it an important area for investigation, and thus it is one of the main factors investigated in this dissertation.

2.7.3 Temperature

Several investigators have studied the effect of temperature on the electrochemical reduction of carbon dioxide. Many have observed a general decrease in hydrogen evolution with decreasing temperature leading to higher Faradaic efficiencies for CO₂ reduction. Increasing the reaction temperature has three main effects: (1) increased exchange current densities for the electrode reactions, (2) decreased solubility of CO₂ in the electrolyte, and (3) increased mass transfer of CO₂. Separating out these effects is difficult. Mizuno et al.⁵¹ studied the reduction of carbon dioxide on indium electrodes at elevated pressures from 20°C -100°C. The pressure was adjusted to keep the solubility of CO₂ approximately constant, thus minimizing the effects of temperature on the concentration of CO₂ in the electrolyte. They observed that hydrogen evolution was significantly lower at lower temperatures, with ~100% Faradaic
efficiency for formic acid at 20°C. Li and Oloman\textsuperscript{47} did a similar study with a Sn catalyst in which the total pressure was constant, but the gas mole % for CO\textsubscript{2} was adjusted to keep the solubility the same. They showed that the Faradaic efficiency for formic acid increased with increasing temperature. These apparently contradictory results could be due to different operating ranges, catalysts, or reactor setups.

2.7.4 Pressure

The primary effect of increasing CO\textsubscript{2} pressure is increasing the concentration of CO\textsubscript{2} in the electrolyte. Thus, it is expected that increasing the pressure will increase the current density and Faradaic efficiency for CO\textsubscript{2} reduction. Several researchers have observed these effects.\textsuperscript{4, 17, 20, 47, 52} Because the solubility of CO\textsubscript{2} decreases as temperature increases, if higher temperature operation is desired it will likely need to be accompanied by elevated pressures.

2.8 Reactor and Cell Designs

Recently several papers have presented designs for complete electrochemical cells or reactors for producing formic acid\textsuperscript{47, 48, 53-56} and syngas.\textsuperscript{25, 26, 32} Most of the reported designs use polymer electrolyte membranes and are similar to fuel cell designs. The key challenge in designing reactors for the electrochemical reduction of CO\textsubscript{2} is ensuring adequate transport of the CO\textsubscript{2} to the catalyst surface, which is difficult due to its low solubility in many liquids. The most common approach to improving mass transport of CO\textsubscript{2} has been to use GDEs for the electrodes.

Yamamoto \textit{et al.}\textsuperscript{25} reported a GDE based electrochemical cell for making syngas at low potentials and moderate current densities. Their design used nickel on activated carbon fibers for the cathode and porous nickel sheets for the anode as catalysts on the GDEs. The GDEs were separated by a sheet of filter paper and electrolyte was allowed to flow down through it by
gravity. Their peak Faradaic efficiency was ~52% at a potential of -0.6V vs. NHE and ~10 mA/cm².

Delacourt et al.26 also recently reported an electrochemical cell for making syngas. They presented several designs based on polymer exchange membranes. The most effective design had a modified configuration with a buffer layer of KHCO₃ between the cathode and the Nafion membrane. This modification allowed much greater efficiency for reduction of CO₂ to CO. With this design, they achieved a CO/H₂ ratio of 1/2 (for methanol synthesis) at about -1.8 V NHE with a current density of 80 mA/cm².

Koleli et al.55 developed a unique fixed bed reactor for reduction of CO₂ to formate, with tin or lead granules as the cathode and a platinum counter electrode. With this design they achieved up to 95% current efficiency on lead at a potential of –1.3 V NHE with a current density of 0.21 mA/cm².

Akohori et al.54 reported a cell using a Nafion membrane to separate a lead cathode and carbon fiber anode. In their design, CO₂ saturated buffer solution (0.2 M K₂HPO₄ + H₃PO₄, pH 6) flowed over the cathode and a solution with sulfite ions was used on the anode. The oxidation of sulfite ions instead of producing oxygen, lowered the total cell potential. They also described the process by which both the CO₂ and sulfite could be absorbed from combustion flue gases. The main products were formate and small amounts of CO, but exact amounts were not reported. Current densities greater than 3 mA/cm² were not obtained.

Subramanian et al. developed a similar reactor using Nafion membranes.56 The cathode used was a lead plated stainless steel mesh and the anode was an iridium oxide film. In their setup the anolyte was 0.2M KOH and the catholyte was CO₂ saturated phosphate buffer (pH ~7). They achieved a maximum current efficiency for formic acid of 93% at a current density of
2 mA/cm² with a cell voltage of 1.4-1.7 V. As mentioned before, the low solubility and diffusivity of CO₂ in the catholyte significantly limits the current density of this type of design.

Some of the most notable work on reactors for CO₂ reduction has been done by Li and Oloman who have published several papers on their design for a continuous flow reactor for the production of formate.⁴⁷, ⁴⁸, ⁵³ Their design uses 2-phase (gas and liquid) flow through a 3-D cathode of tinned copper mesh or tin granules, with a Nafion 117 membrane as separator. Their unique use of two phase flow on the cathode appears to overcome much of the mass transfer limitations. In their work, they also did a study of several parameters including temperature, catholyte species, CO₂ pressure and other reactor parameters. They also achieved high efficiencies (91-63%) and high current densities (60-310 mA/cm²).

Several researchers have reported high temperature electrolysis using solid oxide electrolysis cells (SOEC) ³², ³³, ⁵⁷, ⁵⁸ and molten carbonate electrolysis cells⁵⁹ for the electrochemical reduction of carbon dioxide. As with solid oxide fuel cells and solid oxide water electrolyzers, the high temperatures of SOECs offer substantial improvements in both the kinetics and the thermodynamics of CO₂ reduction. In all cases the reduction products were syngas. Furthermore, analysis suggests that the cathodic reactions are likely dominated by the reduction of steam to form hydrogen, which then produces CO via the reverse water gas shift reaction. Another attractive aspect of SOECs is their ability to operate in both electrolysis and fuel cell modes allowing the products from CO₂ reduction to be consumed later to produce electricity using the same device.

2.9 Summary

As summarized in the sections above, extensive work has been reported to identify promising catalysts for the electrochemical reduction of CO₂. However, significant
improvements in both energy efficiency and current density need to be made either through identifying novel catalysts or optimizing the reaction conditions of these known catalysts. Most of the more thorough studies that include wide potential ranges, effects of electrolyte composition, and alloying effects focused only on copper electrodes, while other parameters such as pH have been left almost completely unexamined. Furthermore, most of the studies have focused on Faradaic efficiency with little mention of overpotentials or energetic efficiency. Hence, the study of CO$_2$ reduction could be greatly advanced with a convenient flexible tool that can investigate the performance of various catalysts in a wide variety of conditions.

2.10 References


Chapter 3

Reactor and Electrode Design

3.1 Introduction

As shown in the previous two chapters, the electrochemical reduction of carbon dioxide is a promising technology than can help address some of the challenges in energy and climate change, but significant improvements in energy efficiency and current densities are needed. To achieve these improvements further study and optimization of numerous parameters including catalysts, temperature, electrolyte composition, and electrolyte pH is needed. To gain the most benefit and understanding, these parameters need to be studied in reactor relevant conditions with high current densities which cannot be achieved in the conventional three-electrode cell.

Figure 3.1: Schematic of the microflue H₂/O₂ fuel cell developed by Kenis et al. The design uses a flowing electrolyte instead of the conventional membrane giving it great flexibility as an analytical platform. (Image courtesy of Fikile Brushett)
Thus, we need a reactor that runs at relevant operating conditions, but still has the flexibility to test this wide variety of parameters. The development and demonstration of such a reactor is the purpose of this dissertation.

3.2 Membraneless Reactor Design

Basis for our electrochemical cell design comes from the microfluidic fuel cell (shown in Figure 3.1) previously developed by Kenis et al.\textsuperscript{1} The microfluidic design uses a flowing liquid electrolyte instead of a membrane to separate the cathode and anode, which gives several advantages and increased flexibility over a membrane based design. This microfluidic cell has been used in a variety of studies including electrode and catalyst characterization\textsuperscript{3-5} and the effects of carbonates on fuel cell performance.\textsuperscript{6} The electrochemical cell developed in this dissertation (see Figure 3.2) is very similar in design. A 1.5-mm thick Poly(methyl methacrylate) (PMMA) sheet with a 0.5cm x 2cm window is placed between 2 catalyst coated gas diffusion electrodes (GDE) to create the channel for the liquid electrolyte. A graphite current collector backs each GDE. Behind the cathode a PMMA chamber is placed for CO\textsubscript{2} to flow through, while the anode is left open to air for oxygen to escape. The entire setup is held together with bolts. As with the microfluidic fuel cell, this electrochemical reactor design has several advantages:

- \textit{Minimizes water management issues associated with membranes and GDEs.} Water is continuously supplied and removed from the GDEs and there is no membrane with hydration requirements.

- \textit{Crossover of reactants and products can be controlled.} Because the microfluidic reactor operates in the laminar flow regime, mixing occurs only through diffusion. The diffusion
distance can be controlled by adjusting electrode distance, channel length and electrolyte flow rate.

- **Composition of electrolyte can be controlled and varied.** Because the electrolyte is a liquid and not a membrane, any solvent and supporting salt can be used allowing the study of various salts and pH on the reduction of carbon dioxide.

- **The flowing design allows for convenient online sampling and product analysis.** The liquid products are obtained by simply collecting the electrolyte as it exits and the exiting gas is sent directly to a GC for gas phase product analysis.

- **Allows easy use of external reference electrode.** Individual electrode potentials can be measured with the reference electrode allowing the performance of each electrode to be studied.

Figure 3.2: Schematic (top) and picture (bottom) of the microfluidic electrochemical cell for the reduction of CO$_2$.\textsuperscript{2}
In addition to these benefits, the microfluidic design provides high surface area to volume ratios enabling a large electrode area in a compact reactor size. The design also places the electrodes close together, which minimizes resistive losses in the cell.

### 3.3 Gas Diffusion Electrode Design

Gas diffusion electrodes are widely used in fuel cells because they provide large improvements in the mass transfer rates of gas reactants to catalyst surface. The faster mass transfer allows the fuel cells to achieve much higher reaction rates (current densities). A typical GDE (see Figure 3.3) consists of a macroporous backing layer made of carbon fibers treated with PTFE to make it hydrophobic. This layer is topped with a microporous carbon layer made of carbon particles also treated with PTFE. The catalyst is then deposited on top of the microporous layer. This GDE structure placed between the gas phase reactants and liquid electrolyte creates a three-phase interface between the solid catalyst, the liquid electrolyte and the gas reactants. The three-phase interface allows the gas phase reactants to diffuse through the backing layer to the catalyst, which minimizes the distance the gases must diffuse through the electrolyte to reach the catalyst.

**Figure 3.3:** MicroCT 3D rendering of a GDE with catalyst showing the different layers of the electrode. (Image courtesy of Fikile Brushett)
For the same reason that they have been used in fuel cells, numerous researchers have used GDEs for the electrochemical reduction of carbon dioxide which has allowed improvements in current densities of 1-2 orders of magnitude.\textsuperscript{8-20} Despite the improvements in current densities that have been achieved with GDEs, issues reported in the literature include the temporal stability and the accumulation of liquid phase products in the macropores of the GDE.\textsuperscript{21} In addition to these issues I have observed in my experiments that gas products which form on the liquid side of the catalyst layer are unable to pass through the wetted catalyst layer to the gas side. As a result they accumulate as bubbles in the electrolyte stream which block the catalyst and cause erratic performance in the cell. While, addressing the first of these three issues is beyond the scope of this dissertation, the latter two needed to be addressed to obtain consistent and reliable data from the reactor. These issues were dealt with by making modifications to the GDEs used in the reactor (see Figure 3.4).

To deal with the issue of bubbles forming in the electrolyte, the cathode catalyst was only painted on the first 1.5 cm of the electrode distance and a porous PTFE filter (10 µm pores) was placed over the last 0.5 cm of the electrode. This provides a hydrophobic path for the bubbles to pass through the electrode to the gas side. Any bubbles that form are carried by the electrolyte.

![Figure 3.4: Schematic of the modified GDEs used in the reactor for the electrochemical reduction of CO$_2$.](image)

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flow and quickly removed by the PTFE separator. This also allows all the gas phase products to be kept together.

The problem of liquid accumulation becomes particularly acute at long run times when liquid will actually pass completely through the electrode and accumulate in the gas chamber. This can ultimately hinder mass transport of the CO$_2$, foul the downstream gas analysis equipment (GC), and represents a loss of liquid product. This was solved by placing a PTFE membrane (200 nm pores) behind the GDE (Sigracet 35BC). This was then backed by another GDE (Sigracet 35BA) which is only the carbon fiber layer (does not have a microporous layer). These three layers are then hot pressed together. The PTFE membrane acts as a barrier to liquid and prevents it from passing completely through the electrode. The membrane is kept slightly smaller than the GDEs to allow electrical contact between the two GDEs. The entire GDE assembly is surrounded by a 10 mil PTFE gasket that acts as a seal to prevent any gas leaking out horizontally through the GDE.

![Figure 3.5: Flow distribution for a 5-channel reactor with a rectangular inlet manifold obtained using a 2D model in COMSOL. The simple design (top) results in unequal flow through the several channels (bottom). The velocity profile shown is at a position halfway down the length of the channels.](image)
While the single-channel reactor is a flexible platform for performing a variety of studies, the design ultimately needs to be scaled to larger electrode areas for practical applications. Researchers have already shown that microfluidic laminar flow fuel cells can be scaled by creating many parallel channels. A similar approach was applied to this CO\(_2\) reduction cell to demonstrate proof of principle scale out. To demonstrate this I designed a multi-channel reactor with 5 channels (0.1cm x 0.5cm x 4.5cm). The key challenge in designing a multi-channel reactor is creating inlet manifolds that ensure equal flow to all channels. To ensure the desired flow was achieved, the flow channels were modeled in COMSOL. As shown in Figure 3.5 a simple rectangular design results in higher flow through the outer channels. To adjust for this, angled inlet manifolds were used. This created nearly equal flow through each channel (see Figure 3.6). An identical design was used for the gas flow fields. Figure 3.7 shows a schematic and picture of the multi-channel reactor. Carbon dioxide and electrolyte flow in from the top (the schematic is flipped to show the gas flow channel better) of the reactor. The electrolyte passes through a hole in the GDE to the liquid layer, while the CO\(_2\) stays on top of the GDE. The CO\(_2\)
and electrolyte flow parallel to each other through the 5 channels on opposite sides of the GDE and exit through the top on opposite corners.

### 3.5 Reactor Modifications for Temperature Control

As discussed in the previous two chapters, temperature is a key parameter that needs investigation in the electrochemical reduction of carbon dioxide. To allow accurate control of the reactor temperature, adjustments to the design were needed. Figure 3.8 shows a schematic of the modified design. In this design, the current collectors and gas chambers were combined and made out of aluminum to allow rapid heat transfer. Cartridge heaters were then placed in the aluminum blocks to supply heating. The temperature was controlled with a PID controller and thermocouple attached to the outside of the cathode gas chamber. To ensure even and accurate temperature at the electrode surface, the heating was modeled using COMSOL. Figure 3.9 shows the results of the COMSOL model. The results clearly show that while most of the reactor is at the desired temperature, flowing the room temperature electrolyte into the
reactor causes “cold spots” on the electrodes. Thus, to have accurate and uniform temperature at the electrodes, the electrolyte needs to be preheated before entering the reactor. This was accomplished with heating tape wrapped around the electrolyte syringe and another PID controller.

3.6 Conclusions

A convenient and flexible reactor is essential to thoroughly studying and understanding

Figure 3.8: Schematic of the modified single-channel reactor with temperature control capabilities.

Figure 3.9: Temperature profile (using COMSOL) for the modified single-channel design. Heaters are at 50°C (323K) while the gas and electrolyte enter at room temperature (20°C/293K). The cold electrolyte entering the reactor causes significant cold spots on the electrodes.
the electrochemical reduction of carbon dioxide. This work developed a microfluidic reactor based on a similar fuel cell design. The flowing liquid electrolyte gives the design enormous flexibility, especially in testing different electrolytes and conditions. A multi-channel reactor was also designed to demonstrate the ability for scaling the microfluidic design to larger electrode areas. Further modifications also enabled control of the reaction temperature which is another critical parameter in the reduction of CO$_2$. The development of this design allows the thorough study of several key parameters including, catalyst, electrolyte, electrolyte pH, and temperature, each of which is critical for understanding and optimizing the efficiency and current density for the electrochemical reduction of CO$_2$.

### 3.7 References


Chapter 4

Catalyst Comparisons for the Electrochemical Reduction of CO$_2$*

4.1 Introduction

As detailed in Chapter 2, several publications have reported thorough surveys of the different metal catalysts for CO$_2$.$^{1-3}$ These publications outline which metals produce the various reduction products. However, many of these catalyst comparisons were done by testing each catalyst at one potential or current, which does not give a thorough comparison of the different catalysts. Thus, while it is clear which catalysts produce formic acid (or any other product), it is not clear which of the several catalysts gives the highest energetic efficiency (highest Faradaic efficiency at the lowest overpotential). Determining this requires a thorough comparison of the various catalysts at a range of potentials. The purpose of this work is to take several of the catalysts that have been reported to have high Faradaic efficiency for formic acid and syngas and compare them at a range of operating potential to determine which have the greatest potential for giving high energy efficiencies. In particular, the Ru-Pd catalyst reported by Furuya$^{6}$ showed promise for having lower overpotentials and was thus chosen along with several more common metals.

4.2 Experimental

4.2.1 Catalysts

Carbon supported Ru-Pd with 17-17 weight percent loading was synthesized in house using a method adapted from the literature$^{7,8}$ (referred to subsequently as “furnace method”).

The synthesis began by adding 0.2874 g of 5 wt% Pd/C catalyst (Sigma Aldrich) to a 20 ml vial. The required amount (0.1353 g) of Pd(NO$_3$)$_2$·2H$_2$O needed to bring the Pd mass % to 17% was then added followed by 10 ml of n-heptane. The mixture was then sonicated by at least 1 hr. The solvent was then removed by applying house vacuum. The catalyst was then transferred to an alumina boat and placed in a tube furnace (Lindberg/Blue, HTF55322). The catalyst was heated under 5% H$_2$ in Ar with the following temperature program: 25°C for 1 hr, ramp to 500°C over 5hrs, 500°C for 18hrs, ramp to 25°C over 5hrs. The catalyst was then transferred back to a vial and 0.1334g RuCl$_3$ was added followed by 10 ml n-heptane. The catalyst was sonicated, dried and heated using the same procedure above to yield the Ru-Pd/C catalyst.

Carbon supported Ru-Pd with a 20-20 weight percent loading was synthesized using another method from the literature$^9$ (referred to later as “beaker method”). The following components were combined in a 1 l beaker: 800 ml deionized water (18 megohm-cm from an in house Barnstead E-Pure), 5.6 ml of 8g Pd/l as Pd Cl$_2$ in 5 M HCl), 5.6 ml of 8 g/l Ru (as RuCl$_3$) in 5M HCl, 1 ml polyvinyl alcohol, 100 mg activated carbon. These were stirred for 30 min and stirring was maintained during subsequent steps. A reducing agent (50 ml of 0.05M NaBH$_4$) was then added drop-wise after which the pH was raised to 11 using 10 M NaOH. The solution was stirred for another 1 hour. The solution was then allowed to settle for 30 minutes, filtered (Whatman 1442), and then dried overnight at 80°C in a vacuum oven (Napco E series 5831). Catalyst with a 30-30 wt % loading was also synthesized with the same method.

Both of the synthesized catalysts were images with TEM and submitted for ICP-MS analysis to determine the actual Ru and Pd loadings. All other catalysts were used as received: Sn powder (<150 nm, Sigma Aldrich), Ag powder (<100nm, Sigma Aldrich), Au powder (0.5-
0.8 micron, Alfa Aesar), Pd powder (0.25-0.55 micron, Alfa Aesar), Ni powder (0.08-0.15 micron), Platinum black (Alfa Aesar), 40% Pt/C (Alfa Aesar).

4.2.2 Gas Diffusion Electrodes

Commercial gas diffusion electrodes were used to make the electrodes for the reactor. The studies for formic acid used ETEK “S” type GDEs, while the studies looking at syngas used Sigracet 35BC modified as described in Chapter 3. The catalyst inks were prepared by mixing the catalyst required for the desired loading with 200 µl deionized water, 200 µl isopropyl alcohol, and 4.6 µl 5% Nafion solution (Ion Power, LQ-1105 1100EW) via sonication (using Branson 3510 overnight or Sonics & Materials Inc, VCX 130PB at 40% amplitude for 10 min). The cathodes had a loading on 2 or 5 mg/cm$^2$ (metal basis) and an area of 1.4 cm$^2$. The anodes had a loading of 2 mg/cm$^2$ and an area of 2 cm$^2$. After sonication the ink was applied with a paintbrush (Tanis 00332 Red Sable size 2) and allowed to dry. The GDEs were then hot pressed (Carver, 3851-0) at 130°C and 2000 kPa for 5 min. The accuracy of the catalyst loading was checked by weighing the GDE before and after applying the catalyst. The GDE was dried under flowing N$_2$ for at least 30 minutes to ensure all the solvent had evaporated. Thorough drying was verified by weighing the GDE periodically until the weight was constant. Table 4.1 shows the loading efficiency for several electrodes. The loading efficiency was typically >80% and was higher for the multichannel electrodes with higher catalyst amounts.

<table>
<thead>
<tr>
<th>Desired loading (mg)</th>
<th>Catalyst Weight (mg)</th>
<th>Mass on electrode (mg)</th>
<th>loading efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>100.6</td>
<td>93.9</td>
<td>93%</td>
</tr>
<tr>
<td>100</td>
<td>102.1</td>
<td>97.6</td>
<td>96%</td>
</tr>
<tr>
<td>40</td>
<td>40.0</td>
<td>40.0</td>
<td>100%</td>
</tr>
<tr>
<td>7</td>
<td>8.6</td>
<td>6.2</td>
<td>72%</td>
</tr>
<tr>
<td>7</td>
<td>7.0</td>
<td>5.8</td>
<td>83%</td>
</tr>
<tr>
<td>7</td>
<td>7.0</td>
<td>5.8</td>
<td>83%</td>
</tr>
<tr>
<td>7</td>
<td>11.5</td>
<td>9.8</td>
<td>85%</td>
</tr>
</tbody>
</table>

Table 4.1: Catalyst loading efficiency for several electrodes.

4.2.3 Cyclic Voltammetry

All the cyclic voltammograms (CVs) were run.
in situ using the microfluidic reactor. All electrolytes were sparged with an inert gas (N\textsubscript{2} or He) for at least 1 hr before being used for any tests. Initially the cell was setup with a mass flow controller (MKS, 1479A11CS1BM) flowing nitrogen at 5 sccm through the cathode chamber and a syringe pump (Harvard Apparatus, PHD 2200) flowing electrolyte at 0.5 ml/min. The gas and electrolyte were allowed to flow for at least 10 minutes before running any CVs. An Autolab potentiostat (EcoChemie, PGSTAT-30) was used to run the CVs. Scans started at -0.5V vs the Ag/AgCl reference electrode (BASi, RE-5B) and scanned at 20 mV/s to -1.5V or -2V. The electrode potential was cycled 3-4 times until the current looked the same from one scan to the next and the final scan was reported. The gas flow was then switched to CO\textsubscript{2} and allowed to flow for another 10 minutes before repeating the CV.

4.2.4 Cell Testing

Formic Acid:

An Autolab potentiostat (EcoChemie, PGSTAT-30) was used to control the cell potential and measure the resulting current. The individual electrode potentials were measured using multimeters (Meterman, 15XP) connected between each electrode and a Ag/AgCl reference electrode (BASi, RE-5B) in the exit stream. A mass flow controller (Cole Palmer, 32907-80) was used to flow CO\textsubscript{2} from a cylinder at 5 sccm and a syringe pump (Harvard Apparatus, PHD 2200) supplied the 0.5M KHCO\textsubscript{3} electrolyte at 0.5 ml/min. The cell was held at each potential for a total of 400s. During the first half the cell was allowed to reach steady state. The electrolyte was collected in a sample vial and the current averaged over the last 200s before stepping to the next potential. All experiments were run at room temperature and ambient pressure and the electrode potentials were not corrected for any IR drop between the electrodes. The cathode catalyst loading for these tests was 2 mg/cm\textsuperscript{2} and the anode was 2 mg/cm\textsuperscript{2} Pt black.
Syngas:

The same equipment was used to control and measure the potentials and currents as with the formic acid studies and were likewise run at ambient conditions. A mass flow controller (MKS, 1479A11CS1BM) supplied the cell with 5 sccm of CO$_2$ while 1M KCl was supplied at 0.5 ml/min with the same syringe pump. The exit gas from the cell passed through the sampling valve of the gas chromatograph and then through a pressure controller (Cole Parmer, 002440W) before exhausting to the house vacuum. Figure 4.1 shows a schematic of the experimental setup used. The pressure controller was used to ensure proper gas liquid balance across the GDE, which was necessary because of the higher pressure drops experienced when hooking the exhaust gas up to the GC. Before each experimental run, the gas pressure was slowly decreased with the pressure controller until no more bubbles were observed in the electrolyte stream. The cell was allowed to reach steady state for 150s at each potential after which the GC took 3 samples spaced at 1 min intervals. The cathode catalyst loadings were all 5 mg/cm$^2$ and the anode was 2 mg/cm$^2$ Pt black.

![Figure 4.1: Schematic of the experimental setup for the electrochemical reduction of CO$_2$ to CO.](image)

The electrolyte was supplied to the reactor from a syringe pump and collected in a beaker after exiting the reactor. Carbon dioxide from a cylinder was supplied via mass flow controller (MFC) to the reactor. The exiting gas from the reactor passed through the GC and then through a back pressure controller before exiting to the house exhaust.
Multi-channel Reactor:

The same equipment was used to control and measure the potentials and currents as with the other studies. A mass flow controller (Cole Palmer, 32907-80) was used to flow CO\textsubscript{2} from a cylinder at 50 sccm and a syringe pump (Harvard Apparatus, PHD 2200) supplied the 1 M KCl electrolyte at 2.5 ml/min. The Ag catalyst was used at a loading of 5 mg/cm\textsuperscript{2} and the cell was run as described in the syngas section above.

4.2.5 Product Analysis

Formate concentrations were analyzed using a method described by Sleat and Mah\textsuperscript{4}. The following reaction solution was made fresh each time: 0.5 g citric acid, 10 g acetamide, 100 ml isopropyl alcohol. The following solutions were mixed and then allowed to react for 1-1.5 hrs: 0.2 ml of sample or standard with formic acid, 0.4 ml reaction solution, 0.02 ml of 30% sodium acetate, 1.4 ml acetic anhydride. After reacting, the solutions were placed in cuvettes (BrandTech Scientific, Brand-UV Cuvettes 7591) and the absorbance at 515 nm was measured using a UV-Vis Spectrophotometer (Perkin Elmer, Lambda 650). A calibration curve of known concentrations was made with each analysis to ensure equal reaction time for the standards and samples. Figure 4.2 shows demonstration of this method to determine the concentration of samples obtained from the reactor.

Figure 4.2: Demonstration of the colorimetric method used for formic acid determination\textsuperscript{4}
Gas product analysis was done using a gas chromatograph (Thermo Finnigan Trace GC with a thermal conductivity detector and Supelco 10072005 Hayesep D column). For the single-channel reactor the carbon dioxide was used as a reference peak and all the products were calibrated against its known flow rate. For the multichannel reactor, 1 sccm of ethylene was added to the gas stream after the reactor and used as the reference peak.

4.3 Results and Discussion

4.3.1 Catalyst Synthesis

TEM images of the catalysts synthesized in house are shown in Figure 4.3. The beaker method produced metal particles of approximately 2-3 nm that are well dispersed on the carbon support. This morphology is what was expected based on the results reported in the literature. In contrast the furnace method produced amorphous catalyst particles in which it was impossible to distinguish the metal particles from the carbon support. It appeared that a high degree of sintering had occurred during heating in the tube furnace. Elemental analysis of the catalysts

![Figure 4.3: TEM images for the 20-20 Ru-Pd catalyst (left) and the 17-17 Ru-Pd catalyst (right) synthesized in the lab using two different methods from literature.](image-url)
was also done using ICP. The results are shown in Table 4.2. The beaker method had nearly equal loading of Ru and Pd at ~55% of the nominal value. In contrast, the furnace method had a much higher loading efficiency for Pd (82%), but almost no Ru (only 5%) was deposited. Thus in reality the 17-17 Ru-Pd was actually closer to a Pd/C catalyst.

4.3.2 Formic Acid Catalysts Performance

Figure 4.4 shows the cyclic voltammograms (CVs) for the three cathode catalysts. For

![20-20 Ru-Pd](image)

![17-17 Ru-Pd](image)

![Sn](image)

**Table 4.2:** ICP analysis of the Ru-Pd catalysts synthesized in house.

<table>
<thead>
<tr>
<th>Synthesis Method</th>
<th>Metal Loading (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Theoretical</td>
</tr>
<tr>
<td><strong>Beaker</strong></td>
<td></td>
</tr>
<tr>
<td>Ru</td>
<td>20</td>
</tr>
<tr>
<td>Pd</td>
<td>20</td>
</tr>
<tr>
<td><strong>Furnace</strong></td>
<td></td>
</tr>
<tr>
<td>Ru</td>
<td>17</td>
</tr>
<tr>
<td>Pd</td>
<td>17</td>
</tr>
</tbody>
</table>

**Figure 4.4:** Cyclic Voltammograms for the three cathode catalysts tested for CO₂ reduction to formic acid. CVs were run in situ in the electrochemical cell at a scan rate of 20 mV/s. Cathode loading was 2 mg/cm² and the counter electrode was 2 mg/cm² Pt black. The electrolyte was 1 M KCl flowing at 0.5 ml/min.
the 20-20 Ru-Pd (beaker method) as we scan more negative under N\textsubscript{2} we see some reduction current. This current is the background hydrogen evolution reaction that is reducing the water into hydrogen. When the gas supply is CO\textsubscript{2} the reduction current increases significantly. This increase in current indicates some CO\textsubscript{2} reduction in addition to the hydrogen evolution seen. The change in current, however, is not conclusive evidence of CO\textsubscript{2} reduction since hydrogen evolution and CO\textsubscript{2} reduction are often interconnected and CO\textsubscript{2} dissolving in the electrolyte will change the pH and can alter the amount of hydrogen evolution that occurs.\textsuperscript{10} With the 17-17 Ru-Pd (furnace method) the background current with N\textsubscript{2} is similar in shape to that for the 20-20 Ru-Pd. For the Sn catalyst, the N\textsubscript{2} scan has very little reduction current, but with CO\textsubscript{2} a strong reduction current begins at about -1.5V, which strongly indicates significant CO\textsubscript{2} reduction.

Figure 4.5a shows the current densities for the three cathode catalysts. As seen in the figure, the current density of the Ru-Pd 30-30 wt\% is highest followed by the Ru-Pd 17-17 wt\% and then the Sn. However, when looking at the partial current density, which is the portion of the current that goes to the desired reaction, we see the opposite trend with the Sn catalyst having the highest performance. Similarly, the Faradaic and energetic efficiencies of the three cathode

![Figure 4.5](image-url)
catalyst are shown in Figure 4.5b. Despite having a much higher overpotential, as indicated by
its peak performance occurring at more extreme cell potentials, the Sn catalyst’s Faradaic and
energetic efficiency still far exceeded that of both Ru-Pd catalysts. This data highlights the
importance of testing the catalysts at a wide range of potentials. Had the experimental conditions
been chosen at lower cell potentials it would likely have appeared that Sn with its higher
overpotential yielded little or no formic acid. However, by testing over a wide range of
potentials it becomes clear that Sn indeed gives large amounts of formic acid and outperforms
the Ru-Pd catalysts.

In this work, neither of the Ru-Pd catalysts synthesized performed as well as what was
reported by Furuya et al. They reported a peak Faradaic efficiency for formic acid of 90%,
while the highest achieved by these Ru-Pd catalysts was <17%. A number of factors could
account for this difference in performance. Most significant is that different catalyst synthesis
methods were used. The method Furuya used was not readily available and thus other methods
were used. In particular, both of the catalysts here were carbon supported, while the catalyst
used by Furuya was not. Also, Furuya used GDEs made in their lab while this work used
commercial GDEs which could also potentially affect the activity of the catalyst. While it is
disappointing that these catalysts were unable to reproduce the exciting results reported, the
extensive catalyst synthesis optimization that would be required to match their results was
outside the scope and emphasis of this dissertation.

4.3.3 Carbon Monoxide Catalyst Performance

Several catalysts were studied for their ability to produce CO (syngas) from the
electrochemical reduction of CO₂. Figure 4.6 shows the CVs for each of these catalysts. For Au
and Ag, both show minimal current in a N₂ atmosphere. However, when exposed to CO₂ both
have strong reduction peaks, indicating they both are likely to reduce CO$_2$. Furthermore, the reduction current appears to begin ~100-200 mV earlier (less negative) for Au than for Ag, which indicates that Au may produce CO$_2$ reduction products at smaller overpotentials than Ag.

**Figure 4.6:** Cyclic voltammograms for the several cathode catalysts used for the electrochemical reduction of CO$_2$ to CO. CVs were run *in situ* in the electrochemical cell at a scan rate of 20 mV/s. Cathode loading was 5 mg/cm$^2$ and the counter electrode was 2 mg/cm$^2$ Pt black. The electrolyte was 1 M KCl flowing at 0.5 ml/min.
In contrast, the other catalysts (Pd, Pt, Ni) have relatively large reduction currents with \( \text{N}_2 \) and only minimal increase in the reduction currents with \( \text{CO}_2 \). This indicates that they are very active for hydrogen evolution and only minimal \( \text{CO}_2 \) reduction occurring on these catalysts. It is known from the literature that these metals favor hydrogen evolution and typically give very low Faradaic efficiencies for \( \text{CO}_2 \) reduction in aqueous electrolytes and ambient conditions.\(^1\)\(^,\)\(^2\) Thus, these catalysts were not expected to be effective at these conditions; however, they have the potential to be effective at different conditions (such as at elevated temperatures in an ionic liquid electrolyte) and these tests were run as a baseline for those future studies.

**Figure 4.7**: Faradaic efficiency for CO (filled symbols) and hydrogen (open symbols) (a), individual electrode potentials (b) and current density (c) as a function of cell potential for three cathode catalysts. Cathode loading was 5 mg/cm\(^2\) and the counter electrode was 2 mg/cm\(^2\) Pt black. The electrolyte was 1 M KCl flowing at 0.5 ml/min. Electrode potentials are not corrected for IR losses.
Figure 4.7b shows the current density as a function of cell potential for three cathode catalysts: Au, Pd, and Ag. Each produces roughly the same current. Figure 4.7a shows the CO Faradaic efficiency for the three catalysts. Au has a peak efficiency of 80% at -2.75V, but quickly decreases at more negative potentials. Pd produced only ~5% efficiency at all potentials. Silver had a peak Faradaic efficiency of 90-100% which was fairly constant from 2.75V – 4V. The data also shows that Au produces more CO at lower (less negative) potentials, which is consistent with the CV results. Pt and Ni were also tested, but gave no detectable amounts of CO and therefore, not plotted. The results show that Ag is the most selective of the catalyst, but Au has the ability to produce CO at lower overpotential, which is important for maximizing the energy efficiency.

The individual electrode potentials for Au, Pd, and Ag are shown in Figure 4.7c. All three have nearly identical polarization curves particularly at higher current densities. Obtaining nearly equal currents from three different catalysts with different particle sizes and properties indicates a shift in the operating regime. While at low currents the cell operates in a “kinetic regime” where the performance is dominated by the kinetic properties of the catalysts (activity, surface area, etc.). At higher currents the cell enters an “ohmic regime” where the performance is dominated by ohmic resistances in the cell (mainly due to electrolyte resistance). This demonstrates that resistances will be an important consideration when trying to operate at current densities above ~100 mA/cm². The easiest ways to minimize resistances are to increase the electrolyte conductivity and to decrease the electrode spacing. Thus, the effect on cell resistance should be considered when selecting the electrolyte and designing the reactor dimensions.
4.3.4 Anode Catalysts Performance

While the anode catalyst does not contribute to the Faradaic efficiency of CO₂ reduction, it is still important since the overpotential of the anode contributes to the energetic efficiency of the reactor. Hence, the performance of various catalysts for oxygen evolution reaction should not be ignored.

Figure 4.8 compares the individual electrode polarization curves for two anode catalysts, Pt black and 40% Pt/C. As seen in the figure, the Pt black catalyst performs better, particularly at high current densities where it experiences much less polarization, i.e., has a lower overpotential, than the 40% Pt/C. The figure also shows significant changes in the cathode potential (likely due to deterioration of the catalyst over time), which highlights a key benefit of the reactor design. By using a reference electrode in the exit stream of the reactor, the performance of the individual electrodes can be assessed, which here provided an explanation of the source of performance decline. Without the reference electrode, the performance of each electrode would be lumped together in the overall cell performance making it impossible to know what portion of any changes in cell performance should be attributed to each electrode.

4.3.5 Multi-channel Reactor

Figure 4.9 compares the performance of the multi-channel reactor with the single channel reactor using a Ag cathode catalyst. Both reactors produce nearly identical current densities. The multichannel reactor has an active electrode area 15 times that of the single channel
which demonstrates the ability to scale the microfluidic design using multiple channels. The Faradaic efficiency for the multi-channel reactor is significantly lower than for the single channel reactor. Besides having more channels, the multi-channel design also has much longer channels (4.5 cm vs. 1.5 cm) which leads to more depletion of CO$_2$ at the end of the reactor. The depletion of CO$_2$ could lead to decreased Faradaic efficiency in the multi-channel reactor. Results reported in Chapter 7 show that decreasing the partial pressure of CO$_2$ by 50% can lead to significant decreases in Faradaic efficiency, while not affecting the current density. This supports the hypothesis that depletion is leading to decreased efficiency and indicates that gas flow field designs capable of minimizing depletion effects will be important in future reactor designs.

The multi-channel reactor was also tested with varying numbers of its channels operating. The unused channels were covered with a thin (0.005”) sheet of PTFE, which allowed all the flow through the reactor to remain unchanged, but only some of the channels actively reducing CO$_2$. The experiments compared the performance with 5, 3, and 1 channel. The center channel(s) were used for the experiments with 3 and 1 channel. Figure 4.10 shows the results of these experiments. Both the Faradaic efficiency for CO and the current density appear to be
independent of the number of channels, although there is high variation (as indicated by the error bars), particularly at high cell potentials. This indicates that each channel is nearly identical as shown in the COMSOL simulations and confirms the ability to scale out with multiple channels.

4.4 Conclusions

This study compared several different cathode catalysts for the electrochemical reduction of carbon dioxide to formic acid and carbon monoxide. The results show that catalysts, such as Au and Ag, which have both been shown to have high Faradaic efficiencies can still have very different performances, making it critical to evaluate catalysts over a wide range of conditions. While Ag gives higher Faradaic efficiencies over a wider potential range, Au begins producing CO at lower overpotentials. In general the study here has been limited to catalysts that are commercially available. However, this reactor would also be an excellent tool for testing and evaluating novel catalysts being developed for the electrochemical reduction of carbon dioxide.

The multi-channel reactor demonstrated that the microfluidic reactor design can be scaled to larger electrode areas by using multiple channels in parallel. This work also indicated two additional parameters that will be important in reactor system design. First these results demonstrated that cell resistance, which is mainly due to electrolyte resistance, is an important
consideration when running at higher current densities. Also, work with the multi-channel reactor showed that CO₂ depletion can become an issue and designs that minimize this issue will be critical.

4.5 References


Chapter 5

Effects of Electrolyte pH on the Electrochemical Reduction of CO₂

5.1 Introduction

As summarized in chapter 2, literature has shown that the pH of the electrolyte can have a significant effect on the Faradaic efficiency of the electrochemical reduction of CO₂.\textsuperscript{1-3} However, these literature studies have not been extensive or systematic despite the fact that pH has been shown to have a large effect in similar situations, such as fuel cells.\textsuperscript{5} The work by Mahmood\textsuperscript{3} was limited to the acidic range (pH 1-5) and the others also had variation in the electrolyte species making it difficult to separate the effects of electrolyte salt and electrolyte pH.\textsuperscript{1,2} The goal of this work is to investigate the effects of pH on the electrochemical reduction of CO₂ over a range of pH without any complicating factors of changing electrolyte species or significant changes in electrolyte conductivity. As discussed earlier, using a flowing electrolyte instead of a membrane allows the flexibility to adjust the pH at will without affecting the performance of a conducting membrane. Two catalysts were selected for this study. Tin was selected as a catalyst for the production of formic acid, and Ag for the production of CO. The Ag catalyst was also tested using nanoparticles supported on carbon nanotubes (CNTs) in place of the standard Nafion binder.

5.2 Experimental

5.2.1 Carbon Nanotube Supported Catalyst

The nanotube cathode catalysts are fabricated by depositing silver onto carbon nanotubes in solution, vacuum filtering the resultant suspension and then hot pressing the fibers together. In detail, 10 mg of single-walled carbon nanotubes powder (Unidym, High Purity HPCO) and 1% (w/v) sodium dodecyl sulfate (SDS) was dispersed in 20 ml of water. Multiple sets of 10-minute low-powered ultrasonication (at 40% power and 90% frequency), 1-hour stirring and 3-hour centrifugations (at 2800 g or 4100 RPM) were performed to homogenize and uniformly disperse the suspension. 10 ml of 5 g/l Ag⁺ (as AgNO₃) was then added to 20 ml of CNT suspension under vigorous stirring at room temperature. After 3 hours vigorous stirring, a freshly prepared reducing agent of 50 mg NaBH₄ in 25 ml of H₂O was also added drop wise to the solution followed by vigorous stirring at room temperature for another 2 hours. This method for reducing the metal nanoparticles onto the support was adapted from several methods in the literature.⁶⁻¹⁶

The solution was then vacuum filtrated directly onto a gas diffusion electrode (GDE) using vacuum filtration to create a mat with an average silver loading on 5 mg/cm². The wet GDE membrane was dried for at least 30 minutes in a vacuum oven. It was then hot-pressed at 130°C and 2000 kPa for 5 min. Figure 5.1 shows SEM images of the synthesized catalyst.

5.2.2 Cell Testing

This study used the same equipment and procedures that were detailed in the previous chapter. For these experiments, 0.5 M or 1 M KCl was used as the electrolyte and was adjusted using 1M HCl or 1M KOH to the desired pH (4, 7, or 10) as indicated by a pH probe (Thermo Electron, Orion 9157BNMD). In these tests the cathode catalyst loadings were 5 mg/cm² and the anode was 2 mg/cm² Pt black. Three cathode catalysts were studied: Sn, Ag, and Ag/CNT.
5.2.3 Electrochemical Impedance Spectroscopy

Electrochemical impedance spectroscopy (EIS) was done on the Sn catalyst to investigate the effects of pH on catalyst performance. The AC impedance spectra were obtained using a Frequency Response Analyzer (FRA) module controlled by the potentiostat (Autolab PGSTAT-30, EcoChemie). The spectra were measured using constant voltage mode with frequencies ranging from 10 kHz to 30 mHz with 9 points/decade and a modulating voltage amplitude of 10 mV root mean squared. The measurements were performed at a cell voltage of -3V which corresponds to points of high efficiency for formic acid at all pHs. The cell was operated under the same conditions (flow rates, etc.) in the EIS studies as were used in the normal cell tests.

5.3 Results and Discussion

5.3.1 Formic Acid

Work in the literature and the experiments detailed in chapter 4 have shown that Sn has high Faradaic efficiency for formic acid production. Because of its high efficiency it was used as a catalyst for studying the effects of pH on the electrochemical reduction of CO$_2$ to CO. The catalyst was tested in 0.5 M KCl that had been adjusted to pH values of 10, 7, and 4. This un-buffered electrolyte requires only minute amounts of acid or base to adjust the pH, causing no
significant change in electrolyte conductivity. Figure 5.2 shows the efficiency and partial current density for the Sn catalyst with the electrolytes with different pHs. The data shows a double benefit of lower, more acidic pH on the reduction of CO$_2$ to formic acid. Decreasing the electrolyte pH gives higher current densities for formic acid, which indicates an improvement in the CO$_2$ reduction reaction kinetics at lower pH. While the onset of formic acid appears to start at the same point (-2.75V) regardless of electrolyte pH, the amount of formic acid produced increases dramatically for more acid electrolytes. Lowering the pH also increases the selectivity of the catalyst as indicated by the increase in Faradaic efficiency. This second observation is in agreement with trends seen by others, however, the prior work was limited to basic pH and also

![Figure 5.2](image)

**Figure 5.2:** Faradaic (filled symbols) and energetic (open symbols) efficiency for formic acid (a), partial current density for formic acid (b), and individual electrode polarization curves using 5 mg/cm$^2$ Sn cathode and 0.5 M KCl adjusted to various pHs. The anode is 2 mg/cm$^2$ Pt. © ECS Reprinted with permission from Whipple *et al.*
had different ionic species, *e.g.* HCO$_3$\(^-\) vs. CO$_3$\(^{2-}\), at the different pHs. The data reported here avoids such complications and extends the range to include acidic pH. Tests were not performed at lower pH because of the instability of Sn at pH < 3.\(^{17}\) The peak Faradaic efficiency and energetic efficiency were 89% and 45%, which are comparable to values achieved in the literature.\(^{18,19}\)

The individual electrode polarization curves in Figure 5.2c confirm that the main effect of lowering the electrolyte pH is on the cathode catalyst. In addition to increasing the efficiency for formic acid production, lowering the pH also results in less polarization on the cathode giving higher current densities. Again, the use of a reference electrode in this design enables us to determine that the effects of decreasing pH are on the cathode and not a side effect on the anode performance.

Figure 5.3 shows the Nyquist plots of the EIS data for the Sn cathode at the three pH values studied. The distance between the vertical axis and the high frequency points (points closest to the origin) represents the ohmic resistance (R$_{\Omega}$) or cell resistance (R$_{\text{cell}}$) of the system and is composed of the electrolyte resistance and any resistance in the components of the cell. As expected, this does not change significantly between the different pH tests since the conductivity of the system is not affected significantly by pH adjustments. The width of the arch formed in the plot corresponds to the charge transfer resistance (R$_{\text{CT}}$) in the system and is a measure of the kinetics of the reaction. Despite significant noise at the low frequency end of the
plots, it is clear that the charge transfer resistance decreases steadily as the pH of the electrolyte is decreased. This confirms the earlier conclusion that decreasing the pH improves the kinetics of the CO₂ reduction reaction on the cathode.

5.3.2 Carbon Monoxide

Because of silver's previously demonstrated ability to produce CO with high Faradaic efficiency, these studies investigating the effect of electrolyte pH on the reduction of CO₂ used a Ag nanoparticle catalyst. As with the formic acid studies above, three pH values, 4, 7, and 10 were used. The electrolyte was 1 M KCl adjusted with HCl or KOH to the desired pH. Figure 5.4a shows the Faradaic efficiency for CO and H₂. Each of the three pH values investigated here produced almost identical Faradaic efficiencies for CO and H₂. Similarly, Figure 5.4b shows the

![Figure 5.4: Faradaic efficiency for CO (filled symbols) and H₂ (open symbols) (a), partial current density for CO (b) and individual electrode polarization curves using 5 mg/cm² Ag cathode and 1 M KCl adjusted to various pHs. The anode is 2 mg/cm² Pt.](image)
partial current density for the Ag catalyst as a function of cell potential and pH. This shows that pH has minimal effect on the rate of CO₂ reduction to CO. Finally, Figure 5.4c reports the individual electrode potentials at each of the pH values, and likewise shows no significant variation with pH. The results demonstrate that, over the range from 4-10, pH has no significant effect on the electrochemical reduction of CO₂ to CO.

These observations are very different from those reported in the previous section for CO₂ reduction to formic acid. The dramatic differences in pH dependence can likely be attributed to differences in the reaction mechanism for formic acid production versus carbon monoxide. While several researchers have reported on the reaction mechanism for CO₂ the details are still not well understood and depend on many factors including, catalyst, electrolyte, temperature and electrode potential.¹⁰⁻²⁶ Despite the uncertainty in details of the reaction, the general mechanism proposed by Hori²⁴ provides insight into the key differences between CO and formic acid. In the cases where formic acid is formed (metals such as Pb, Hg, In, Sn, Cd, Tl) the key intermediate, CO₂⁻, is a free anion radical in solution. In contrast, when CO is the product (metals such as Au, Ag, Zn) the same intermediate is stabilized by adsorption on the catalyst surface. Because the intermediate is adsorbed on the surface the reaction is dependent on the conditions on the surface, which can be significantly different from bulk conditions. This could result in the production of CO being unaffected by the bulk electrolyte pH in these experiments, while reduction to formic acid shows a strong dependence because of the free intermediate in solution.

Figure 5.5 shows the Faradaic efficiencies, partial current densities, and individual electrodes for the Ag catalyst supported on carbon nanotubes, with the same electrolyte conditions as the Ag catalyst above. The results show the same general trend as the original silver catalyst with the Nafion binder. The pH has no measurable effect on the reaction. The
only significant differences between the performances of the two Ag catalysts are slightly lower current densities and Faradaic efficiencies for CO with the Ag/CNT catalyst.

5.3.3 Catalyst Durability

Tests were also done to investigate the performance of the two Ag catalysts over time. Each of the catalysts was run continuously in the reactor at -3V with samples taken every 30 min to measure the Faradaic efficiencies. Figure 5.6 shows the performance of the two catalysts. Both show significant decreases in performance over the time period investigated. Both started with a CO Faradaic efficiency of >90%. The Ag/CNT catalyst dropped to ~55% CO Faradaic efficiency in <3hrs, while the Ag catalyst with Nafion maintained a CO Faradaic efficiency of

Figure 5.5: Faradaic efficiency for CO (filled symbols) and H₂ (open symbols) (a), partial current density for CO (b) and individual electrode polarization curves using the Ag/CNT catalyst and 1 M KCl adjusted to various pHs. The anode is 2 mg/cm² Pt.
Figure 5.6: Faradaic efficiency for CO (filled symbols) and H$_2$ (open symbols) (a) and current density (b) over ~6 hrs for two Ag catalysts running continuously at a cell potential of -3V.

~60% after almost 6hrs. Similarly, both catalysts showed significant decreases in current density over time. The Ag/CNT catalyst dropped from 70 mA/cm$^2$ to 50 mA/cm$^2$ over 3 hrs while the Ag catalyst with Nafion dropped from 75 mA/cm$^2$ to 40 mA/cm$^2$ over 6 hrs. Figure 5.7 shows SEM images of the Ag/CNT catalyst before and after use. The catalyst layer changes significantly after use. Most of the smaller catalyst particles are gone and only a few of the larger catalyst particles remain. This loss of catalyst indicates that the long term stability and durability of the catalyst will be an important consideration in future development for the electrochemical reduction of carbon dioxide.

Figure 5.7: SEM images of the Ag/CNT catalyst before (left) and after (right) being used in the reactor.
5.4 Conclusions

While not yet fully studied or understood, the electrolyte pH is an important factor in the electrochemical reduction of carbon dioxide. The microfluidic reactor used here provides a convenient and flexible platform for studying parameters such as the pH of the electrolyte. These results demonstrate that the pH can have a very strong impact on the rate and efficiency of CO₂ reduction. However, whether the electrolyte pH has an effect depends on the reduction product being formed. In this work, formic acid production showed a strong dependence on the pH. In the pH range studied (4-10), decreasing the pH significantly increased the partial current density and Faradaic efficiency for formic acid. The individual electrode potentials and EIS analysis confirmed that these improvements are due to more facile kinetics on the cathode. In contrast, the production of CO using a Ag catalyst was completely unaffected by changes in the pH. These varying dependences on pH are likely due to the differences in the mechanisms for each product. Thus, optimization of the electrolyte pH depends on the catalyst used and the desired product. This work also performed initial investigation of durability for Ag catalysts. The catalyst showed significant loss in catalyst particles and performance over a few hours of operation, indicating that catalyst durability will be an important area for future study and development.

5.5 References


Chapter 6

Amine Based Electrolytes for the Electrochemical Reduction of CO₂

6.1 Introduction

As discussed in chapter 1, one of the biggest challenges for the electrochemical reduction of carbon dioxide is achieving high energy efficiencies at reasonable current densities. The energy efficiency is composed of two components: Faradaic efficiency (selectivity) and the overpotential. While high Faradaic efficiencies have been achieved by many researchers on various catalysts, high overpotentials consistently limit the energy efficiency. The cause of these high overpotentials is the formation of a high energy CO₂∙⁻ intermediate. This intermediate has a standard potential of -1.9V, which is much more negative than the standard potentials for the common reduction products. However, stabilization of this intermediate can lower its energy and reduce the overpotential required to CO₂ reduction. Stabilization can occur with catalysts and potentially through electrolyte interactions.

As discussed previously, the tendency for hydrogen evolution in many electrolytes limits catalysts for CO₂ reduction to those with high hydrogen overpotentials. The use of an electrolyte that effectively suppresses hydrogen evolution could expand the range of potential catalysts to include those that readily catalyze hydrogen evolution and potentially lead to CO₂ reduction at lower overpotentials through the use of catalysts which are currently ineffective because of their tendency for hydrogen evolution. Furthermore, direct reduction of the overpotential could be achieved through the use of catalysts that interact with and stabilize the key intermediates in CO₂ reduction.
This study investigates two potential electrolytes for improving the electrochemical reduction of CO$_2$: (1) 1-ethyl-3-methyl-imidazolium tetrafluoroborate (EMIM BF$_4$) and (2) choline chloride (see Figure 6.1).

Ionic liquids, such EMIM BF$_4$, have several properties that make them attractive for electrochemical applications:

- **Low melting points** – they are liquid at room temperature without needing to dissolve in a solvent
- **Non-volatility** – because they are ionic compounds they have negligible vapor pressure
- **High conductivity** – their high ion concentrations give them relatively high conductivities
- **“Tunability”** – because they are organic ions, their properties can be tuned by varying the organic groups attached to the cation

Furthermore, ionic liquids have relatively high solubilities (see Table 6.1) for carbon dioxide

![Chemical structures for choline chloride and EMIM BF$_4$ used as electrolytes in this study.](image)

**Figure 6.1:** Chemical structures for choline chloride and EMIM BF$_4$ used as electrolytes in this study.

<table>
<thead>
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<th>Solvent</th>
<th>$S_{CO_2}$</th>
</tr>
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<tr>
<td>CH$_3$CN</td>
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</tr>
<tr>
<td>acetone</td>
<td>6.6</td>
</tr>
<tr>
<td>THF</td>
<td>6.2</td>
</tr>
<tr>
<td>MeAc</td>
<td>6.0</td>
</tr>
<tr>
<td>DMF</td>
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</tr>
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</tr>
<tr>
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<tr>
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<td>3.6</td>
</tr>
<tr>
<td>DMSO</td>
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</tr>
<tr>
<td>$n$-hexane</td>
<td>2.1</td>
</tr>
<tr>
<td>EMIM BF$_4$</td>
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</tr>
<tr>
<td>water</td>
<td>0.8</td>
</tr>
<tr>
<td>1 M NaCl$^{17}$</td>
<td>0.6</td>
</tr>
</tbody>
</table>

**Table 6.1:** Solubility of CO$_2$ in several organic solvents compared to EMIM BF$_4$ and water. Data is take from Bara et al.$^{21}$ except where indicated.
making them promising absorbents for CO$_2$ sequestration$^{20-22}$ which could facilitate integration if the adsorbent could also serve as the electrolyte supplying CO$_2$ for electrochemical reduction.$^{23-25}$ They also have been shown to interact with CO$_2$ indicating the possibility for achieving the desired stabilizing effects.$^{24,26}$

Similarly, the choline cation is a tertiary amine and thus has potential for interacting with carbon dioxide. Also, several researchers have reported the ability of quaternary ammonium salts to suppress hydrogen evolution$^{27-29}$, which is advantageous since hydrogen evolution is the main competing reaction with CO$_2$ reduction. Furthermore, choline chloride is a food additive for livestock and also sold as a dietary supplement for humans making it an inexpensive and non-toxic alternative to ionic liquids.

Both of these electrolytes have been investigated by researchers in Professor Masel’s group here at Illinois. The electrochemical studies done by these researchers have shown that EMIM BF$_4$ electrolytes can reduce CO$_2$ at significantly lower overpotentials$^{30}$ and that choline chloride can effectively suppress hydrogen evolution.$^{31}$ This work seeks to build on their work and evaluate the effects of these electrolytes in an operating reactor. The flexibility of this microfluidic reactor enables the use of these unusual electrolytes.

6.2 Experimental

6.2.1 Cell Testing

This study used the same equipment and procedures that were detailed in chapter 4. For these experiments the electrolytes were 0.5M choline chloride and 18 mol % EMIM BF$_4$ in deionized water. In these tests the cathode catalyst loadings were 5 mg/cm$^2$ and the anode was 2 mg/cm$^2$ Pt black. Four cathode catalysts (Ag, Au, Pd, Sn) were tested in choline chloride while four catalysts (Ag, Au, Ni, Pt) were tested in EMIM BF$_4$. 

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6.2.2 Reference Electrode

For the experiments with EMIM BF$_4$ a non-aqueous reference electrode was used instead of the standard Ag/AgCl electrode. The electrode consisted of a non-aqueous reference electrode kit (BASi, MF-2062) filled with 0.1 M tetrabutlyammonium perchlorate (TBAP) and 0.01M AgNO$_3$ in acetonitrile (ACN). The potential of this electrode was determined by referencing to the Fe$^+/\text{Fc}$ redox couple. However, as described by Pavlishchuk\textsuperscript{32} there is uncertainty in the assumption that the potential of the Fe$^+/\text{Fc}$ redox couple is unchanged between electrolytes, which makes comparing potentials between the ionic liquid and aqueous systems difficult. For the experiments with choline chloride, a Ag/AgCl reference electrode was used as in the previous chapters.

**Figure 6.2:** Cyclic Voltammograms for several catalysts in 0.5 M choline chloride compared with 1 M KCl. CVs were run in situ in the electrochemical cell at a scan rate of 20 mV/s. Cathode loading was 5 mg/cm$^2$ and the counter electrode was 2 mg/cm$^2$ Pt black. The electrolyte was flowing at 0.5 ml/min.
6.3 Results and Discussion

6.3.1 Choline Chloride

Figure 6.2 shows the CVs for Ag, Au, Sn, and Pd in choline chloride compared with potassium chloride electrolytes. The effect of choline chloride varies with each metal. The current in the nitrogen CV decreases (Au) stay the same (Sn) or increases (Ag and Pd) when choline is used, making it difficult to draw conclusions regarding its effect on hydrogen evolution. However, for all metals, the current in the CO₂ CV decreases when choline chloride is used as the electrolyte. This decrease could come from suppression of the hydrogen evolution side reaction, or changes in the CO₂ reduction reaction rate.

Figure 6.3: Faradaic efficiency for formic acid (open symbols) and CO (filled symbols) (a), total current density (filled symbols) and partial current density for CO₂ reduction (open symbols) (b), and individual electrode potentials (c) of the Sn catalyst with 0.5 M choline chloride compared to 1 M KCl. Cathode loading was 5 mg/cm² and the counter electrode was 2 mg/cm² Pt black. The electrolyte was flowing at 0.5 ml/min.
Figure 6.3 shows the performance of the Sn catalyst in 0.5 M choline chloride compared with 1 M KCl. Both formic acid and CO production were measured and compared. Using choline chloride as an electrolyte significantly increased the Faradaic efficiency for both formic acid and CO indicating that choline improves the selectivity for CO$_2$ reduction over hydrogen evolution. However, despite the increase in Faradaic efficiency, the overall reaction rate decreases. Figure 6.3b shows the total current density as well as the partial current density for CO$_2$ reduction (formic acid and CO). Both are significantly lower for choline chloride compared with KCl. The individual electrode potentials (Figure 6.3b) show that the increased polarization occurs on the cathode. Thus, choline chloride appears to increase the selectivity for CO$_2$ but

**Figure 6.4:** Faradaic efficiency (a) partial current density (b) and individual electrode potentials (c) of the Ag catalyst with 0.5 M choline chloride compared to 1 M KCl. Cathode loading was 5 mg/cm$^2$ and the counter electrode was 2 mg/cm$^2$ Pt black. The electrolyte was flowing at 0.5 ml/min.
decreases the reaction rate.

Figure 6.4a shows the Faradaic efficiency for CO with a Ag catalyst in 0.5 M choline chloride compared with the efficiency in 1 M KCl. The Faradaic efficiency at low cell potentials (-2.25V) is significantly higher in choline chloride than KCl; however at higher potentials, both electrolytes give ~100% Faradaic efficiency. While there is some improvement in the Faradaic efficiency, the current density (shown in Figure 6.4b) shows a large drop of ~50% when using choline chloride instead of KCl. Because the Faradaic efficiency is ~100% for most of the potentials, the partial and total current densities are nearly the same and thus only the partial current density is shown. The individual electrode potentials in Figure 6.4c show that the reason

**Figure 6.5:** Faradaic efficiency for CO (a), total (filled symbols) and partial (open symbols) current density (b), and individual electrode potentials (c) of the Au catalyst with 0.5 M choline chloride compared to 1 M KCl. Cathode loading was 5 mg/cm² and the counter electrode was 2 mg/cm² Pt black. The electrolyte was flowing at 0.5 ml/min.
for the decreased current density is increased polarization on the cathode. Figure 6.5 shows the corresponding data for a Au catalyst and similar trends are seen as with the Ag catalyst. At potentials where the Faradaic efficiency for CO is low (> -2.5V and < -3V) the Faradaic efficiency increases. However, the overall rate decreases significantly as evidenced by the current densities. As with Ag, the individual electrode potentials show that the cathode experiences much more polarization and if the potentials are IR corrected (Figure 6.6) the anode curves overlay showing that all the increased polarization comes from the cathode. Zhu et al.\textsuperscript{31} showed with SERS experiments that a thin layer of choline forms on the surface, which is likely the mechanism for hydrogen suppression. These results show the additional effect of an overall decrease in the CO\textsubscript{2} reduction rate. Because of the two effects a net positive effect on the Faradaic efficiency occurs only at potentials where the Faradaic efficiency for CO\textsubscript{2} reduction is low.

6.3.2 EMIM BF\textsubscript{4}

Figure 6.7 shows the CVs for Pt, Ag, Au and Ni in 18 mol\% EMIM BF\textsubscript{4}. The Pt and Ni CVs show no significant difference between the N\textsubscript{2} and CO\textsubscript{2} scans indicating that significant amounts of CO\textsubscript{2} reduction on Pt are unlikely even in the EMIM BF\textsubscript{4} solution. In contrast, both the Ag and Au catalysts show a shift in the reduction potentials in EMIM BF\textsubscript{4} compared to 1M KCl. The reduction peak in the presence of CO\textsubscript{2} begins approximately 200 mV earlier (less negative) in 18 mol\% EMIM BF\textsubscript{4} compared with 1 M KCl. This supports the results reported by

![Figure 6.6: IR corrected electrode potentials for the Au cathode catalyst in 0.5 M choline chloride compared with 1 M KCl.](image)
Rosen et al.\textsuperscript{30} showing that EMIM BF\textsubscript{4} reduces the overpotential for CO\textsubscript{2} reduction. However, as mentioned earlier, because of the difficulty in comparing potentials between aqueous and non-aqueous systems, the potentials in EMIM BF\textsubscript{4} have significant uncertainty. Further, more rigorous validation of the potentials is necessary to be certain of lower overpotentials in the ionic liquid.

Figure 6.8 shows the performance of the Ag catalyst in 18 mol\% EMIM BF\textsubscript{4} compared with 1 M KCl. Instead of increasing the Faradaic efficiency, using EMIM BF\textsubscript{4} as an electrolyte significantly decreased the Faradaic efficiency for CO. Also, as with choline chloride, the partial current density decreases significantly with the EMIM BF\textsubscript{4} electrolyte compared to the KCl.

\textbf{Figure 6.7:} Cyclic Voltammograms for several catalysts in 18 mol\% EMIM BF\textsubscript{4} compared with 1 M KCl. CVs were run \textit{in situ} in the electrochemical cell at a scan rate of 20 mV/s. Cathode loading was 5 mg/cm\textsuperscript{2} and the counter electrode was 2 mg/cm\textsuperscript{2} Pt black. The electrolyte was flowing at 0.5 ml/min.
electrolyte. The individual electrode potentials again identify the cause for the decreased performance. Figure 6.8c shows that using an EMIM BF₄ electrolyte causes a large increase in the polarization on the anode. Thus, contrary to the results for choline chloride, EMIM BF₄ appears to have a strong negative effect on the anode performance. This explains the decrease in current density, but does not fully address the decreased selectivity with the EMIM BF₄ electrolyte.

While the cyclic voltammetry experiments done here and by others³⁰ indicate that EMIM BF₄ improves the kinetics of CO₂ reduction on Ag, the electrolysis experiments do not show any improvement. The cathode polarization curves for EMIM BF₄ and KCl electrolytes overlap

![Graphs showing Faradaic efficiency, partial current density, and electrode potentials for KCl and EMIM BF₄ electrolytes.]

**Figure 6.8:** Faradaic efficiency for CO (a) partial current density (b) and individual electrode potentials (c) of the Ag catalyst with 18 mol% EMIM BF₄ compared to 1 M KCl. Cathode loading was 5 mg/cm² and the counter electrode was 2 mg/cm² Pt black. The electrolyte was flowing at 0.5 ml/min.
nearly exactly and the Faradaic efficiency in EMIM BF$_4$ decreases significantly. The lack of improvements in the electrolysis experiments, despite the CVs indicating improved kinetics, suggest that there are other factors that are dominating performance. One likely factor that could be limiting performance is mass transfer of CO$_2$ to the catalyst surface. Although EMIM BF$_4$ has a higher solubility for CO$_2$ than for water, the diffusivity of CO$_2$ is much lower in ionic liquids than many other solvents. Table 6.2 shows the diffusivity of several ionic liquids (the diffusivity for EMIM BF$_4$ was not available in the literature) along with the diffusivity in water and some organic solvents. The diffusivity in ionic liquids is an order of magnitude smaller than the organic liquids and ~2-5 times smaller than in water. The decreased diffusivity counteracts the benefits of higher solubility and could lead to decreased mass transfer of CO$_2$ to the catalyst surface, thus decreasing the Faradaic efficiency for CO$_2$ reduction. However, mass transfer limitations would become more important at higher current densities, but these results show higher efficiency at higher currents. Thus, mass transfer effects do not appear to completely account for the trends seen and the use of ionic liquids needs much more extensive investigation to understand the various factors influencing performance.

6.4 Conclusions

This study investigated two electrolytes for their potential to improve the electrochemical reduction of carbon dioxide. Choline chloride appeared to be effective at suppressing hydrogen evolution as has been previously reported.$^{31}$ However, it also decreased the rate of CO$_2$ reduction by ~50%. The CV’s indicated that EMIM BF$_4$ was effective at reducing CO$_2$ at lower
overpotentials. However, the electrolysis experiments showed a decrease in Faradaic efficiency and a sharp decrease in current densities. The latter appears to be a result of increased polarization on the anode, while the reason for decreased efficiency is not yet fully understood. These preliminary results using choline chloride and EMIM BF$_4$ demonstrate the need for further study to understand the effects of these electrolytes on all relevant parameters including the cathode and anode kinetics, solubility and diffusivity of CO$_2$, and conductivity of the electrolyte stream.

6.5 References


Chapter 7

Effects of Reaction Temperature on the Electrochemical Reduction of CO₂

7.1 Introduction

Temperature is a critical parameter in any chemical reaction. In general, reaction rates depend on temperature in accordance with the well known Arrhenius equation\(^1,2\):

\[
k_A(T) = A e^{-E/RT}
\]  

This equation states that the reaction rate is expected to increase with increasing temperature. However, surface reactions, such as reaction on a catalyst, have much more complex rate equations and can even decrease with increasing temperature.\(^3\) Extensive work in fuel cells has shown that increasing temperature can greatly enhance the performance of even “low temperature” fuel cells operating between 20°C and 100°C.\(^4,5\) However, in the case of competing reactions (as is the case with CO₂ reduction), the selectivity, \(i.e.,\) Faradaic efficiency, will depend on the relative magnitudes of the activation energies, \(E.\)\(^1\) Furthermore, changing the reaction kinetics is not the only way that temperature affects the electrochemical reduction of CO₂. Increasing the reaction temperature has three main effects: (1) increased exchange current densities for the electrode reactions in accordance with equation 1; (2) decreased solubility of CO₂ in the electrolyte; and (3) increased diffusivity of CO₂.\(^6\) Separating out these effects is often difficult.

Several investigators have studied the effect of temperature on the electrochemical reduction of carbon dioxide and many have observed a general decrease in hydrogen evolution with decreasing temperature leading to higher Faradaic efficiencies for CO₂ reduction.\(^7-10\)
Mizuno et al.\textsuperscript{10} and Li and Oloman\textsuperscript{6} performed studies in which they adjusted the pressure of CO\textsubscript{2} to keep the solubility the same, thus eliminating that effect from the results. Their results, however, were contradictory with Mizuna et al. reporting increasing efficiency with decreasing temperature and Li and Oloman reporting the opposite trend. These apparently contradictory results could be due to different operating ranges, catalysts or reactor setups. Thus, our understanding of the effects of temperature on the electrochemical reduction of carbon dioxide is still limited. This study seeks to further that understanding by studying the effects of temperature using a microfluidic reactor with various catalysts and electrolytes.

7.2 Experimental

This study used the same equipment and procedures that were detailed in Chapter 4 with a few changes which are detailed here. Instead of the original reactor, these experiments used the modified design with an aluminum body (see Chapter 3). The flow channels for both the gas and liquid are identical in dimensions to the original design. The reactor was heated using a 1/8” diameter 50 watt cartridge heater (McMaster-Carr, 8376T22) in both the cathode and anode sides of the reactor. The temperature was controlled using a PID controller (Omega, CSI32K) with a K-type thermocouple (McMaster-Carr, 3648K24) bolted to the back of the cathode chamber. The electrolyte was preheated before entering the reactor using heating tape (Barnstead/Thermolyne, BS0051-040) wrapped around the electrolyte syringe with a controller and thermocouple identical to those used on the reactor. The electrolyte was allowed to “warm-up” for at least 15 minutes before running an experiment. As detailed in Chapter 3, this setup was modeled with COMSOL to achieve accurate and uniform temperature on the reactor electrodes. Finally, a small steam trap consisting of a 1 ml vial was inserted in the gas line
between the reactor and the GC to capture any water condensing out of the hot gas stream as it cools and prevent it from entering the GC and pressure controller.

7.3 Results and Discussion

7.3.1 Tin

Figure 7.1 presents the performance of the microfluidic reactor with a Sn catalyst and 1 M KCl electrolyte at several temperatures. According to these results, increasing temperature appears to increase the Faradaic efficiency for formic acid at small potentials (-2.5V), but has minimal effect at larger potentials. The individual electrode potentials and overall current density show that higher temperatures increase the current density slightly due to less

![Figure 7.1](image-url)

**Figure 7.1:** Faradaic efficiency for CO (filled symbols) and formic acid (open symbols) (a), individual electrode potentials (b), total current density (c), and partial current density for CO (filled symbols) and formic acid (open symbols) with a Sn catalyst at temperatures ranging from 20°C - 90°C. Cathode loading was 5 mg/cm² and the counter electrode was 2 mg/cm² Pt black. The electrolyte was flowing at 0.5 ml/min.
polarization on the cathode. Looking at the partial current densities for formic acid and CO at low potentials (Figure 7.1d) reveals that at these potentials, increasing the temperature increases the rate of CO$_2$ reduction to both formic acid and CO.

7.3.2 Silver

Figure 7.2 shows the temperature dependence of a Ag catalyst with 1 M KCl electrolyte. In contrast to the results for the Sn catalyst, the Faradaic efficiency for CO steadily decreases with increasing temperature. The peak Faradaic efficiency decreases from ~100% at 20°C to <30% at 90°C. Similar to the Sn catalyst, there appears to be an increase in the reaction rate with increasing temperature particularly at smaller potentials. Table 7.1 shows the partial current

Figure 7.2: Faradaic efficiency for CO (a), individual electrode potentials (b), and total current density (c) with a Ag catalyst and 1 M KCl electrolyte at temperatures ranging from 20°C - 90°C. Cathode loading was 5 mg/cm$^2$ and the counter electrode was 2 mg/cm$^2$ Pt black. The electrolyte was flowing at 0.5 ml/min.
density for CO with the Ag catalyst as a function of cell potential and temperature. At small potentials (before -2.75V) and temperatures less than 90°C, the rate of CO₂ reduction to CO increases with increasing temperature. Beyond these ranges, increasing temperature begins to decrease the rate of CO₂ reduction. These results are consistent with the multiple affects of temperature outlined in the introduction. At small cell potentials (or currents) and low to moderate temperatures, the cell is operating in a “kinetic” regime where the performance is dominated by the kinetics of the reaction. Since higher temperature improves the kinetics, there is an increase in CO₂ reduction rate with increasing temperature in this region. Outside this region, i.e., large potentials (currents) or very high temperatures, mass transfer becomes much more important due to decreasing solubility and high reaction rates depleting the CO₂ near the electrode. Thus, the reactor is operating in a “mass transfer” regime where increasing the temperature, which decreases mass transfer of CO₂, decreases the reaction rate.

To further investigate whether the decrease in Faradaic efficiency seen at higher temperatures is due to decreased solubility of CO₂, the cell was run with 50% each CO₂ and N₂ in the gas stream. Similar to the experiments done by Li and Oloman⁶, this simulates a decrease in solubility by decreasing the partial pressure. Decreasing the partial pressure by 50% is approximately equal to decreasing the solubility of CO₂ 50% by increasing the temperature by 30°C¹¹, i.e., from 20°C to 50°C. Figure 7.3 shows the results for these experiments. Similar to

### Table 7.1: Partial current density for CO as a function of potential and temperature using a Ag catalyst.

<table>
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<tr>
<th>Potential (V)</th>
<th>Partial Current Density (mA/cm²)</th>
<th>Partial Current Density (mA/cm²)</th>
<th>% Increase</th>
<th>Partial Current Density (mA/cm²)</th>
<th>Partial Current Density (mA/cm²)</th>
<th>% Increase</th>
<th>Partial Current Density (mA/cm²)</th>
<th>Partial Current Density (mA/cm²)</th>
<th>% Increase</th>
</tr>
</thead>
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<tr>
<td>-2.00</td>
<td>0.0</td>
<td>0.0</td>
<td>0%</td>
<td>-2.25</td>
<td>-0.7</td>
<td>-1.5</td>
<td>129%</td>
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<td>-2.50</td>
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</tr>
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</tr>
</tbody>
</table>

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the effects of increasing temperature, decreasing the partial pressure of CO\textsubscript{2} decreases the Faradaic efficiency of the reactor. Partial pressure has essentially no effect on the current density or polarization of either electrode. A key difference between decreasing the partial pressure and increasing the temperature is the improvements seen with temperature in the small potential “kinetic” region are not observed with decreased partial pressure. This supports the assertion of two regimes, one in which kinetic effects are important and one where mass transfer effects dominate.

The effects of temperature were also investigated using a Ag catalyst in 0.5 M choline chloride electrode. These results are reported in Figure 7.4. Similar to the KCl electrolyte, the

![Figure 7.3: Faradaic efficiency for CO (a), individual electrode potentials (b), and total current density (c) with a Ag catalyst and 1 M KCl electrolyte with varying CO\textsubscript{2} partial pressure. Cathode loading was 5 mg/cm\textsuperscript{2} and the counter electrode was 2 mg/cm\textsuperscript{2} Pt black. The electrolyte was flowing at 0.5 ml/min.](image-url)
Faradaic efficiency decreases sharply as temperature is increased. The choline chloride electrolyte experiences more significant increases in current density as the reaction temperature increases, but the current densities are still well below those achieved in KCl. The individual electrode potentials show that the increased current densities with temperature appear to be coming from decreased polarization on the cathode. It is not yet known how temperature may affect the hydrogen suppression by the adsorbed layer of choline chloride reported by Zhu et al.\textsuperscript{12}, however the decrease in CO Faradaic efficiency and change in cathode polarization suggest that is it significantly impacted.

\textbf{Figure 7.4:} Faradaic efficiency for CO production (a), individual electrode potentials (b), and total current density (c) with a Ag catalyst and 0.5 M choline chloride electrolyte at temperatures ranging from 20°C - 90°C. Cathode loading was 5 mg/cm\textsuperscript{2} and the counter electrode was 2 mg/cm\textsuperscript{2} Pt black. The electrolyte was flowing at 0.5 ml/min.
7.3.3 Gold

Further studies on temperature were done using a Au catalyst. The results for the Au catalyst in Figure 7.5 show significant deviations from the results seen with Ag and Sn. Unlike the other catalysts, the Au catalyst exhibits a large increase in Faradaic efficiency at 50°C before decreasing at 90°C. Furthermore, the current density and partial current density increase dramatically between 20°C and 50°C, which is due to decreased polarization on the cathode. When increasing the temperature further from 50°C to 90°C the current density and cathode polarization show no significant improvement, but a sharp decrease in Faradaic efficiency results

Figure 7.5: Faradaic efficiency for CO (a), individual electrode potentials (b), total current density (c), and partial current density for CO production (d) with a Au catalyst and 1 M KCl electrolyte at temperatures ranging from 20°C - 90°C. Cathode loading was 5 mg/cm² and the counter electrode was 2 mg/cm² Pt black. The electrolyte was flowing at 0.5 ml/min.
in a large decrease in partial current density. The difference seen between the Sn, Ag and Au catalysts are likely due to the different adsorption strengths and resulting kinetic properties of these metals. Because of the different kinetic properties, they have different “kinetic” regimes, which for Au extends across the entire potential range explored for temperatures up to at least 50°C. Thus, the same trends in the competing effects of kinetics and mass transfer are seen on the different metals, but the areas for which each effect dominates depends on the catalytic properties of the metal.

7.3.4 Platinum and Nickel

Platinum and nickel catalysts were also tested with 0.5 M H₂O in EMIM BF₄ at 110°C and 120°C. The approach was to suppress hydrogen evolution by using only minimal amounts of water in EMIM BF₄ and prevent CO from poisoning the catalysts by operating at elevated temperatures where the CO desorbs. However, neither catalyst produced detectable amounts of CO. Figure 7.6 shows the Faradaic efficiency for H₂ with these two catalysts. The efficiency for H₂ on Pt is nearly 100% indicating there is very little if any CO₂ reduction. The Faradaic efficiency on Ni is much less than 100%, indicating that there could be some liquid CO₂ reduction products, however, this was not pursued at this time.

![Figure 7.6](image_url)  
*Figure 7.6: Faradaic efficiency for H₂ production with Ni at 120°C (a) and Pt at 110°C (b) with 0.5 M H₂O in EMIM BF₄.*
7.4 Conclusions

Temperature is a critical parameter in the electrochemical reduction of carbon dioxide, however, because the many ways in which temperature affects the system and the limited studies investigating temperature, its effects are complicated and poorly understood. Temperature affects the kinetics of the various surface reactions and it affects the mass transfer of CO$_2$ by changing its solubility and diffusivity in the electrolyte. The studies here have shown that the reactor operates in two regimes. The first is the “kinetic” region at lower temperatures and potentials (current densities) where the kinetics of the reaction is important. In this region, temperature tends to increase the reaction rate as indicated by the partial current density and sometimes also leads to improved Faradaic efficiency. The second region is the “mass transfer” region where the performance is dominated by mass transfer of CO$_2$ to the catalyst. In this region Faradaic efficiency and partial current density tend to decrease with temperature due to decreasing solubility at higher temperature. The relative size and location of the two regions depends on the properties of the catalyst being used and thus different catalysts may have different optimum temperatures. Also, as discussed above, the improved kinetics is counteracted by lower solubility at higher temperatures. The simplest way to counteract this decrease in solubility is to increase the CO$_2$ pressure. Thus elevated pressures will likely be needed to realize the full benefits of improved kinetics at higher temperatures and pressure control should be incorporated into future iterations of the microfluidic reactor design.

7.5 References


Chapter 8

Conclusions and Future Directions

8.1 Summary and Conclusions

Diminishing supplies of conventional energy sources and growing concern over greenhouse gas emissions present significant challenges to supplying the world’s rapidly increasing demand for energy. The electrochemical reduction of carbon dioxide has the potential to address many of these issues by providing a means of storing electricity in chemical form. Storing electrical energy as chemicals would help solve the challenges in leveling the output of clean, but intermittent renewable energy sources such as wind and solar. An effective means of storing the electricity, such as CO$_2$ reduction is necessary for intermittent resources to expand beyond 15-20% of the electricity supply.\textsuperscript{1} The electrochemical reduction of CO$_2$ also enables renewable electricity to produce carbon neutral fuels for portable applications.

However, to be a viable technology, the electrochemical reduction of carbon dioxide needs to have current densities and energetic efficiencies that are competitive with other means of converting electricity into chemicals, \textit{e.g.,} water electrolysis.\textsuperscript{2-7} Many researchers have studied the electrochemical reduction of CO$_2$ including parameters such as catalysts,\textsuperscript{8-10} electrolytes\textsuperscript{11-16} and temperature,\textsuperscript{8, 17-20} but further study is needed to further the understanding of this process and optimize the performance. Studying the electrochemical reduction of CO$_2$ is greatly facilitated by a reactor setup with excellent flexibility and control over the reaction conditions.

This dissertation reports the development and validation of a microfluidic reactor for the electrochemical reduction of CO$_2$. The design uses a flowing liquid electrolyte instead of the
typical polymer electrolyte membrane. In addition to other benefits, this flowing electrolyte
gives the reactor great flexibility, allowing independent analysis of each electrode and the testing
of a wide variety of parameters including catalysts, electrolyte, electrolyte pH, and temperature.
Scaling of the microfluidic design was demonstrated with a multi-channel reactor. Modeling in
COMSOL aided development to ensure equal flow through the channels of the multi-channel
reactor and accurate and uniform temperature in the single-channel reactor. In this work,
experiments using the microfluidic reactor studied the following areas:

- **Comparison of different metal catalysts for the reduction of CO$_2$.** Several catalysts
  including Sn, Pd, Ru-Pd, Pt, Ni, Ag, Au, were tested for the production of formic acid
  and CO. Of these catalysts, Sn had the highest Faradaic efficiency for formic acid. Both
  Ag and Au catalysts gave high Faradaic efficiencies for CO, but Au appeared to give CO
  at lower overpotentials. These results also showed that resistance from the electrolyte
  can have a significant effect on performance at high current densities, and that longer
  channels, such as those in the multi-channel reactor can lead to depletion of CO$_2$ and
decrease the Faradaic efficiency.

- **Investigation of the effects of the electrolyte pH on the reduction of CO$_2$.** Both the
  Sn and Ag catalysts were tested in electrolytes with varying pH. With the Sn catalyst, the
  Faradaic efficiency and partial current density depended strongly on the pH of the
  electrolyte. In contrast, the Ag catalyst was completely unaffected by the electrolyte pH.
  These differences are attributed to the different reaction pathways for CO and HCOOH
  on the two catalysts.\(^9\)

- **Study of amine based electrolytes for suppressing side reactions and lowering the
  overpotentials for CO$_2$ reduction.** Two amine based electrolytes, choline chloride and
EMIM BF₄, were investigated for their effect on CO₂ reduction. Choline chloride has been shown to be effective at suppressing hydrogen evolution. In this work it did significantly suppress hydrogen evolution, but also significantly decreased the rate of CO₂ reduction. Ionic liquids such as EMIM BF₄ have been shown to interact with CO₂ and have the potential to help stabilize high energy intermediates in the reaction pathway for CO₂ reduction. Cyclic voltammetry experiments indicated the possibility for significant improvements, however, uncertainty in the potential of non-aqueous reference electrodes prevents firm conclusions. Furthermore, the Faradaic efficiency in the cell was low and the anode appeared to experience poisoning from the ionic liquid. Thus, EMIM BF₄ has potential, but needs further investigation and will likely require more advanced reactor configurations such as a dual electrolyte reactor to minimize negative effects on the anode.

- **Investigation of the effects of reaction temperature on CO₂ reduction.** Experiments tested the performance of the reactor at temperatures ranging from 20°C to 90°C. In agreement with some other researchers, increasing temperature appeared to improve the CO₂ reduction reaction. However, additional temperature effects, e.g., the decreasing solubility of CO₂ with increasing temperature, limited the performance of the reactor. Increasing the CO₂ pressure will likely be effective at counteracting this effect and elevated pressure operation should be included in future reactor development.

8.2 Future Directions

The flexibility of the microfluidic reactor design and the relatively immature nature of research on the electrochemical reduction of carbon dioxide create endless possibilities for future
research. This section highlights just a few of those areas with a focus on questions and topics stemming from the results of this work:

- Results from this work showed that depletion of carbon dioxide in the gas chamber and electrolyte resistance can have a significant impact on the reactor performance. Improved reactor configurations, such as minimizing electrode distance and more efficient flow field designs can minimize these effects. Further exploration of reactor designs and these effects will allow them to be understood and accounted for, thus improving the reactor’s utility as an analytical tool in studying other parameters. This knowledge will also be important when ultimately moving from an analytical tool to an actual reactor design.

- Ionic liquids show significant possibility for improving the electrochemical reduction of CO$_2$. Further investigation is needed to fully understand their effects and evaluate their potential for application in CO$_2$ reduction. One of the clearest results from this work is that EMIM BF$_4$ has a negative effect on the anode and means of minimizing this effect are necessary. Several approaches, including alternative catalysts and a dual electrolyte configuration with an ionic liquid catholyte and aqueous anolyte, may prevent poisoning of the anode. Furthermore, there are a wide variety of other ionic liquids and organic electrolytes that could be explored as catholytes.

- This work has already shown temperature to be an important parameter, but further investigation incorporating operation at elevated CO$_2$ pressures would show whether significant improvements at higher temperature could be achieved without being hampered by the lower solubility of CO$_2$.  

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• The catalysts used in this study were limited to simple metal catalysts. However, more advanced catalysts including alloys, and nanostructured catalysts have enormous possibility for improved performance. All of these are readily incorporated and tested with this microfluidic reactor as previously demonstrated with the microfluidic fuel cell.25, 26

• Preliminary experiments in this dissertation investigated the long term performance of a Ag catalyst in the microfluidic cell. As development of the electrochemical reduction of CO\textsubscript{2} continues, the durability of catalyst and components, \textit{e.g.}, the gas diffusion electrode, will be critical. Similarly, the effect of contaminants on the operation of the reactor will be important, particularly as CO\textsubscript{2} captured from flue gases is envisioned as the ultimate source of CO\textsubscript{2} for the process. The flexibility of a microfluidic design makes this an excellent tool for such studies.

Ultimately, immediate work needs to focus on achieving improved performance through improved catalysts, novel electrolytes, and optimized reactions conditions, \textit{e.g.}, temperature and pressure. As improved performance makes industrial application more feasible, long term durability and resilience to contaminants will become critical areas of research.

8.3 References


