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MICROFLUIDIC REACTOR FOR THE ELECTROCHEMICAL REDUCTION OF
CARBON DIOXIDE

BY

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THESIS

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ABSTRACT

The electrochemical reduction of CO₂ has the potential to address many of the intertwined issues of energy security and climate change. Efficient conversion of CO₂ into hydrocarbons using renewable electricity would provide a renewable source of these chemicals and would also provide a high energy density means of storing renewable energy. However, to make the electrochemical reduction of CO₂ a viable process, significant improvements are needed to increase the efficiency and current density. This thesis reports the design and demonstration of a microfluidic reactor for the electrochemical reduction of CO₂ that uses a flowing liquid electrolyte. This flowing electrolyte provides enormous flexibility and control over the reaction conditions and enables the use of a reference electrode to study individual electrode performances. These characteristics make the reactor an excellent tool for studying and optimizing catalysts and reaction parameters. The utility of this design is demonstrated by: (i) comparison of several catalysts for reduction of CO₂ to formic acid, and (ii) investigation of the effects of pH on Sn catalyst for production of formic acid.

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CHAPTER 1

INTRODUCTION

1.1 Challenges in Energy and Climate Change

In recent years the large amounts of greenhouse gases, in particular CO₂, that are being released into the atmosphere as a result of human activity have caused increased concern in the global community. The large increase in emissions over the past couple centuries has resulted in the substantial accumulation of CO₂ in the atmosphere. These elevated levels of greenhouse gases, if allowed to persist, will likely lead to further elevation in global temperatures and significant changes in global climate. These changes in climate could cause problems in many areas such as human health, agriculture, natural ecosystems, and coastal areas [1].

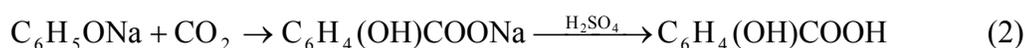
The largest source of CO₂ emissions, by far, is the consumption of fossil fuels. In the United States, 85-90% of CO₂ emissions are a result of fossil fuel use [2]. Thus, efforts to reduce emissions should focus on fossil fuels. Fossil fuels are used in a variety of areas. About 30-35% is used for transportation while 35-40% is used for electricity generation. An additional 7% [3] is used for non-energy purposes, e.g. as feedstock for chemical synthesis, and most of the remainder is used for heating. In addition to causing large CO₂ emissions, the heavy dependence on fossil fuels causes problems in energy security since many of our fossil fuels are imported and they are inherently nonrenewable.

One approach for reducing CO₂ emissions that has received a lot of attention in recent years is carbon capture and sequestration (CCS). In this process, CO₂ is removed from the flue gases of large emitters, such as power plants, using membrane separation or an absorbent/adsorbent, e.g., monoethanolamine (MEA) [4]. The captured CO₂ is then stored either

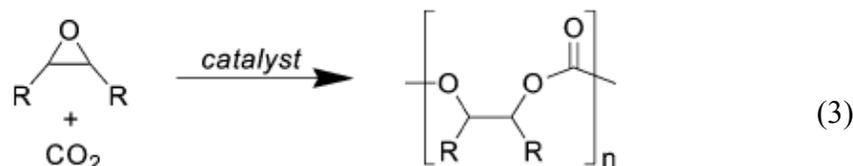
deep in the ocean or underground in geological formations such as depleted oil and gas reservoirs. While this has the potential for reducing the amount of CO₂ entering the atmosphere, this approach has a number of issues. First, CCS requires a suitable sequestration site near the CO₂ source or the CO₂ must be transported to a suitable site. Furthermore, carbon storage does not address the fact that fossil fuels are non-renewable and will ultimately be depleted. While CCS may be an easily implemented method for reducing CO₂ emissions, because of these issues, alternative solutions will ultimately be needed and should be actively investigated.

1.2 CO₂ Utilization and Conversion

One alternative to CO₂ sequestration is to use CO₂ as a feedstock in producing other salable products. This approach eliminates the need for sequestration sites and improves the economics of carbon capture by making value-added chemicals. There are a number of processes in which CO₂ can be used to make other products. Carbon dioxide is currently used industrially to make urea and salicylic acid via the reactions shown in Eqns (1) and (2) [5].



Carbon dioxide can also be used as a co-polymer with epoxides to form polycarbonates as shown



in Eqn (3) [6]. While these processes are ideal in that they consume CO₂ to produce valuable chemicals, it is unlikely that the demand for these chemicals will ever be large enough to consume a significant amount of CO₂.

Carbon Dioxide can also be used in reforming with methane to produce syngas as shown in Eqn (4) [5]. This reaction is endothermic but can be combined with steam reforming and partial oxidation of methane in a process called tri-reforming to provide the energy needed to drive the reaction and produce the desired H₂/CO ratio [7, 8]. The syngas produced from this process can then be used to produce liquid fuels. While, methane reforming with CO₂ provides a means of producing liquid fuels using CO₂ it relies on non-renewable methane from natural gas.



Another alternative that has been extensively studied is to react CO₂ with hydrogen to form methanol [9-12]. This reaction (shown in Eqn 5) is the reverse of steam reforming of methanol and is well understood with several catalysts [8]. By using H₂ from the electrolysis of water with renewable electricity, this process allows for the storage of renewable energy in a liquid chemical.



In addition to these chemical methods of CO₂ conversion, significant work has also been done on photochemical [8, 13, 14] and biochemical [15] means for converting CO₂ into useful products. However, photochemical means are generally limited by low rates and efficiencies for CO₂ reduction, while the biochemical routes face challenges in immobilization and stability of enzymes as well as the cost of these enzymes. The last major method for converting CO₂ is electrochemical reduction, which uses electrical potential (rather than heat or sunlight) to drive the reduction of CO₂. This method is the focus of this thesis and is described in detail in the following section.

1.3 Electrochemical Reduction of CO₂

Another alternative to CO₂ sequestration is to use renewable electricity to electrochemically reduce CO₂ into useful products such as methanol, formic acid, and syngas [16]. As with the other methods of CO₂ conversion previously mentioned, this approach of CO₂ utilization has the advantages of producing a useful product and eliminating the need for high pressure compression and a suitable site for sequestration. Furthermore, using renewable electricity to reduce CO₂ provides a renewable source of hydrocarbons that are currently almost exclusively derived from fossil fuels. Such a renewable source could help both in reducing CO₂ emissions and reducing our dependence on non-renewable fossil fuels.

The final key benefit from electrochemical reduction of CO₂ is the ability to store electrical energy in a chemical form, which provides a convenient and high energy density form of storage. The CO₂ can be converted to fuels such as formic acid or methanol, which can be used in fuel cells to recover the energy, or the CO₂ can be converted to CO along with hydrogen, a mixture referred to as synthesis gas (syngas), which in turn can be converted through Fischer-Tropsch synthesis to make liquid fuels that can be used in conventional internal combustion engines. The ability to store electricity is important when considering the task of matching electricity production with electricity demand, particularly when using intermittent renewable sources such as wind and solar. Without a means of storing electrical energy, intermittent sources such as wind and solar would likely be limited to 15-20% of the total electricity supply to avoid stability issues in the electricity supply [10]. The electrochemical reduction of CO₂ could potentially provide a means of storing electrical energy to overcome the issues of intermittent supply. Furthermore, storing renewable electricity in chemical form would provide

more opportunities for use in transportation, which currently only has 3% coming from renewable sources [17].

While the electrochemical reduction of CO₂ has the potential to help with a number of challenges, significant advances still need to be made in order for this process to be viable. First, the reduction of CO₂ into other chemicals must be accomplished with reasonably high energetic efficiency, which is a measure of how much energy is stored in the desired product relative to the energy supplied. The energetic efficiency is a combination of two factors: the Faradaic efficiency (also called current efficiency) and the overpotential [18]. Thus an efficient process is accomplished by achieving high selectivity for the desired product while avoiding the need for a high driving force in the form of large cell potentials. In addition to achieving high efficiency, CO₂ reduction needs to be accomplished at high current densities. The current density is important because it determines the reactor size for the process. To avoid unreasonable reactor sizes, the electrochemical reduction of CO₂ must be able to run a reasonably high current densities. The realization of both high energy efficiency and high current density can be achieved through the optimization of several aspects including catalysts for both the CO₂ reduction and the oxidation reaction, reactor design and operating conditions such as pH, electrolyte composition and temperature. To optimize these parameters a convenient and very flexible tool for studying the CO₂ reduction reaction is required.

1.4 Objectives of this Work

The goal of this thesis is to present the development of a microfluidic reactor for the electrochemical reduction of CO₂ and to demonstrate its flexibility and utility in the study and optimization of the CO₂ reduction process. The cell design consists of a flowing liquid

electrolyte between two gas diffusion electrodes (GDE) and utilizes a reference electrode in the exit stream to allow for in depth analysis. This design is based closely on a microfluidic H₂/O₂ fuel cell that was previously designed in our research group and shown to be effective in similar studies for fuel cells [19, 20]. In the following chapter a thorough review of the literature on electrochemical reduction of CO₂ is presented. In chapter 3 a more detailed description of the reactor design is given and the benefits of this flexible design are demonstrated by comparing the performance of different catalyst for CO₂ reduction to formic acid and showing the effects of electrolyte pH on the efficiency of formic acid production for a Sn catalyst. These studies show the significant impact that operating conditions can have on the efficiency of CO₂ reduction and thus the importance of studying and optimizing these parameters. Finally, chapter 4 summarizes the key conclusions from this work and describes the future directions of this project.

CHAPTER 2

LITERATURE OVERVIEW

2.1 Introduction

The electrochemical reduction of carbon dioxide has been studied for a number of years and several good reviews have been written on the subject [16, 21, 22] as well as papers investigating the reaction mechanisms for CO₂ reduction [23, 24]. Most of the focus has been investigating different products that can be formed using various catalysts with the majority of the work being done on metal electrodes in either aqueous [25-28] or organic media [29-32]. The main products of CO₂ reduction are methane, ethylene, formate (formic acid), carbon monoxide and some alcohols (methanol, ethanol, propanol) [16]. Since hydrogen evolution is a competing reaction, metals with high overpotential for hydrogen evolution, such as Hg, In, Pb, Cd, have higher efficiencies for CO₂ reduction. Because of their aprotic nature, organic electrolytes also help suppress hydrogen evolution in addition to having higher solubility of CO₂. Furthermore, several researchers have found that lower temperatures suppress hydrogen evolution and increase efficiency for CO₂ reduction [25, 33, 34].

Copper has received a lot of attention because it produces appreciable amounts of hydrocarbons and alcohols from CO₂ reduction [25, 27, 30, 34-37]. There has also been some work on making alloy catalyst, most of which has been Cu alloys [34-36]. However, copper and its alloys tend to give a mix of products, including hydrogen, rather than one product at high efficiency. At least a couple groups have also looked at the effect of the supporting electrolyte on the selectivity of CO₂ reduction at copper electrodes and have shown that it has a significant effect in both aqueous [37] and organic [30] media. Work has also been done to increase the

reaction rate using gas diffusion electrodes (GDEs) [33, 38-46], and high CO₂ pressures [32, 33, 42, 47-49], which has allowed current densities up to several hundred mA/cm² to be achieved.

2.2 Formic Acid

Formic acid is attractive because it can be produced at very high Faradaic efficiencies (>90%) on several catalysts [16, 25, 27, 41, 43]. The results for formic acid production from several groups are summarized in Table 2.1. 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.[43] who achieved 100% efficiency on Pb GDEs with high current density (115 mA/cm²) as well as that of Furuya et al.[41] who achieved 90% 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 Alcohols

Unlike formic acid and other products, little work has directed at electrochemical reduction of CO₂ to methanol, and only a few have reported high current efficiencies [50-53]. Those that have reported high current efficiency have either had very low current densities or not reported them. A summary of the results in the literature for electrochemical reduction of carbon dioxide to methanol is shown in Table 2.2. Another approach that is more common than direct electrochemical reduction of CO₂ to methanol is to take H₂ from the electrolysis of water and react it with CO₂ to form methanol [9, 11, 12, 54]. CO₂ can also 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.

2.4 Hydrocarbons

As mentioned in the introduction, copper has the ability to reduce CO₂ to hydrocarbons and as a result has received lot of attention. However, one of the main problems 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]. Significant amounts of hydrocarbons have also been produced on Pt GDEs at elevated pressures [33]. Despite the amount of work that has been done, high efficiencies (>75%) have yet to be obtained. Furthermore, the higher Faradaic efficiencies reported also have had very high over potentials, which lowers the energetic efficiency. Significant results in reducing CO₂ to hydrocarbons are shown in Table 2.3.

2.5 CO and Syngas

Carbon monoxide is another product that has been produced with high efficiency by reducing CO₂ at various electrodes [27, 39]. Carbon monoxide is useful as a reactant with H₂ in a Fischer-Tropsch reaction 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 that has been 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 [46, 55]. Notable in this area is the work by Yamamoto et al.[46] who produced a roughly 1:1 ratio of hydrogen and carbon

monoxide at a relatively low potential of -0.6V RHE . They estimated the energy efficiency for the cell (producing oxygen at the anode) to be roughly 45%. They also demonstrated that the ratio of CO to H₂ can be controlled by the potential applied to the cell. Zhao et al. have also done work reducing supercritical CO₂ in ionic liquids. The main products were CO and H₂ with the efficiencies ranging from 25%-50% and 40%-65% respectively [49]. The relevant literature data for CO and syngas production is summarized in Table 2.4.

2.6 Reactor and Cell designs

Recently several papers have present designs for complete electrochemical cells or reactors for producing formic acid [56-61] and syngas [46, 55, 62]. Most of the reported designs use proton exchange membranes and are similar to fuel cell designs.

As mentioned above, Yamamoto et al.[46] have 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.

Delacourt et al.[55] 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 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 $\sim -1.8\text{ V NHE}$ with a current density of 80 mA/cm^2 .

Koleli et al.[60] 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.[59] 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 [61]. 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.

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 reactor for the production of formate [56-58]. 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. In their work they also did a limited study of several parameters such as temperature, catholyte species, CO₂ pressure and other reactor parameters. They also achieved high efficiencies (91-63%) and high current densities (60-310 mA/cm²).

2.7 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. Many of the studies that compared several catalysts only tested them at one fixed potential or current, which does not allow for an accurate comparison of the catalysts since their peak performance may be at different potentials. 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 CO₂ reduction could be greatly advanced with a convenient flexible tool than can investigate the performance of various catalysts in a wide variety of conditions.

2.8 Figures and Tables

Catalyst	Electrolyte	CO ₂		Current Density (mA/cm ²)	Pressure (atm)	T (°C)	Ref
		Eff (%)	Potential (V NHE)				
Pb (GDE)	50g/L NaSO ₄	100	-2.0	45	1	20	[43]
Pb (GDE)	50g/L NaSO ₄	100	-2.4	115	1	20	[43]
Hg	0.1 M KHCO ₃	99.5	-1.51	0.5	1	18.5	[27]
Pb	0.1 M KHCO ₃	97.4	-1.63	5.0	1	18.5	[27]
Tl	0.1 M KHCO ₃	95.1	-1.6	5.0	1	18.5	[27]
In	0.1 M KHCO ₃	94.9	-1.6	5.0	1	18.5	[27]
Hg	0.05 M KHCO ₃	90.2	-2.0		1	0	[25]
Ru-Pd (GDE)	0.5 M KHCO ₃	90	-1.1	80	1	25	[41]
Pb (GDE)	50g/L NaSO ₄	89	-1.6	56	1	20	[43]
Sn	0.1 M KHCO ₃	88.4	-1.5	5.0	1	18.5	[27]
Hg	0.05 M KHCO ₃	87.6	-2.0		1	20	[25]
In	0.1 M TEAP/H ₂ O	87.6	-2.0		1		[28]
In (GDE)	50g/L NaSO ₄	87	-2.3	100	1	20	[43]
In	0.1 M TEAP/H ₂ O	83.2	-2.4		1		[28]
Cu(Hg)	10% NaSO ₄ sat w NaHCO ₃	81.5	3.5*		1		[63]
Pb (GDE)	0.5 M KHCO ₃ + 0.02 M KNO ₃	80	-1.9		1	25	[64]
Pb	0.1 M TEAP/H ₂ O	78.9	-2.4		1		[28]
Cd	0.1 M KHCO ₃	78.4	-1.6	5.0	1	18.5	[27]
Pb	0.3M KOH in MeOH	77	-2.0	~5	1	15	[29]
Cd (GDE)	0.5 M KHCO ₃ + 0.02 M KNO ₂	75	-2.9		1	25	[64]

Pc = Phthalocyanine

Table 2.1: Summary of literature results for electrochemical reduction of CO₂ to formic acid

Catalyst	Electrolyte	Efficiency (%)			Potential (V NHE)	Current Density (mA/cm ²)	CO ₂		Ref
		MeOH	EtOH	PrOH			Pressure (atm)	T (°C)	
Ru-GCE	0.2M Na ₂ SO ₄	100			-0.5	0.2	1		[50]
Mo	0.2M Na ₂ SO ₄	84			-0.6	0.12	1	22	[53]
Ru	0.2M Na ₂ SO ₄	42			-0.3	<0.3	1	60	[51]
Ru	0.2M Na ₂ SO ₄	25			-0.31	<0.3	1	61	[51]
RuO ₂ /TiO ₂ NT	0.5 M NaHCO ₃	60.5			-0.56		1	25	[52]
RuO ₂ /TiO ₂ NP	0.5 M NaHCO ₃	40.2			-0.56		1	25	[52]
Cu/Ni	0.05 M KHCO ₃	10			-0.65		1	2	[36]
La _{1.8} Sr _{0.2} CuO ₄	0.5 KOH	1	30.7	10		180	1	25	[45]
Cu	0.1 M KHCO ₃		5.7	3	-1.44	5.0	1	18.5	[27]
Pt(GDE)	0.5 M KHCO ₃		2.9		-1.69	600	5	25	[33]
Pt(GDE)	0.5 M KHCO ₃		2.8		-1.7	600	10	25	[33]
Pt(GDE)	0.5 M KHCO ₃		2.6		-1.73	600	20	25	[33]
Pt(GDE)	0.5 M KHCO ₃		2.3		-1.73	600	30	25	[33]
Pt(GDE)	0.5 M KHCO ₃		2.3		-1.7	600	50	25	[33]
Pt(GDE)	0.5 M KHCO ₃		1.9		-1.62	500	30	25	[33]

Table 2.2: Summary of literature results for electrochemical reduction of CO₂ to methanol and other alcohols

Catalyst	Electrolyte	Efficiency (%)		Potential (V NHE)	Current Density (mA/cm ²)	CO ₂	T (°C)	Ref
		CH ₄	C ₂ H ₄			Pressure (atm)		
Cu	0.5M LiClO ₄ in MeOH	71.8	1.6	-2.78	27	1	-30	[30]
Cu	0.25M NaClO ₄ in MeOH	70.5	3.1	-2.78	22.7	1	-30	[30]
Cu	0.5M LiCl in MeOH	68.4	4	-2.78	16.4	1	-30	[30]
Pt (GDE)	0.5 M KHCO ₃	38.8		-1.73	600	20	25	[33]
Pt (GDE)	0.5 M KHCO ₃	36.3		-1.7	600	10	25	[33]
Pt (GDE)	0.5 M KHCO ₃	33.4		-1.73	600	30	25	[33]
Cu	0.1 M KHCO ₃	33.3	25.5	-1.44	5.0	1	18.5	[27]
Pt (GDE)	0.5 M KHCO ₃	31.2		-1.69	600	5	25	[33]
Ru	0.2M Na ₂ SO ₄	30		-0.31	<0.3	1	61	[30]
Cu (GDE)	1M KOH	9.1	69	-2.788	400	1	2	[38]
Cu (GDE)	1M KOH	6.7	65	-3.238	467	1	2	[38]
Cu (GDE)	1M KOH	6.3	65	-3.668	533	1	2	[38]
Cu (GDE)	1M KOH	7.4	60	-4.318	600	1	2	[38]
Cu (GDE)	1M KOH	7.5	53	-4.528	667	1	2	[38]

Table 2.3: Summary of literature results for electrochemical reduction of CO₂ to hydrocarbons

Catalyst	Electrolyte	Efficiency (%)		Potential (V NHE)	Current Density (mA/cm ²)	CO ₂		Ref
		H ₂	CO			Pressure (atm)	T (°C)	
Ni-Pc(GDE)	0.5 M KHCO ₃	2	100	-1.75	61.3	1	23	[39]
Co-Pc(GDE)	0.5 M KHCO ₃	3	98	-1.3	54.1	1	23	[39]
Pd-Pc(GDE)	0.5 M KHCO ₃	9.5	81.4	-1.5	31.8	1	23	[39]
Cu-PcCl(GDE)	0.5 M KHCO ₃	42.3	37.9	-1.82	48	1	23	[39]
Au	0.1 M KHCO ₃	10.2	87.1	-1.14	5.0	1	18.5	[27]
Ag	0.1 M KHCO ₃	12.4	81.5	-1.37	5.0	1	18.5	[27]
Zn	0.1 M KHCO ₃	9.9	79.4	-1.54	5.0	1	18.5	[27]
Cu	0.1M TBABF ₄	5	67	-2.3?	~400	40	25	[32]
Cu	0.1M TBABF ₄	5	39	-2.3?	200	30	20	[32]
Ni/ACF(GDE)	0.5 M KHCO ₃	48	52	-0.6	10-20	~1?		[46]
Pd(GDE)	0.5M KHCO ₃ +0.02M KNO ₃		45	-0.9		1	25	[64]
Ru	0.2M Na ₂ SO ₄		45	-0.31	<0.3	1	61	[51]
Ag	0.05 M KHCO ₃	32.6	40.7	-1.96		1	0	[25]

Table 2.4: Summary of literature results for electrochemical reduction of CO₂ to CO and syngas

CHAPTER 3

CATALYSTS AND pH EFFECTS FOR CO₂ REDUCTION TO FORMIC ACID

3.1 Introduction

As discussed in detail in the opening chapter, the efficient electrochemical conversion of CO₂ to useful products has the potential to address many of the intertwined problems in energy and climate change. The use of renewable electricity to convert CO₂ into compounds such as formic acid, methanol and CO (syngas) provides a number of key benefits. First, it provides a renewable, carbon neutral source of organic compounds that are currently almost solely derived from fossil fuels. This would help both with reducing CO₂ emissions and reducing our dependence on importing non-renewable fossil fuels. The other main advantage of CO₂ reduction is that it provides a means of storing electrical energy in a convenient chemical form, which is important as we try to increase the amount of electricity from intermittent sources such as wind and solar and increase the penetration of renewable energy into areas such as transportation that require high energy density fuels.

While extensive work has been done exploring various catalysts for the reduction of CO₂ to various products including formic acid [25, 27, 41, 43], CO [27, 39, 46], methane [30, 38] and methanol [50, 53], much work is still required to optimize catalysts and reaction conditions to maximize the energy efficiency and current density. This optimization requires the thorough comparison of different catalysts at a wide range of reaction conditions such as electrolyte composition and pH. In this chapter we report the development of a microfluidic reactor with a flowing liquid electrolyte as the separator between the cathode and anode. This design is similar to the microfluidic fuel cell previously designed in the Kenis group [20] and in addition to being

an efficient reactor for the electrochemical reduction of CO₂ it also serves as an effective analytical tool for study of catalysts and operating conditions [19]. Its flexibility and effectiveness in studying CO₂ reduction is demonstrated by comparing different catalysts for electrochemical reduction of CO₂ to formic acid and investigating the effects of electrolyte pH on reduction efficiency.

3.2 Reactor Design

A schematic of the reactor design used in this study is shown in Fig. 3.1 and is similar to the microfluidic fuel cell previously reported [19, 20]. A 1.5mm thick Poly(methyl methacrylate) (PMMA) sheet with a 0.5cm x 2cm window is placed between 2 catalyst coated gas diffusion electrodes (GDE). On the cathode side the catalyst was applied only to the first 1.5cm and a PTFE filter (Pall life sciences 10 micron) was added to cover the last 0.5cm. This facilitates the removal of bubbles (from oxygen evolution on the anode) that enter the electrolyte stream and would otherwise collect and block electrolyte contact with the catalyst. A graphite current collector backs each GDE. Behind the cathode a PMMA chamber is placed for CO₂ to flow through, while the anode is left open to air for oxygen to escape. Ten bolts hold the entire setup together. The electrolyte flows out of the cell to a beaker containing a reference electrode (Ag/AgCl in saturated NaCl, BAS), which is used to measure the individual cell potentials.

3.3 Experimental

3.3.1 Catalyst Synthesis

Ru-Pd was chosen as a cathode catalyst because the work by Furuya [41] showed it to have high Faradaic efficiency for formic acid and low over potential. The catalyst synthesis

method was not reported in the paper so carbon supported Ru-Pd was synthesized using two different methods from the literature [65, 66] resulting in catalysts with Ru-Pd weight percents of 17-17 and 30-30. The first method involved synthesis from commercial Pd/C catalyst (Sigma Aldrich) by sonication with RuCl₃ in *n*-heptane followed by slow evaporation of the solvent and then activation at 500 500 °C for 18 h under a nitrogen flow. The second method consisted of metal chloride reduction in solution with NaBH₄. Commercial Tin nanopowder (Sigma Aldrich) was used as a convenient catalyst for comparison with the Ru-Pd catalysts.

3.3.2 Gas Diffusion Electrode Preparation

Three cathode catalysts were used in this study: Ru-Pd 17%, Ru-Pd 30%, and commercial Sn nanoparticle. The catalyst was painted on a 1.4 cm² area of a 4cm x 2.5 cm GDE. The catalyst loading was either 2 or 5 mg/cm² (metals basis) with 0.1 mg/cm² Nafion as a binder. Catalyst ink was prepared by sonicating the catalyst overnight with 4.6 µl of 5% Nafion solution in 200 µl Millipore water and 200 µl isopropyl alcohol. This study used two different anode catalysts, Pt black and 40% Pt/C. The catalysts loadings for the anodes were all 2 mg/cm² and painted on a 2 cm² area. The inks were prepared in the same manner as for the cathodes and all electrodes were hot pressed at 130 °C and 300 psi for 5 min.

3.3.3 Cell Testing

An Autolab potentiostat (PGSTAT-30, EcoChemie) was used to control the cell potential and measure the resulting current. The individual electrode potentials were measured using multimeters connected between each electrode and a Ag/AgCl reference electrode in the exit stream. 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 potential drop between the reference electrode and the cathode and anode since not significant drop was observed. A mass flow controller (32907-80, Cole Palmer) was used to flow CO₂ from a cylinder at 5 sccm and a syringe pump (HPD 2200, Harvard Apparatus) supplied the electrolyte at 0.5 ml/min. The formate concentrations were analyzed using the method reported by Sleat and Mah [67]. For the catalysts comparison tests 0.5M KHCO₃ was used as the electrolyte for the cell. The catalyst loading for these tests was 2mg/cm². For the pH studies 0.5M 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 test the cathode was 5 mg/cm² Sn and the anode was 2mg/cm² Pt black.

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.

3.4 Results and Discussion

Initially three cathode catalysts (Ru-Pd 30 wt%, Ru-Pd 17 wt%, and Sn nanopowder), and two anode catalysts (Pt black and 40% Pt/C) were tested in the microfluidic cell for efficiency of CO₂ reduction to formic acid and the current density achieved. Subsequently, the

effect of pH on reactor performance was tested using a Sn cathode and Pt black anode for pH values of 4, 7, and 10.

3.4.1 Cathode Catalyst Comparison

Figure 3.2 shows the current densities for the three cathode catalysts. As seen in the figure, the current density of the Ru-Pd 30% is highest followed by the Ru-Pd 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 catalyst are shown in Figure 3.3. Despite having a much higher overpotential, as indicated by its peak performance occurring at more extreme cell potentials, the Sn catalysts Faradaic and energetic efficiency still far exceeded that of both Ru-Pd catalysts. This data highlights the inadequacies of some of the prior studies published that compared catalysts by testing them at only one potential (or current). 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. Because of its superior performance, the Sn catalyst was used in the subsequent experiments investigating pH effects.

3.4.2 Anode Catalyst Comparison

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 3.4 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 points out another key benefit of the reactor designs. 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.

3.4.3 Comparison of Performance at different pH

One factor that has not been significantly studied in the electrochemical reduction of CO₂ is the effect of pH, despite the fact that pH has been shown to have a large effect in similar situations, such as fuel cells [68]. The flexibility of the reactor configuration with its flowing liquid allows for the thorough characterization of the effects of reaction conditions on reactor performance without the issue of decreased membrane performance in different conditions. Figures 3.5 and 3.6 show the partial current densities and efficiencies of the Sn catalyst in 0.5M KCl electrolyte that has been adjusted with 1M HCl or 1M KOH to a pH of 4, 7, and 10. This unbuffered electrolyte requires only minute amounts of acid or base to adjust the conductivity, causing no significant change in electrolyte conductivity. The data shows a double benefit of lower, more acidic pH on the reduction of CO₂ to formic acid. Lowering the pH results in higher current densities for formic acid, which indicates an improvement of reaction kinetics at lower pH. 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 [57], however, the prior work was limited to basic pH and also had different ionic species, e.g. HCO₃⁻

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 $\text{pH} < 3$ [69]. The peak Faradaic efficiency and energetic efficiency were 89% and 45%, which are comparable to values achieved in the literature [58, 61].

The individual electrode polarization curves in Fig. 3.7 show 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.

3.4.4 Electrochemical Impedance Spectroscopy

Figure 3.8 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_Ω) or cell resistance (R_{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_{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 CO_2 reduction reaction on the cathode.

3.5 Conclusions

This study demonstrates the utility of a microfluidic cell as an effective reactor and a versatile analytical tool to study the electrochemical reduction of CO₂. The flowing liquid electrolyte stream employed in this design offers a number of benefits: (i) provides media flexibility in both composition and pH, (ii) supplies reactant (H₂O) to anode and eliminates any water management issues, and (iii) allows a reference electrode in the exit stream for analysis of individual electrodes. These advantages make it a useful tool for investigating different catalysts, electrolytes, and other operating conditions. This work demonstrated the versatility of the cell design by effectively comparing different catalysts for both the cathode and anode and being able to isolate the effects of each using the reference electrode. This study also investigated the effects of electrolyte pH on the electrochemical reduction of CO₂, showing that lower pH increases the kinetics of CO₂ reduction giving higher current densities and better selectivity reduction of CO₂ to formic acid. Furthermore the cell also serves as an effective reactor with high efficiencies (89% Faradaic and 45% energetic) and current densities, on the order of 100 mA/cm².

3.6 Figures and Tables

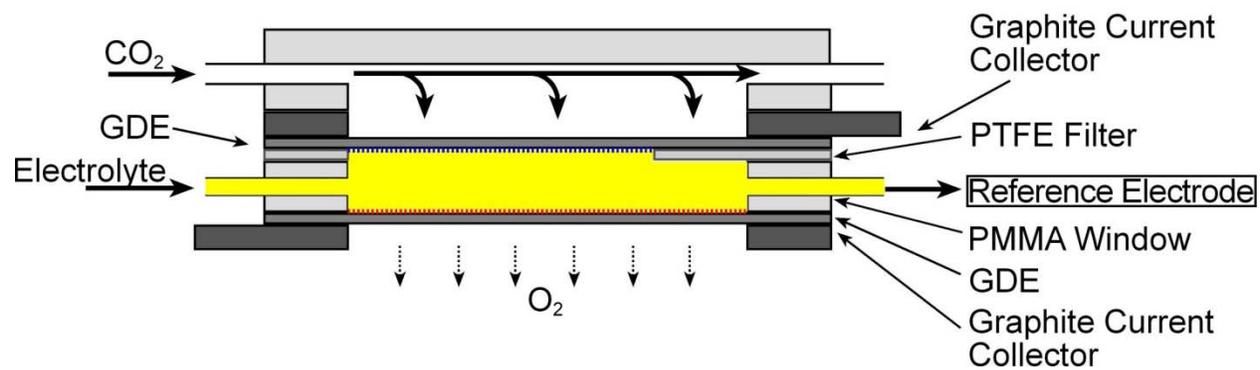


Figure 3.1. Schematic diagram of the microfluidic reactor.

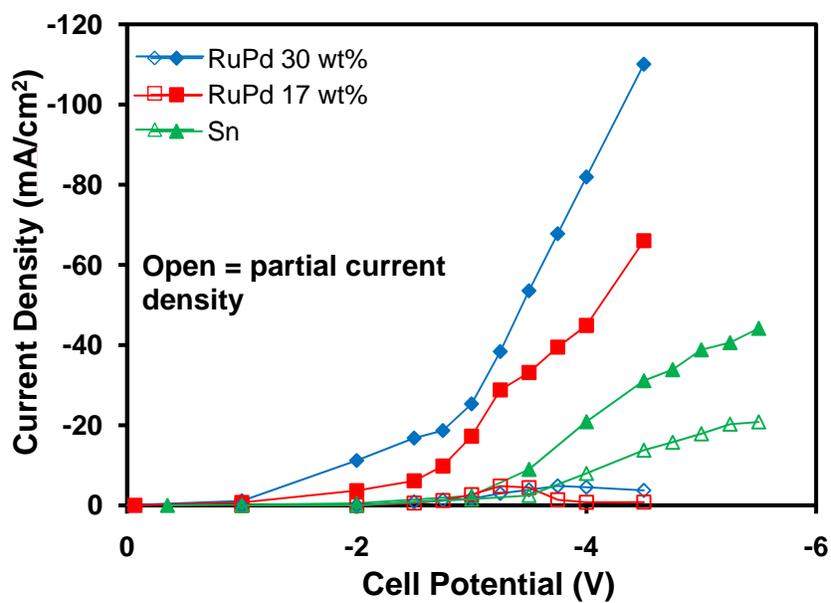


Figure 3.2. Current densities of three different cathode catalysts using 0.5M KHCO₃ as the electrolyte and Pt black as the anode catalyst. Filled symbols indicate the total current density, while the open symbols show the partial current density for CO₂ reduction to formic acid.

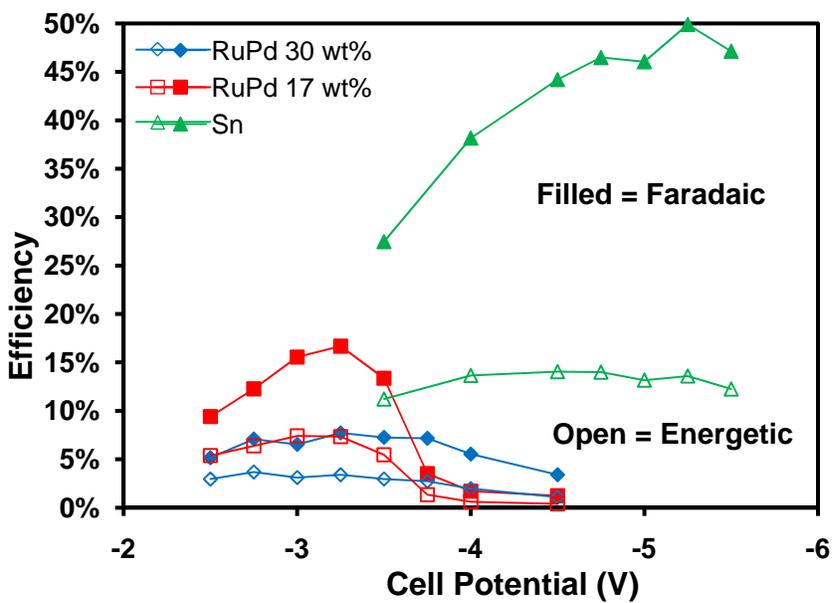


Figure 3.3. Efficiencies of three different cathode catalysts using 0.5M KHCO_3 as the electrolyte and Pt black as the anode catalyst. Filled symbols indicate Faradaic efficiency, while the open symbols show the energetic efficiency for CO_2 reduction to formic acid.

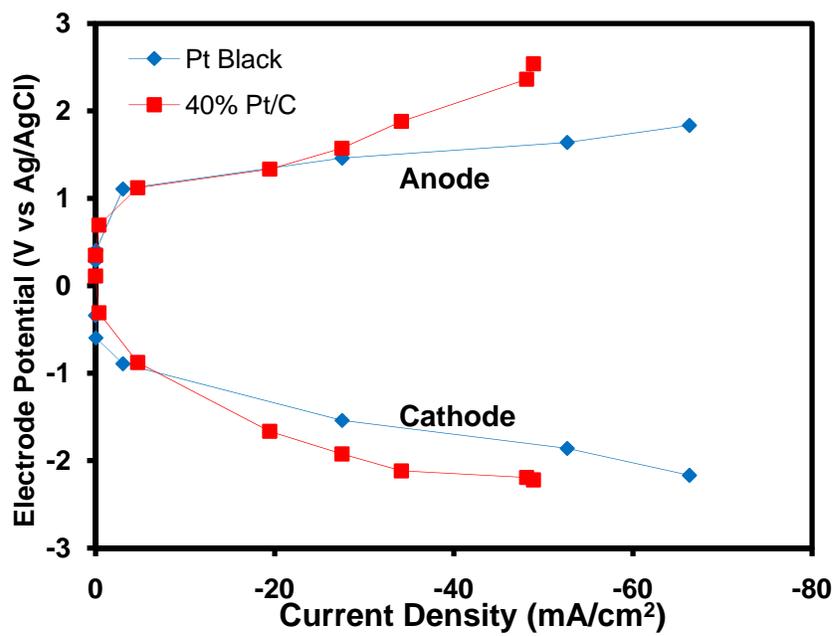


Figure 3.4. Individual electrode potentials for Pt black and 40% Pt/C as anode catalysts.

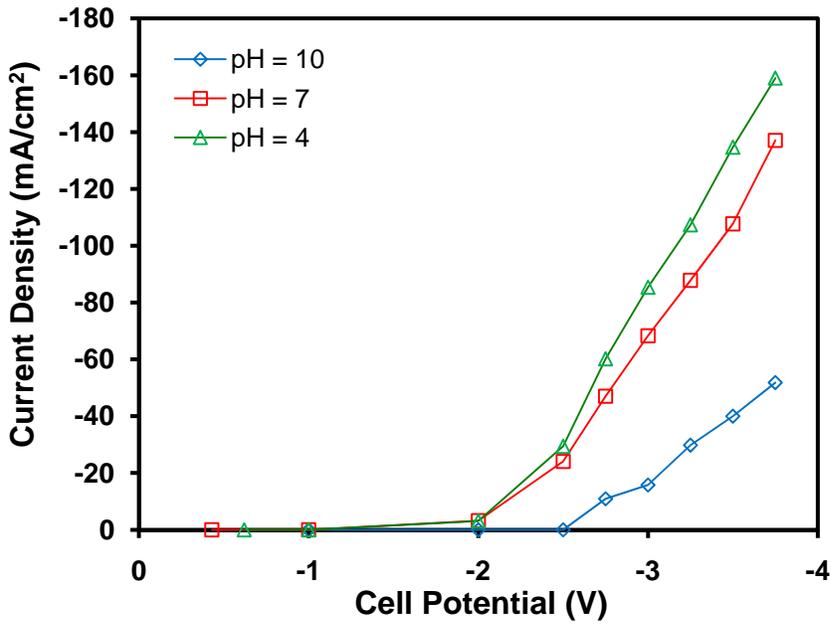


Figure 3.5. Partial current density as a function of pH with a Sn cathode and Pt black anode

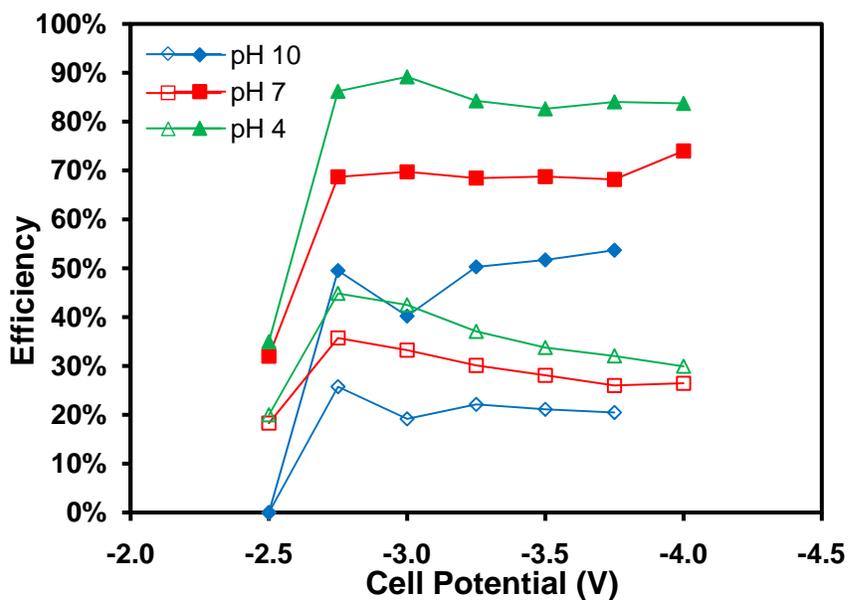


Figure 3.6. Efficiencies for Sn cathode catalyst using 0.5M KCl adjusted with HCl or KOH to different pHs. Closed symbols represent the Faradaic efficiency, while open symbols are the energetic efficiencies.

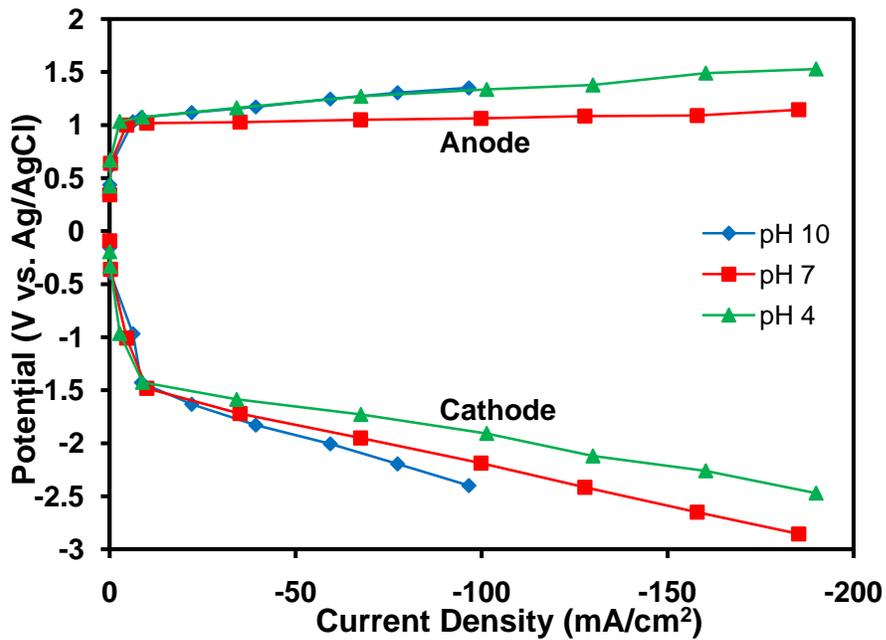


Figure 3.7. Individual electrode polarization curves for Sn cathode catalyst using 0.5M KCl adjusted with HCl or KOH to different pHs.

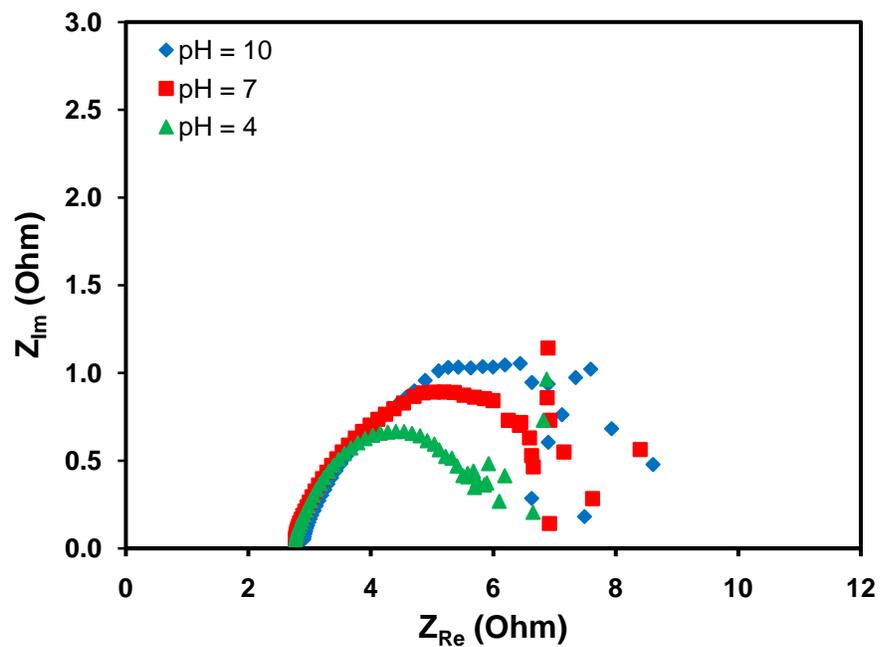


Figure 3.8. Nyquist plots for electrochemical cell at different pHs using a Sn cathode and Pt anode.

CHAPTER 4

CONCLUDING REMARKS AND FUTURE DIRECTIONS

4.1 Conclusions

The electrochemical reduction of CO₂ has the potential to help with many of the issues faced in energy and climate change by providing both a renewable, carbon neutral source of organic compounds that are currently derived from fossil fuels and a means of storing renewable electricity in a convenient, high energy density chemical form. In order for this process to become economically viable, significant improvements are needed in both the energy efficiency of the process and the current densities of the CO₂ reduction reaction. Currently, high Faradaic efficiencies have been achieved, but only at high overpotentials, which has kept energetic efficiencies low. To accomplish these improvements, a thorough study and optimization of catalysts and reactions conditions needs to be done. In this work we demonstrated a microfluidic electrochemical reactor as a convenient, flexible tool for performing these studies. The design uses a flowing liquid electrolyte to replace the membrane typically used to separate the cathode and anode. This flowing stream provides enormous flexibility in controlling the reaction conditions (e.g. pH, electrolyte composition) as well as providing convenient online sampling or analysis of reaction products. The liquid stream also allows the use of a reference electrode which enables individual analysis of each electrode's performance. In this thesis the utility of this flexible design has been demonstrated by:

1. Comparison of the performance of multiple cathode and anode catalysts over a wide range of cell potentials for the electrochemical reduction of CO₂ to formic acid.

2. Investigation of the effects of electrolyte pH on the current density and energetic efficiency of CO₂ reduction to formic acid on a Sn catalyst.

In each of these studies the use of the reference electrode was key in isolating the effects on, and performance of, the cathode and anode individually.

4.2 Future Directions

The work in this thesis demonstrates the versatility of a microfluidic reactor with a flowing liquid electrolyte for studying the electrochemical reduction of CO₂. This versatility makes the reactor useful for studying a variety of parameters and problems. Areas for future study using this system include the following:

1. *Syngas Production* - As discussed earlier, CO₂ can be reduced into a number of different products. One attractive option is CO, which combined with H₂ makes synthesis gas (syngas) and can be used through established Fischer-Tropsch synthesis to make a variety of hydrocarbons, including high energy density liquid fuels such as gasoline. Such a process of using renewable electricity to make syngas from CO₂ and water and then converting it to gasoline or other liquid fuels would provide a simple way of allowing renewable electricity to supply transportation energy without the need of completely turning over the vehicle fleet from internal combustion engines to fuel cell and/or battery powered vehicles. The electrochemical cell presented here is equally suited to study the reduction of CO₂ to gas or liquid products, and because of its value as a feedstock for production of other chemicals, syngas is a prime target for further study. With the use of a GDE as the cathode in this design, gas phase products diffuse out the back of the GDE and leave with the flowing CO₂ stream.

This makes sample analysis easy as the exit stream can be directed to a GC for immediate determination of product concentrations. Key parameters for investigating syngas production from CO₂ include those covered in this thesis, such as pH and catalyst.

2. *Ionic liquid electrolytes* - In this work the electrolytes used for CO₂ reduction have been limited to simple, common aqueous solutions. However, researchers have shown that electrolyte species can have a significant impact on the selectivity of the CO₂ reduction reaction [30, 37]. Furthermore, recent work has shown that using room temperature ionic liquids can significantly decrease the overpotential for CO₂ reduction [70]. Significant reductions in overpotential are needed to achieve higher energetic efficiencies. Because of the flowing liquid electrolyte used in this design, the system is media flexible and can accommodate different electrolytes, including ionic liquids. Future work with this system will investigate various electrolytes, particularly ionic liquids, to improve the selectivity (Faradaic efficiency) and decrease the overpotentials, thereby increasing the energetic efficiency of CO₂ reduction.
3. *Reaction Temperature Optimization* - Temperature is a key parameter in nearly every reaction. While some work has reported that decreasing the reaction temperature can increase the Faradaic efficiency of CO₂ reduction [25, 33, 34], it is anticipated that higher temperatures will increase the rate of reaction and allow for higher current densities to be achieved. As a result of this, optimization of the operating temperature will likely be important in maximizing performance. Studying temperature effects can easily be done either by heating or cooling the reactants before entering the

reactor or by placing the compact cell into a temperature controlled device, such as an oven.

In summary, if the energetic efficiency and current density of the electrochemical reduction of CO₂ can be enhanced sufficiently through the optimization of catalysts and reaction conditions, CO₂ reduction has the potential to help with many of the challenges faced in energy and climate change. Because of its use of a flowing liquid electrolyte, the microfluidic reactor presented here has the flexibility needed to perform these studies and achieve the necessary performance improvements.

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