DESIGN AND CHARACTERIZATION OF CATALYSTS AND ELECTRODES FOR ELECTROCHEMICAL ENERGY CONVERSION APPLICATIONS

BY

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DISSERTATION

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Abstract

The modern world faces immense challenges associated with meeting its energy needs, due to its current dependence on fossil fuels. At the same time, the world faces the threat of global climate change linked to CO\(_2\) emissions. Indeed, global energy consumption has risen significantly since the industrial revolution and is expected to double again in the next 50 years. This is accelerating the depletion of conventional fossil fuels and has led to a steady increase in atmospheric CO\(_2\) levels. Taken together, the dual challenges of finding alternative energy sources and curbing CO\(_2\) emissions are daunting. Multifaceted approaches are needed to produce, store, and utilize energy in more efficient and environmentally sustainable ways. This thesis researches two energy conversion technologies that show promise to help address both challenges: fuel cells for efficient electrical power generation, and electrolysis of carbon dioxide into value-added intermediates for chemical production.

Fuel cell technologies are expected to play an important role in many alternative energy conversion strategies, particularly for automotive applications. Detailed investigation of the relationship between the physical structure and electrochemical activity of fuel cell electrodes is a critical, yet often poorly reported or proprietary step in the manufacturing of cheaper and more durable configurations. This thesis employs X-ray micro-computed tomography (MicroCT) to visualize the architecture and buried interfaces of fuel cell electrodes in a non-destructive fashion. By coupling MicroCT-based visualization with microfluidic-based electrochemical characterization, variation in catalyst layer morphology can be directly correlated to electrode performance. Depositing catalyst layers via a fully-automated air-brushing method led to a 56% improvement in fuel cell performance and a significant reduction in electrode-to-electrode variability.

Electrochemical reduction of CO\(_2\) into value-added chemicals potentially offers an economically viable route to recycle CO\(_2\) towards reducing CO\(_2\) emissions and dependence on fossil fuels. However, the current performance levels of CO\(_2\) electrolyzers are insufficient for commercialization due to the lack
of catalysts with adequate activity and selectivity. This thesis researches the effects of catalyst layer deposition methodology on electrode performance. Air-brushing catalyst layers for CO$_2$ reduction led to a 3-fold increase in partial CO current density and enhanced product selectivity (94%) and a 10-fold decrease in catalyst loading as compared to previous reports. Furthermore, this thesis reports carbon nanotube-supported gold catalysts for CO$_2$ reduction exhibiting both higher activity and higher Faradaic efficiency for CO production. The 160 mA/cm$^2$ partial current density for CO production achieved for this supported gold catalyst is to date the highest performance reported under ambient conditions. Such high activity can be attributed to enhanced catalyst utilization, evidenced by the high electrochemically-active surface area of gold on this material. Finally, the development of no-metal-added nitrogen-doped carbon catalysts for CO$_2$ reduction is reported. Pyrolyzed carbon nitride supported on carbon nanotubes exhibit excellent selectivity for CO production over H$_2$ production (98% CO and 2% H$_2$) as well as high throughput (90 mA/cm$^2$ CO partial current density). Together, these studies present the framework for developing catalytic materials to help CO$_2$ reduction achieve performance benchmarks for commercialization.
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Chapter 1

Introduction*

1.1 Addressing Global Energy Challenges

Global energy consumption is expected to double in the next 50 years, further accelerating the depletion of the world’s fossil fuel reserves [1]. New, more sustainable strategies must be implemented to meet energy demand [2]. The development of electrochemical energy conversion technologies for efficient production, storage, and utilization of energy has the potential to improve society’s sustainability with respect to energy.

Catalysts are often needed in electrochemical energy conversion devices to overcome the overpotential of an electrochemical reaction through the activation of reactant molecules and stabilization of reaction intermediates. When the electrocatalytic reaction involves gaseous reactants, a gas diffusion electrode (GDE) is often used to immobilize and support the catalyst as it functions to (i) deliver reactant gas from flow-field channels to the catalyst layer, (ii) to drain product from the catalyst layer into flow channels or the electrolyte, and (iii) to conduct electrons with low resistance [3]. The performance and durability of these electrochemical energy conversion devices is largely determined by catalysts and electrodes.

This thesis researches catalysts and electrodes for two energy conversion technologies: polymer electrolyte membrane fuel cells for efficient electrical power generation, and electrolysis of CO$_2$ into value-added intermediates for chemical production.

1.2 Overview of Polymer Electrolyte Membrane Fuel Cells

In polymer electrolyte membrane fuel cells (PEMFCs), hydrogen is electro-oxidized on the anode to produce protons and electrons. These electrons travel around an external circuit powering a load whereas the protons travel through a conductive electrolyte which separates the two electrodes. On the cathode, oxygen combines with the protons and electrons and electro-reduces to produce water. At present, PEMFCs have been extensively investigated as alternative power sources due to their high efficiency, high energy density and low emissions [4]. Unfortunately, commercialization of PEMFCs has been deterred by high cost associated with high loadings of expensive platinum (Pt) required for the cathodic oxygen reduction reaction (ORR) [5,6]. Significant research efforts have focused on discovery and development of new ORR catalysts that reduce Pt loading or replace Pt [7]. Furthermore, intensive efforts have studied these catalysts after immobilization on gas diffusion electrodes (GDEs). Indeed, a variety of catalyst layer deposition methods have been reported to prepare electrodes for fuel cell reactions. These focused efforts have resulted in loadings of ca. 0.4 mg Pt/cm² for state-of-the-art fuel cell cathodes, compared to 4-10 mg/cm² in the first generation of PEMFCs in the 1990s. Though this represents a significant improvement, an approximately 4-fold further reduction is needed to meet the Department of Energy 2017 targets for large-scale automotive applications (i.e., a total loading of 0.125 mg Pt/cm²) [6]. Developing an improved understanding of how different catalyst layer deposition methods impact electrode performance is key to enhancing overall performance of the electrochemical process. The rational development of better cathodes with lower precious metal catalyst loading would benefit from analytical methodology that integrates structural and electrochemical techniques. This is one of the topics of this thesis.
1.3 Overview of Electrochemical Reduction of CO₂ to Useful Chemicals

Global energy consumption has risen significantly since the industrial revolution and is poised to steadily increase over the next several decades due to economic growth in industrialized and developing countries. Society currently consumes 16.0 TW$_{avg}$ of primary power, of which 87% is derived from burning fossil fuels [8]. By 2050 the demand for primary power is estimated on the order of 30 TW$_{avg}$ [8]. This increased energy consumption is accelerating the depletion of the world’s fossil fuel reserves and has led to a steady increase in atmospheric levels of carbon dioxide (CO₂), which has been linked to climate change. Recently, atmospheric CO₂ levels surpassed 400 parts per million (ppm). To curb the rise, and eventually to reduce atmospheric CO₂ levels, multiple approaches need to be implemented concurrently to avoid further climate change. Approaches to reduce CO₂ emissions include switching from coal to natural gas, carbon capture and sequestration (CCS) from point sources such as power plants, increasing fuel efficiency of cars and energy efficiency of buildings, and increasing the utilization of renewable energy sources such as wind and solar [9]. Particularly, there is a strong incentive to exploit clean, renewable energy sources. However, because of their intermittent nature, the fraction of energy that can be supplied from renewable sources will be limited to 30%, unless approaches for large scale energy storage or on-demand utilization become available to avoid wasting energy.

Electrochemical conversion of CO₂ offers a potentially economically viable route to recycle CO₂ towards reducing CO₂ emissions and dependence on fossil fuels [10-12]. This process can be driven by renewable electricity, providing a carbon-neutral method to utilize otherwise wasted excess energy from intermittent sources such as wind and solar. Technically, electrochemical reduction of CO₂ is analogous to running a fuel cell in reverse. The CO₂ reduction reaction takes
place at the cathode, whereas the water oxidation reaction or chlorine evolution reaction takes place at the anode. Over the past few decades, efforts have mostly focused on the half-reaction of the cathode (i.e., the CO₂ reduction reaction) [13-20]. Four distinct classes of metal catalysts have been identified for CO₂ reduction: (i) metals that selectively form carbon monoxide, CO (Au, Ag, Zn, Pd, Ga); (ii) metals that mainly produce formic acid, HCOOH (Pb, Hg, In, Sn, Cd, Tl); (iii) metals that form a wide range of hydrocarbons such as methane and ethylene (Cu); and (iv) metals that primarily form H₂ (Pt, Ni, Fe, Ti) [13]. Prior reports and reviews have provided an excellent overview of possible products of electrochemical CO₂ reduction at a wide range of current densities, energetic efficiencies, and selectivities for the desired product [14,15,21].

Despite the potential of electrochemical CO₂ reduction, current performance levels are insufficient for commercialization. The performance of CO₂ electrolyzers needs to be improved significantly by developing better catalysts in combination with optimized electrodes, electrolyte formulations and cell configurations, all topics of study in this dissertation.

1.4 Topics Studied in this Dissertation

This thesis describes a suite of studies undertaken to better understand the structure-performance relationships of electrodes and the application of this knowledge to the design of new, supported catalysts to improve electrode performance. Chapter 2 discusses the current status and opportunities for catalyst design, electrolyte choice and electrode structure for electrochemical reduction of CO₂. Chapters 3 and 4 report on the proof-of-concept utilization of MicroCT for detailed characterization of the 3D structure of fuel cell electrodes in a non-destructive fashion. Coupled with electrochemical analysis in a microfluidic fuel cell, variations in electrode structure (catalyst layer uniformity, electrode compression) can be directly correlated to differences in electrode performance. Chapters 5-7 describe results on the synthesis,
characterization, and testing of catalysts, electrodes, and electrolysis cells for the electrochemical conversion of CO$_2$ to CO, an intermediate that can be used in subsequent Fischer-Tropsch processes for the synthesis of value-added chemicals such as diesel fuels.

1.5 References


Chapter 2

Electrochemical Reduction of CO\textsubscript{2} to Useful Chemicals: Current Status, Remaining Challenges, and Future Opportunities\textsuperscript{*}

2.1 Chapter Overview

The rise of atmospheric CO\textsubscript{2} levels must be slowed, or better reverted, to avoid further undesirable climate change. Electrochemical reduction of CO\textsubscript{2} into value-added chemicals using renewable energy is one approach to help address this problem as it will recycle ‘spent’ CO\textsubscript{2} (carbon neutral cycle) and it provides a method to store or utilize otherwise wasted excess renewable energy from intermittent sources, both reducing our dependence on fossil fuels. Current electrolysis cells accomplish either high Faradaic efficiency (often >95\% selectivity) for a desired product (\textit{e.g.}, CO), or reasonable current density (conversion), whereas both need to be high for a commercial process. This review will discuss current status and opportunities for catalyst design, electrolyte choice, and electrode structure.

2.2 Introduction

Carbon dioxide (CO\textsubscript{2}) emissions into the atmosphere will need to be drastically reduced to curb the various undesirable effects of climate change. One approach is to switch from fossil fuel burning power plants to renewable sources like solar, wind, and water, which has the added benefit that we reduce our dependency on dwindling global supplies of fossil fuels. However, due to their intermittent nature, the fraction of energy that can be supplied from renewable sources will be limited to 30\%, unless approaches for large scale energy storage become available. Alternatively, CO\textsubscript{2} could be captured from point sources such as power plants,

\textsuperscript{*} This chapter has been adapted from the following publications: H.R.M. Jhong, S. Ma, P.J.A. Kenis, ‘Electrochemical conversion of CO\textsubscript{2} to useful chemicals: Current status, remaining challenges, and future opportunities,’ \textit{Curr. Opin. Chem. Eng.}, 2013, 2, 191-199.
followed by conversion into chemicals of economic value [1-3]. Potential products include formic acid [4,5], methanol, CO [4,6-13], and ethylene [4,14] which can be formed using processes such as homogeneous catalysis [15,16], heterogeneous catalysis [17,18], photocatalysis [19], photoreduction [20], or electrochemical reduction – the topic of this review. In addition to reducing greenhouse gas emissions, CO₂ conversion processes will reduce our dependency on fossil fuels for chemical synthesis. At this point, however, it is unclear which of these strategies are technologically feasible and make economic and practical sense [1]. Electrochemical CO₂ reduction has the advantage that it may be an approach to utilize excess energy from intermittent renewable sources in lieu of large scale energy storage.

This chapter will summarize the current status, remaining challenges, and future opportunities for electrochemical conversion of CO₂ into value-added chemicals or intermediates at low temperatures. Prior reviews and reports have provided an excellent overview of possible products of electrochemical CO₂ reduction, including CO, formate, methane, ethylene, ethanol, n-propanol, allyl alcohol, acetaldehyde, propionaldehyde, acetate, methanol, ethylene glycol, glycolaldehyde, hydroxyacetone, acetone, and glyoxal [14,17,21]. In an electrolyzer CO₂ is reduced on the cathode while the oxygen evolution reaction (OER) takes place on the anode. Half-reactions of the cathode for electrochemical CO₂ reduction into major products such as CO, formate, methane, and ethylene are listed below.

\[
\begin{align*}
\text{CO}_2 + 2\text{H}^+ + 2\text{e}^- & \rightarrow \text{CO} + \text{H}_2\text{O} \\
\text{CO}_2 + \text{H}^+ + 2\text{e}^- & \rightarrow \text{COO}^- \\
\text{CO}_2 + 8\text{H}^+ + 8\text{e}^- & \rightarrow \text{CH}_4 + 2\text{H}_2\text{O} \\
2\text{CO}_2 + 12\text{H}^+ + 12\text{e}^- & \rightarrow \text{C}_2\text{H}_4 + 4\text{H}_2\text{O}
\end{align*}
\]
The process of CO$_2$ electrolysis is basically running a fuel cell in reverse; so indeed, many lessons learned over the last five or so decades in the development of catalysts, electrodes and cell configurations of fuel cells do apply also to the development of efficient CO$_2$ processes, but certain aspects will be very different and will require different optimization strategies. For example, both low-temperature fuel cells and CO$_2$ electrolysis cells are often limited by cathode performance, so both seek to improve slow cathode kinetics by developing more active catalysts. However, in addition to activity, the catalyst for CO$_2$ reduction needs to exhibit high product selectivity so the formation of desired products is heavily favored while suppressing unwanted reactions. Moreover, effective removal of products from the catalyst layer to avoid blocking active sites is important in both fuel cells and CO$_2$ electrolysis cells, but the technical strategies to do so can be very different due to the different nature of products. Specifically, the oxygen reduction reaction in acidic fuel cells generates water which often leads to water management issues, whereas the CO$_2$ reduction reaction in CO$_2$ electrolysis cells often leads to the formation of both gaseous (e.g., CO, H$_2$) and liquid products and thus effective gas / liquid phase separation is vital. The subsequent sections will briefly review the technological requirements for catalysts, electrodes, electrolytes, and cell configurations.

2.3 Terminology and Figures of Merit

For electrochemical reduction of CO$_2$ to be performed in an efficient manner, highly active and durable electrocatalysts for both the cathode (CO$_2$ reduction reaction) and the anode (O$_2$ evolution reaction), as well as electrodes and electrolytes that have high conductivity and allow for sufficient mass transport of the reactants and products to/from the catalyst layers are required. Key figures of merit of the process that characterize its performance and thus assist in determining its economic feasibility are (i) the **Energetic Efficiency (EE)** – a measure of the
overall energy utilization towards the desired product; (ii) the \textit{Current Density (CD)} – a measure of the rate of conversion; (iii) the \textit{Faradaic Efficiency (FE)} – a measure of the selectivity of the process for a given product; (iv) \textit{the catalyst stability}; and (v) \textit{process costs} [22] – including material consumption costs, capital cost and electricity cost. In this review, we will focus on the first three figures of merit (EE, FE, and CD) because currently neither standard protocols for durability tests of catalysts nor cost models for major products exist for electrochemical CO\textsubscript{2} conversion.

The energetic efficiency can be calculated using equation 1:

\[
\varepsilon_{\text{energetic}} = \sum_k \frac{E_k^o \cdot \varepsilon_{k,\text{Faradaic}}}{E_k^o + \eta} 
\]

(1)

where \(E_k^o\) is the equilibrium cell potential for a certain product. For example, \(E^o = E^o_{\text{cathode}} - E^o_{\text{anode}} = -0.10 \text{ V} - 1.23 \text{ V} = -1.33 \text{ V}\) for converting CO\textsubscript{2} to CO and \(E^o = E^o_{\text{cathode}} - E^o_{\text{anode}} = 0 \text{ V} - 1.23 \text{ V} = -1.23 \text{ V}\) for H\textsubscript{2} evolution). \(\varepsilon_{k,\text{Faradaic}}\) is the Faradaic efficiency of product \(k\) and \(\eta\) is the cell overpotential (or the sum of overpotentials on the cathode and anode). From this equation it becomes clear that high energy efficiency is achieved through a combination of high Faradaic efficiency for the desired product, and low overpotentials on the cathode and anode, because that will lead to a low cell potential. Note that at times researchers use a slightly different approach to determine the energy efficiency of their experimental setup [23].

The Faradaic efficiency (sometimes also referred to as the current efficiency) for a given product is calculated using equation 2:

\[
\varepsilon_{\text{Faradaic}} = \frac{z \cdot n \cdot F}{Q} 
\]

(2)
where $z$ is the number of electrons exchanged (for example, $n = 2$ for reduction of CO$_2$ to CO), $n$ the number of moles for a given product, $F$ Faraday’s constant ($F = 96485$ C/mol), and $Q$ the charge passed (C) [14,23,24].

The overall current density, defined as the current at a given cell potential divided by the active cathode electrode area (geometric surface area of the cathode), is a measure of the electrochemical reaction rate (conversion), so it helps determine the electrode area (and thus the electrolyzer size and capital investment) needed to meet the desired rate of producing the product. One can also calculate partial current densities for the individual products formed by multiplying overall current density by the corresponding FE.

2.4 Current Status and Remaining Challenges

Figure 2.1 shows plots of the energetic (Figure 2.1a) and Faradaic (Figure 2.1b) efficiencies versus current densities for CO$_2$ reduction to formic acid, syngas, and C1-C2 fuels (methane, ethylene and methanol) for data published in the literature from 1985 to December 2012. The data points that went into Figure 1 were chosen based on three criteria: the highest Faradaic efficiency, highest energetic efficiency, or highest current density achieved in a single report for the particular product. Note that many variables such as catalyst, electrode (plate, mesh, or gas diffusion electrode), electrolyte (composition and pH), cell configuration, temperature, and pressure are not consistent so this plot is only intended to provide a bigger picture of which figures of merit need most improvement. From these plots it is evident that for each of the different products, many examples have been reported exhibiting a high EE or a high FE, or a high CD, but that optimizing all three figures of merit has been a challenge. For example, for several cases of C1-C2 fuel production a high Faradaic efficiency in combination
with a high current density has been achieved (as high as 70% FE with a CD of 600 mA/cm$^2$; Figure 1a), but these same cases exhibit energetic efficiencies of less than 22%.

### 2.4.1 Catalysts

Electrocatalysts are needed to bind and activate CO$_2$ in order to reduce the high overpotentials typically encountered. Also, catalysts can drive selective formation of desired products. During the past few decades efforts have mostly focused on different metal catalysts and the various products that can be formed using those metals [4,6,25,26]. Four distinct classes of metal catalysts have been identified for CO$_2$ reduction: (1) metals that mainly form formic acid, HCOOH (Pb, Hg, In, Sn, Cd, Tl); (2) metals that mainly form carbon monoxide, CO (Au, Ag, Zn, Pd, Ga); (3) metals that form significant amounts of hydrocarbons such as methane and ethylene (Cu); and (4) metals that mainly form H$_2$ (Pt, Ni, Fe, Ti) [4]. Other potential products formed using metal catalysts include alcohols [17] and oxalic acid [27]. Over the last few years, researchers have also started to study other materials, including metal oxides [28-30], metal organic frameworks (MOF) [31], as well as organometallic catalysts [32]. In this chapter, we summarize work on heterogeneous catalysts that mainly form formic acid, CO, hydrocarbons, and methanol.

**Formic Acid:** Formic acid can be produced with very high Faradaic efficiencies on metals with high overpotential for H$_2$ production, e.g., Hg, Pb [4]. Metal oxides [30], alloys [33,34] and MOF catalysts [31] have also been found active for HCOOH production. Chen et al. found that a Sn/SnO$_x$ catalyst exhibits much higher partial current density and Faradaic efficiency for HCOOH whereas Sn$^0$ only produces H$_2$ [30]. This result suggests the participation of SnO$_x$ in the CO$_2$ reduction pathway. Agarwal et al. showed that Sn-alloy catalysts yield higher Faradaic efficiencies than pure Sn at lower polarization [33]. Hinogami et al. synthesized a copper
rubeanate metal organic framework (CR-MOF) catalyst which was able to decrease the onset for CO$_2$ reduction by 0.2 V compared to a plain Cu electrode [31].

**Hydrocarbons:** Copper catalysts seem uniquely capable of reducing CO$_2$ to hydrocarbons at ambient pressure and temperature [4,14,21,35,36]. Recently, Jaramillo and coworkers have identified the many hydrocarbon products that form, and elucidated the mechanism by which these products form, using a flow cell with a Cu-based cathode [14]. In a number of other studies, modifying copper surfaces has been shown to lower the overpotential and increase the selectivity for hydrocarbon formation. For example, Tang *et al.* found that a Cu electrode covered with Cu nanoparticles exhibits higher selectivity towards hydrocarbons due to a greater abundance of under-coordinated sites[37]. Li *et al.* modified Cu electrodes by annealing Cu foil in air, which resulted in a stable electrode that lowered the overpotential for CO$_2$ reduction by 0.5V compared to polycrystalline Cu [29]. Schouten *et al.* studied two single-crystal copper electrodes and observed two different mechanisms for ethylene formation [38].

**Carbon Monoxide:** CO can also be produced with high Faradaic efficiency on various metal electrodes [4], and when combined with H$_2$ liquid fuels can be produced via the Fischer-Tropsch process. H$_2$ can be produced at less negative potential than CO, using fairly efficient processes (*e.g.*, water electrolysis, biomass conversion, or the water gas shift reaction), so most efforts focus on optimizing the CO$_2$ conversion process with respect to maximizing CO production, although in some application scenarios a single reactor for cogenerating CO and H$_2$ may be preferred over two separate but more efficient reactors. Ag catalysts have long been the state of the art for CO production, with recently reported current densities as high as 91 mA/cm$^2$ [39], but other systems are also actively being studied. Rosen *et al.* reported being able to decrease the overpotential for CO production to 0.17 V, *i.e.*, they observed CO evolution at an cell
potential of -1.5 V, close to the theoretical equilibrium cell potential of -1.33 V (difference between the equilibrium cathode potential of -0.10 V and the equilibrium anode potential of 1.23 V), by using an aqueous ionic liquid solution, in which the 1-ethyl-3-methylimidazolium (EMIM+) cation serves as a co-catalyst, in combination with Ag nanoparticles immobilized on the electrode [13]. Unfortunately, the current densities reported in this work are low; less than 5 mA/cm². We have recently studied diaminotriazole-based organometallic silver catalysts, which decreased Ag loading by a factor of 20, while maintaining similar performance [32]. Furthermore, a co-catalyst mechanism was also suggested by using those ligands. Interestingly, it is not clear whether the organometallic species is actually the catalytically active species on the electrode surface at this point. Salehi-Khojin et al. investigated the effect of Ag particle size on CO₂ reduction activity and observed maximum activity for particles with an average size of 5 nm Ag [40]. In another interesting lead, Chen et al. showed that Au nanoparticles synthesized by reduction of Au oxide films are highly selective for reduction of CO₂ to CO at overpotentials of about 0.14V [28].

**Methanol:** While methanol is a desirable product due to its wide range of application, including direct use as a fuel for a fuel cell, there are few reports on its formation from CO₂ via heterogeneous, electrochemical methods and these typically reported low current densities and/or low Faradaic efficiencies [41,42]. In contrast, homogeneous catalysis efforts for the conversion of CO₂ into methanol have been quite successful [43-45].

In summary, catalysts for the selective reduction of CO₂ into different interesting products have been developed, but catalysts that simultaneously exhibit overpotentials (e.g., < -0.2 V) and current densities (e.g., >100 mA/cm²) needed for commercial applications are still lacking. The quest for such catalysts could be aided by (i) more fundamental studies focusing on elucidation
of reaction mechanisms for distinct catalysts, an area in which reports are few [38,46,47], and (ii) more in-depth modeling efforts, ideally linked directly with experimental work, so pathways for CO₂ reduction on different catalysts can be better understood, which in turn will assist the design and synthesis of novel catalysts that have both low overpotential and high activity for CO₂ reduction reactions.

2.4.2 Electrode Structure

Electrodes play a vital role in all devices based on heterogeneous electrochemical reactions, including those for CO₂ conversion. The performance and durability of the reactor is largely determined by the processes occurring at the electrode-electrolyte interface and within the electrode. In general, electrodes comprised of a catalyst layer and a backing layer/substrate serve multiple functions: (i) to deliver reactant gas, CO₂, from flow-field channels to the catalyst layer, (ii) to transport product from the catalyst layer into flow channels or the electrolyte/membrane, and (iii) to conduct electrons with low resistance [48,49]. Maximizing electrode performance, and consequently reactor performance, requires optimizing all of these transport processes that strongly depend on the complex structure of the electrode.

Despite their importance, to date only a few efforts have studied the interplay between electrode structure and performance [4,7,12,39,50]. In early work, Hori et al. extensively studied the CO₂ reduction reaction on planar metal electrodes (Cu, Au, Ag, Zn, Pd, Ga, Pb, Hg, In, Sn, Cd, Ti, Ni, Fe, Pt, Ti) at low current densities of about 5 mA/cm² [4]. Low surface area and low CO₂ concentrations at the electrode surface due to the limited CO₂ solubility in the aqueous electrolytes used limits the performance of such planar electrodes. Yano et al. proposed the use of a metal (Ag, Cu) mesh as the cathode for CO₂ reduction in a modified H-type cell in which the reaction can take place at a three-phase gas/solid/liquid interface by delivery of gaseous CO₂
from a gas chamber [12,50]. The lack of current density data in this report prevents quantification of the beneficial effects of this approach. More recently, Delacourt et al. hand- or spray-painted Ag catalyst inks on gas diffusion layers (GDLs) commonly used in polymer electrolyte membrane fuel cells, to generate cathodes with a Ag (particle size of 1 µm) loading of 8-10 mg/cm² [7]. When this Ag nanoparticle-covered GDE (cathode) was mounted in a fuel cell-like CO₂ electrolysis cell with a buffer layer of 0.5 M KHCO₃ in contact with the Ag cathode, current densities as high as 20 mA/cm² were obtained, in combination with product selectivities for CO and H₂ that are comparable to the findings by Hori et al. [4] and Yano et al. [12] using similar catalysts (Ag) and electrolytes (0.5 M KHCO₃). We recently reported a current density as high as 91 mA/cm² in combination with 94% Faradaic efficiency for CO, and 46% energetic efficiency using a gas diffusion electrode (GDE) covered with a catalyst layer of Ag nanoparticles (particle size of 70 nm) [39]. The data was collected at room temperature and ambient pressure using a microfluidic CO₂ electrolysis cell in which a flowing aqueous KCl electrolyte separated the cathode (a GDE covered with a Ag catalyst layer) and anode (a GDE covered with a Pt catalyst layer). Deposition of the catalyst using a fully-automated airbrushing method yielding a very thin (7 ± 2 µm measured using X-ray micro-computed tomography), crack free layer with a Ag loading of only 0.75 mg/cm² (Figure 2.2) was key to achieving this state-of-the-art performance, while simultaneously drastically reducing the amount of metal catalyst needed compared to planar metal electrodes, metal meshes, as well as other approaches to deposit metal nanoparticle-based inks. Furthermore, Salehi-Khojin et al. investigated how Ag particle size has a profound effect on CO₂ reduction activity [40]. They observed that the reaction rate of the reduction of CO₂ to CO increases as the particle size decreases from 200 to 5 nm, but then drops again as the particle size decreases to 1 nm. Thus, a diameter of about 5 nm
is likely an optimal particle size for Ag catalysts. In summary, use of a GDE in combination with optimized catalyst layer deposition methods has led to significant improvement in electrode performance for CO$_2$ reduction. Further efforts should probably focus on assessing, via experiment and modeling, to what extent the structure and chemical composition of the catalyst layer (e.g., pore size and distribution, the choice of binder materials such as Nafion) and the porous backing layer (e.g., porosity, hydrophobicity, layer thickness) impact the transport of reactants (sufficient supply of CO$_2$?) and products (active sites blocked?).

**2.4.3 Electrolyte**

Few efforts to date have focused on the effects of electrolyte composition on electrochemical CO$_2$ reduction, despite the fact that electrolytes have been known to affect almost every electrochemical process dating back to the days of Frumkin [51].

The heterogeneous electrochemical reduction of CO$_2$ employs aqueous electrolytes commonly comprised of alkali cations (e.g., Na$^+$, K$^+$), various anions such as halide anions (e.g., Cl$^-$), bicarbonate (HCO$_3^-$), or hydroxide (OH$^-$), and water [4,35,52,53]. These inorganic salts are often used due to their high conductivities in water. Additionally, the water in aqueous electrolytes provides protons for the necessary electrochemical proton transfer steps involved in the reaction pathway [4,47]. A number of prior reports have shown that electrolyte choice has profound effects on current density, product selectivity, and energetic efficiency in CO$_2$ reduction [35,52,53]. For example, Hori et al. reported that cation choice (i.e., Li$^+$, Na$^+$, K$^+$, and Cs$^+$) for bicarbonate (HCO$_3^-$) electrolytes significantly impacts the distribution of product formed on copper (Cu) electrodes [52]. Hori et al. also reported that anion choice (i.e., Cl$^-$, ClO$_4^-$, SO$_4^{2-}$, HCO$_3^-$, H$_2$PO$_4^-$), each with different buffer capacities, influences the local pH at the Cu electrode and thus the nature and the amount of products formed [35]. Similar to these findings
by Hori *et al.*, Wu *et al.* observed significant differences in activity and selectivity of tin (Sn) electrodes when different electrolytes (KHCO$_3$, K$_2$SO$_4$, KCl, Na$_2$SO$_4$, Cs$_2$SO$_4$, NaHCO$_3$, and CsHCO$_3$) are used [53]. Previously, we reported that the size of the cation (Na$^+$ < K$^+$ < Rb$^+$ < Cs$^+$) of the salt used in the electrolyte plays a significant role in CO$_2$ reduction on silver (Ag) electrodes. Specifically, larger cations favor CO production and suppress H$_2$ evolution [54].

In summary, these studies show that (i) cation size impacts the propensity for cation adsorption on the electrode surface, which affects the potential of the outer Helmholtz plane (OHP) in the electrical double layer (EDL), and in turn impacts reaction energetics and kinetics; and (ii) the buffer capacity of anions impacts the local pH at the electrode and thus the availability of protons, which in turn affects reaction kinetics. Furthermore, depending on reactor configuration, electrolyte composition may enhance performance by improving the solubility of CO$_2$, for instance by using ionic liquids instead of aqueous solution, thereby reducing mass transport limitations.

### 2.4.4 Electrolyzers

No standard experimental setup or methodology for studying electrochemical CO$_2$ reduction currently exists. Different labs have used a variety of flow cells or electrolyzers for the various studies reported here. Jaramillo and coworkers [14], as well as our lab [32,39,54,55], use a microfluidic flow cell in which the electrodes are separated by a flowing liquid electrolyte, which enables analysis of individual electrode performance by using an external reference electrode. Delacourt *et al.* based their design on an alkaline fuel cell [7], while Dufek *et al.* used a more traditional electrolyzer design [10,11,56,57]. Interestingly, three of these systems exhibit similar behavior when comparing their performance for CO production (*Figure 2.3*). All data plotted in *Figure 2.3* were collected at room temperature and ambient pressure to allow for fair
comparison (identical kinetics) although these conditions might not be optimal for the reactors reported by Delacourt et al. and Dufek et al. Indeed, Dufek et al. [10,57] have reported improved reactor performance at elevated temperature and/or pressure. The key difference between our recent data [39], and the data by the two other groups is that the same CDs and EEs can be achieved at much lower cell potentials. This difference can be completely attributed to the optimized structure of the catalyst layer in our flow cell-based electrolyzer. This suggests that electrolyzer design, which has a profound effect on mass transport, is presently not limiting the performance of CO$_2$ electrolyzers. Indeed, one would expect even better performance if these optimized catalyst layers would be used in reactors such as those reported by Delacourt et al. and Dufek et al. Still, further optimization of operating conditions (e.g., electrolyzers operated at elevated pressure and temperature) will continue to improve reactor performance in CO$_2$ reduction. Specifically, multiple labs have reported enhanced current densities in pressurized electrolyzers (e.g., 20 atm) [58,59]. For example, Furuya et al. reported that a total current density as high as 300-900 mA/cm$^2$ can be achieved under 20 atm using a pressurized electrolyzer operated with GDEs coated with different metals (Pt, Ag, Cu, Ni, Co, Pd) [58].

### 2.5 Key Opportunities and Conclusions

Recent reports on a variety of promising catalysts for CO$_2$ reduction (MOFs, organometallics, etc.) suggest that significant strides will be made to enhance catalyst activity while reducing overpotential. Such efforts will greatly benefit from fundamental mechanistic studies, as well as modeling of new classes of catalytic materials. Fine-tuning the electrolyte composition for a given catalyst offers a further opportunity for performance enhancement.

A key opportunity resides in optimization of electrode structure and/or composition. Based on our experience, CO$_2$ electrolysis is much more sensitive to the structure and composition of
the microporous layer, than similar electrodes in an identical cell operated as a fuel cell. Further efforts should probably focus on assessing, via experiment and modeling, to what extent the physical properties of these gas diffusion layers (e.g., porosity, hydrophobicity, layer thickness) impact effective gas-liquid phase separation while facilitating transport of reactants (sufficient supply of CO₂?) and products (active sites blocked?).

The above shows that multiple opportunities for further improvement of the EE, FE, and CD for electrochemical reduction of CO₂ to (intermediates for) value-added chemicals are available, but a few key questions remain: What combination of optimized figures of merit will be sufficient for economic feasibility? How fast do the component materials (particularly catalysts) degrade over long periods of time? What are the sources of CO₂ and how will potential contaminants such as sulfur-containing compounds impact electrolyzer design, as well as cell performance and catalyst durability [11]? Answering these questions requires a full system and life cycle analysis, well beyond the scope of this review. However we did start to develop a crude process cost analysis model [57] for the electrochemical reduction of CO₂ to CO to get an idea of how the cost to produce CO scales with current density (Figure 2.4). Many assumptions, including capital cost (e.g., non-linear correlation of capital cost and production rate) and the cost of electrical power (e.g., linear correlation of energy cost and production rate) went into this model, so on the y-axis we only show the specific cost to produce CO ($/unit mass of CO produced) as well as the costs of capital investment and energy in arbitrary units. Critically, the cost to produce a given amount of CO is relatively high and dependent on the current density at which the electrolyzer is being operated below CD values of ~250 mA/cm², whereas the cost levels off if the process can be operated at higher current densities. One may conclude that the present state of the art performance of CDs around 100 mA/cm² (see for example [37]), is still
far from a performance level where the cost to produce CO starts to level off. So indeed the performance of CO₂ electrolyzers needs to be improved significantly by development of better catalysts in combination with optimized electrode and electrolyte formulations. As mentioned above, estimation of the actual cost to produce CO (or other products) via electrochemical reduction of CO₂ will require the development of much more in depth cost and life cycle analysis models.
2.6 Figures

Figure 2.1. Summary of electrochemical performance for CO$_2$ conversion from selected literature in the period from 1985 to December 2012. (a) Faradaic efficiencies and (b) energetic efficiencies as a function of current density for three different (types of) products: formic acid \([4,14,28,29,31,32,51,58-64]\), syngas \([4,6,10,11,13,26,27,30,35,38,53,54,62,64-72]\), and C1-C2 fuels (methane, ethylene, and methanol) \([6,14,35,40,61,62,64,67,72]\).
Figure 2.2. Example of the effect of catalyst layer deposition method (airbrushing vs. hand-painting) on electrode performance for converting CO\textsubscript{2} into CO [37]. Depositing Ag nanoparticle-based catalyst layers via fully-automated air-brushing method led to a 3-fold increase in partial CO current density (not shown) and enhanced product selectivity (94% CO), despite a 10-fold decrease in catalyst loading compared to prior reports [37].
Figure 2.3. Comparison of different electrolyzer configurations for electrochemical conversion of CO$_2$ to CO. Jhong et al.: a microfluidic flow cell [37]; Dufek et al. a traditional electrolyzer [10]; and Delacourt et al.: a modified alkaline fuel cell [68]. The data from the literature plotted here were all collected at room temperature and ambient pressure.
Figure 2.4. Schematic representation of the results of a crude cost analysis model for the electrochemical conversion of CO$_2$ to CO: the relative cost of energy, capital investment, and the resulting CO cost as a function of the current density. The purpose of this graph is to visualize that the cost to produce CO is strongly dependent on current density below ~250 mA/cm$^2$, but levels off for higher current densities.
2.7 References


Chapter 3

Combining Structural and Electrochemical Analysis of Electrodes Using Micro-Computed Tomography and a Microfluidic Fuel Cell*

3.1 Chapter Overview

Detailed investigation of the relationship between the physical structure and electrochemical activity of state-of-the-art fuel cell electrodes is a critical, yet often poorly reported or proprietary, step in the manufacturing of cheaper and more durable configurations. Here we demonstrate the utility of X-ray micro-computed tomography (MicroCT) for detailed characterization of the architecture and buried interfaces of fuel cell electrodes in a non-destructive fashion. We employ a combined thresholding and filament tracing based analytical protocol for image analysis which enables more accurate quantification of GDE structures as compared to previously-used thresholding-only methods. Furthermore, we report on a methodology of combining in-situ electrochemical analysis in a microfluidic fuel cell and ex-situ structural analysis in a MicroCT which enables direct correlation of changes in electrode performance to changes in physical structure, in this case, porosity. As a demonstration, the effects of electrode compression are investigated. We observed that both subtle shifts in structure in the microporous and catalyst layers at low compression pressures (< 1x10^3 lbf) and more drastic structural densification of the macroporous carbon fiber layer at moderate compression pressures (≥ 1x10^3 lbf) impact electrode performance.

3.2 Introduction

* This chapter has been adapted from the following publications:
Low temperature fuel cells, such as polymer electrolyte membrane fuel cells (PEMFCs), have been extensively investigated as alternative power sources due to their high efficiency, high energy density and low emissions [1,2]. Unfortunately, commercialization of these technologies has been hampered by high cost and insufficient durability [3]. Reducing cost and improving durability of these fuel cell systems requires detailed studies of each component (e.g., electrodes, membranes, flow-fields) and of the interfaces between those components (e.g., membrane-electrode). Of particular importance are gas diffusion electrodes (GDEs), which consist of a catalyst layer, a microporous layer (MPL) of teflonized carbons, and a macroporous layer of carbon fibers [4]. The GDE structure plays a pivotal role in fuel cell operation as it functions (i) to deliver reactant gas from flow-field channels to catalyst layer, (ii) to drain liquid water from the catalyst layer into flow channels or the electrolyte / membrane, and (iii) to conduct electrons with low resistance [4]. Maximizing electrode performance, and consequently fuel cell performance, requires optimizing all of these transport processes that strongly depend on the complex three-dimensional (3D) structure of the GDE. Unfortunately, these structure-activity relationships remain poorly-understood as (i) present state-of-the-art electrodes are often manufactured using proprietary methods and (ii) physical changes in electrode structure, both macro and micro, during fuel cell operation have not been extensively studied. The rational design of novel high-performance electrodes requires a detailed understanding of how GDE structure and performance change as a function of preparation methods and operational conditions. Therefore, a systematic characterization of electrode structure and subsequent performance as a function of processing parameters, including electrode compression during pretreatment, catalyst deposition, and membrane-electrode assembling, is needed. However, in
the absence of non-destructive 3D imaging techniques, gaining a comprehensive understanding of GDE structure-activity relationships is difficult.

Traditional methods for analyzing electrode structure such as scanning electron microscopy (SEM) probe two-dimensional (2D) surfaces / cross-sections and thus provide limited information on how buried interfaces are interconnected in 3D. SEM imaging coupled with ion milling (i.e., focused ion-beam-scanning electron microscopy, FIB-SEM) can be used to generate 3D microstructural renderings, albeit in a destructive fashion. This technique has been applied successfully to solid-oxide fuel cell (SOFC) anodes [5] as well as the catalyst layer and the MPL of PEMFCs [6,7]. Unfortunately, FIB-SEM is not suitable for studying dynamic GDE structure-activity relationships due to (i) destructive sample preparation, (ii) limited field of view, 10 μm × 10 μm at most, in comparison to typical GDE thicknesses of 200 – 500 μm, and (iii) computational costs (i.e., more time needed to analyze a dataset with nanoscale pixels). X-ray tomography is an emerging analytical technique in fuel cell science that enables non-destructive multiscale 3D imaging of electrode architecture and liquid water transport through that architecture [6,8-20]. In X-ray tomography, an X-ray beam travels through a rotating sample and its intensity gets attenuated. The transmitted signals are then collected by a detector to generate a 3D map of variations in X-ray absorption within the sample, from which different phases / elements as well as heterogeneity in density can be identified [8]. Two X-ray tomography methods are available: X-ray micro-computed tomography (MicroCT) and X-ray nano-computed tomography (NanoCT) provide resolutions of 1-10 μm and ≤ 100 nm, respectively [17]. While NanoCT has been employed to analyze electrode structure, particularly to analyze features at the sub-micron length scale, its utility is limited to evaluating sub-millimeter size samples [6,17,21]. Furthermore, NanoCT is also more computationally
expensive than MicroCT. To date, most MicroCT investigations of fuel cells have focused on the study of water management in PEMFC cathodes [10,11,13] and, more recently, the structural analysis of electrode architectures with a focus on providing more accurate parameters for numerical models [15,18,20]. To our knowledge, to date no efforts have focused on the systematic investigation of structure-activity relationships as a function of electrode preparation methods, in which individual electrode performance is directly linked with electrode structure.

Here, we report an analytical methodology that directly correlates changes in electrode performance, as measured in-situ using a microfluidic H₂/O₂ fuel cell, to changes in physical structure (i.e., porosity), as determined ex-situ using MicroCT. In specific, we demonstrate the utility of MicroCT to characterize buried interfaces of fuel cell electrodes in detail in a non-destructive fashion.

3.3 Experimental

3.3.1 Gas Diffusion Electrode (GDE) Preparation and Fuel Cell Testing

EFCG Phosphoric Acid Fuel Cell Electrodes (E-Tek) were used as gas diffusion layers (GDLs) in this study. This GDL consists of a polytetrafluoroethylene (PTFE)-treated Toray carbon paper TGP-H-120 with a teflonized microporous layer on one side. Catalyst inks were prepared by mixing 12 mg Pt/C catalyst (50 wt% Pt) and 9.2 μL Nafion solution (5 wt%, Solution Technology, 30:1 catalyst-to-Nafion ratio), and adding the carrier solvents: 200 μL Millipore water (18.2 MΩ), and 200 μL of isopropyl alcohol. All catalyst inks were sonicated (Branson 3510) for at least two hours to ensure uniform mixing and were hand-painted on the teflonized carbon side of the GDL to create a gas diffusion electrode (GDE) covered with catalyst over a geometric surface area of 4 cm². So the catalyst loading is 3 mg Pt/C/cm². Some of the fabricated GDEs were hot-pressed (Carver 3851-0) at varying pressures (0, 1x10³, 2x10³,
5x10^3 and 10x10^3 lb) and at a temperature of 125 ± 10 °C for 5 min. Detailed descriptions of fuel cell assembly and testing procedures can be found in our previous work [22,23].

### 3.3.2 Acquisition, Reconstruction, and Segmentation of MicroCT Data

In this study, the whole GDE was clamped in a rotating sample holder and a corner was exposed to the X-ray beam field (Figure 1b, top left). During MicroCT imaging (Micro-XCT 400, Xradia), the sample was scanned using an X-ray source at 40 kV and 200 μA, and 745 projections, typically called shadowgraphs or shadow images, were collected as the sample was rotated stepwise over 180° with a 10 second exposure time for each projection. The shadow images were then processed to reconstruct 2D radiographic cross-sectional image stacks and 3D tomographic virtual models of the GDE. The initial reconstruction of MicroCT data was carried out using the *TXM Reconstructor* reconstruction software (Xradia), which accompanies the MicroCT hardware. The distances of the sample to the X-ray source (76 mm) and the X-ray detector (28 mm) resulted in a voxel (volume pixel) size of 1 μm^3. The field of view (FOV) was approximately 1000 μm × 1000 μm. Further image processing was performed using the *Amira* visualization software package (Version 5.3, Visage Imaging) for subsequent quantitative analysis of the GDE microstructure.

### 3.4 Results and Discussion

#### 3.4.1 Qualitative Visualization of GDE Structure

*Figure 3.1* shows comparative GDE imaging by SEM and MicroCT. Obtaining cross-sectional images of a GDE using a SEM without physically slicing off the material is difficult. Breaking the GDE via liquid nitrogen cracking (*Figure 3.1a*) or cutting thin slices off of the GDE using a razor blade tends to cause damage to or smearing of the porous structure [7].
**Figure 3.1a2** shows the 2D SEM micrograph of a GDL in a bottom up view which provides only information on the surface of the macroporous backing layer. In contrast, MicroCT as a non-destructive imaging technique does not require destructive sample preparation to generate cross-sectional images. The initial data reconstruction obtained with MicroCT allows for inspection of 2D radiographic cross-sectional image stacks and of 3D tomographic virtual models of the GDE, which provides detailed information about layer thickness, internal architecture, and material distribution. In particular, **Figure 3.1b1 and 3.1b2** shows through-plane (YZ-plane) and in-plane (XZ-plane) 2D radiographic images of the GDE, respectively. In these images, one can easily distinguish the catalyst layer, the microporous layer, and the macroporous carbon fiber layer by comparative layer thicknesses as well as brightnesses (**Figure 3.1b1**), and within the layers one can distinguish the distribution of different materials, *e.g.*, carbon fibers vs. PTFE (**Figure 3.1b2**). We confirm that the bright catalyst layer in **Figure 3.1b1** is not an artifact of beam hardening. In addition to layer thickness provided by through-plane images, buried layer interfaces can also be characterized from examination of in-plane images. For example, **Figure 1b2** shows the interface between the macroporous backing layer comprised of fibrous carbons and the hydrophobic MPL comprised of a polytetrafluoroethylene (PTFE) and carbon particle mixture. In addition, the 3D tomographic virtual model of the GDE (**Figure 3.1b3**) visualizes the internal architecture and organization in false color. The brightness of the false color indicates X-ray absorption intensity of materials, so materials with high atomic numbers or densities such as metallic catalyst particles tend to be brighter. While the microporous layer and the macroporous layer are both carbonaceous, the macroporous, fibrous layer tends to be much brighter due to its higher carbon density whereas the microporous layer that consists of low-density teflonized carbon particles appears relatively invisible. In sum, MicroCT imaging
provides information on (i) buried interfaces, (ii) 3D architecture, and (iii) material distribution, which is critical in understanding transport processes within the electrode.

### 3.4.2 Methodology for Quantitative Analysis of GDE Structure

Computing microstructural properties of GDEs, such as porosity and pore size distribution, from MicroCT data has gained a lot of interest to validate numerical models of electrode material properties [15,20,24]. Here, we quantify these structural properties to understand the extent to which physical changes in electrode structure correlate to changes in electrode performance. We have developed an analytical methodology to post-process the 2D radiographic cross-sectional images obtained from the initial reconstruction to extract critical structural parameters from the MicroCT data, including information of the bulk porosity of and local porosity within the macroporous layer.

**Figure 3.2a** shows the flowchart of this quantitative analysis procedure. First, the 2D cross-sectional image stack is cropped to a discrete volume that is of analytical interest, here a $862 \, \mu m \times 658 \, \mu m \times 345 \, \mu m$ section of the macroporous layer. The analytical volume is selected based on two criteria: (i) the analytical volume is the majority of the total image volume of the macroporous layer (i.e., $862 \, \mu m \times 685 \, \mu m \times 400 \, \mu m$), and (ii) the analytical volume does not include or is not close to either the macroporous layer – air interface or the macroporous layer – MPL interface. Sensitivity analysis is performed on 10 samples of the same GDL material to determine if this volume is representative of the material properties and similar results are obtained, for example, the bulk porosity is $70.6 \pm 0.9\%$.

Second, each 2D grayscale image is segmented to a 2D binary image to help identify and separate voxels predominantly filled with materials (white) from those that are predominantly void (black). Two segmentation techniques are investigated: the *thresholding method* and the
filament tracing method. In the most commonly used segmentation method, image thresholding, the threshold value of the grayscale range is determined either by visual inspection or by an algorithm (i.e., Otsu’s method) that attempts to simultaneously account for all of material without capturing excessive void space [17,20,25]. However, this thresholding method does not accurately filter out image noise, e.g., due to the effects of X-ray beam hardening. Consequently, grayscale values can be found in the fibrous masses and also in the void space, especially close to the edges of the fibers (Figure 3.2b). Figure 3.2b shows the raw grayscale image as well as an overlay of the binary images generated by each of the two segmentation methods. The overlaid binary images highlight the differences between the material voxels identified using the thresholding method (red) and the filament tracing method (white). The pink and black areas represent method overlap and void space, respectively.

In this study, we perform segmentation using the filament tracing method, available in Amira v5.3 visualization software, which utilizes a grayscale threshold value in combination with structural connectivity, rather than a threshold range alone [26]. As a result, this method better differentiates fibrous masses from void space. Connected carbon fibers are identified in a single slice using a semi-automated operation, comprised of threshold masking followed by edge detection. Specifically, threshold masking permits the user to first select a grayscale range (i.e., in this case, by visual inspection) prior to employing further segmentation algorithms. The grayscale threshold (a range) is determined by subjective visual inspection that is considered more effective than automated methods when distinctive and easily computer-recognizable boundaries are not present [27,28], which is the case here in the analysis of GDEs. The threshold masking limits which grayscale values can or cannot be selected, effectively creating a new sub-volume of available intensity values for segmentation. This type of masking is especially helpful
when applying subsequent algorithms such as edge detection, which rely upon the computational ability to automatically distinguish between structural components in an image. The edge detection we used relies upon the three-dimensional region growing algorithm [26], which starts from a user-defined seed point and segments images by incrementally recruiting voxels based on predefined criteria, including grayscale value similarity and spatial proximity. The voxels that are connected and have similar grayscale values are assumed belonging to the same material. These connected fibers that are identified in a single slice are then automatically traced throughout the entire analytical volume such that only connected volumes, within the threshold grayscale range, are captured.

After segmentation, in the third and final step, a 3D reconstructed volume of these binary images is rendered for subsequent quantitative analysis. For example, the properties of the macroporous layer can be investigated with a focus on determining both bulk porosity and layer-to-layer changes in porosity. The porosity $\varepsilon$ is defined as:

$$\varepsilon = 1 - \frac{\text{material}_{\text{vox}}}{\text{material}_{\text{vox}} + \text{void}_{\text{vox}}}$$

where $\text{material}_{\text{vox}}$ is the number of material voxels filled with carbon fibers, binder, or PTFE (all of which are assumed to be impermeable) and $\text{void}_{\text{vox}}$ is the number of void voxels.

With the porosity data obtained directly from MicroCT, critical transport properties such as tortuosity, relative diffusivity, and permeability that govern the delivery of reactant gases and removal of products within the GDL can be calculated using equations proposed by numerical models such as the Bruggeman model [29] as well as the Tomadakis & Sotirchos model [30,31]. Accurate knowledge of these transport properties is needed to improve the power density and efficiency of PEMFCs. Moreover, these parameters are necessary input for all numerical models simulating multi-phase mass transport within the GDL [15].
In PEMFCs, the mass transport of reactant gases from the flow channels to the catalyst layer is dominated by diffusion [32]. Binary diffusion of species a and b in a porous medium can be described by Fick’s first law and effective media theory:

\[ j = -D_{ab}^{\text{eff}} \nabla c \tag{1} \]

where \( c \) is the concentration, and \( j \) is the molar flux. \( D_{ab}^{\text{eff}} \) is the effective diffusion coefficient tensor, which is split into an effective relative diffusivity \( f(\varepsilon) \) and a bulk diffusivity \( D_{ab} \):

\[ D_{ab}^{\text{eff}} = f(\varepsilon)D_{ab} = \frac{\varepsilon}{\tau} D_{ab} \tag{2} \]

where \( \varepsilon \) is the porosity and \( \tau \) is the tortuosity, a measure for the connectivity of the pores. Mathematically the tortuosity is defined as the arc-to-chord ratio, which is the ratio of the length of a curve to the distance between the end points [33]. Typically, the Bruggeman model (Eq. 3) [29], which is based on an idealized morphology of spherical agglomerates, is used for tortuosity and effective relative diffusivity prediction due to its simplicity. However, application of this model to fibrous agglomerates is known to be not very accurate [24,33]. Tomadakis & Sotirchos developed a model for randomly oriented fibrous media [30,31]. This model uses Monte Carlo simulation on constructed fibrous media to compute tortuosity and effective relative diffusivity as a function of porosity and proposes the following equations with porosity as the only input parameter:

\[ \tau = \left( \frac{1 - \varepsilon_p}{\varepsilon - \varepsilon_p} \right)^\alpha \quad \text{and} \]

\[ f(\varepsilon) = \varepsilon \left( \frac{\varepsilon - \varepsilon_p}{1 - \varepsilon_p} \right)^\alpha . \tag{4} \]
where $\varepsilon_p$ is the percolation threshold porosity, the porosity with the least required open void space connectivity for diffusion or permeation through the porous media (here $\varepsilon_p = 0.11$), and $\alpha$ is a fitting parameter for through-plane diffusion (here $\alpha = 0.785$). $\varepsilon_p$ was determined by extrapolating the simulation results of effective relative diffusivity to the minimum porosity that allows mass transfer to occur. $\alpha$ was determined using a parameter estimation procedure based on the minimization of the square error between the simulations and the proposed equations.

Although diffusion is considered the primary mode of gas-phase transport within the GDE, convection needs to be accounted for when a pressure difference exists between neighboring flow channels [32,34]. Convection in a porous medium can be described by Darcy’s law:

$$ u = -\frac{\kappa}{\mu} \nabla P , \quad [5] $$

where $\kappa$ is the permeability tensor, $\mu$ the dynamic viscosity of the fluid, $u$ the velocity of the fluid, and $P$ is the pressure. Tomadakis & Sotirchos[30,31] predicts the permeability using:

$$ K = \frac{\varepsilon}{8(\ln \varepsilon)^2 \left(1 - \varepsilon_p\right)^2 [\alpha + 1] \varepsilon - \varepsilon_p} \left[ (\varepsilon - \varepsilon_p)^{\alpha + 2} r_f^2 \right] $$ \quad [6]

where $r_f$ is the carbon fiber radius. We use $r_f = 4.6 \, \mu m$, which is in agreement with values reported in literature[34] as well as our observations in SEM. The applicability of the Tomadakis & Sotirchos model to GDLs has been validated by experimental data and observations[34].

Recently, Fishman et al. [24] employed the Tomadakis & Sotirchos model to calculate heterogeneous through-plane distributions of tortuosity, relative permeability, and permeability for GDLs. These analyses provided insight into the impact of GDL porosity on transport properties. Here, we exploited a similar analysis for the calculation of transport properties using
porosity data we obtained from MicroCT using the filament tracing segmentation procedure described above (Figure 3.2a). Specifically, we wished to get a better understanding on how these transport properties respond to electrode preparation methods, for example, the mechanical compression of the GDE. Due to the non-destructive nature of MicroCT imaging, the exact same GDE can be investigated multiple times after being exposed to and tested at different conditions for different periods of time. For example, we studied the relation between changes in electrochemical performance and changes in electrode structure by sequentially exposing the same electrode to higher compression levels. This MicroCT-based method allows for porosities to be measured and, from that, for the determination of the corresponding physical properties of tortuosity, relative diffusivity, and permeability, without the need to perform destructive measurements like mercury intrusion porosimetry (MIP).

3.4.3 An Example Study of Linking Electrode Structure and Performance

Combined ex-situ MicroCT imaging and in-situ fuel cell analysis can be used to systematically probe the impact of physical changes to the electrode structure on its electrochemical performance. Furthermore, the use of a microfluidic fuel cell enables structure-activity relationships to be determined for individual electrodes within an operating fuel cell. To demonstrate the utility of such investigations, we studied the effects of hot-pressing on fuel cell electrode performance. Prior to use, fuel cell electrodes and membrane-electrode assemblies (MEAs) are hot-pressed to compact the interfacing layers together in order to minimize electrical contact resistances and to avoid delamination. In addition, pressure is also applied to the fuel cell stack during operation to prevent gas leaks and to ensure minimal contact resistance losses between electrodes or MEAs and current collectors. However, over-compression of or uneven pressure distribution across GDEs can damage the intricate electrode microstructure leading to
losses in porosity and consequently to a reduction in performance and durability. Thus, understanding and balancing these competing effects is important for the design and development of next-generation electrode materials and fuel cell systems. Despite its importance, to date relatively few papers have been published on the effects of mechanical compression on electrode performance. Lee et al. studied the effect of GDL compression on PEMFC performance by adjusting the bolt torque for different GDL materials and found optimal bolt torque values [35]. Ge et al. found that the amount of compression has a significant impact on PEMFC performance and the optimal compression varies for different GDL materials [36]. Bazylak et al. studied the influence of GDL compression on the morphology of the GDL using SEM and suggested the irreversible damage to carbon fibers as well as PTFE in the macroporous layer results in preferential pathways for excess water transport, which leads to electrode flooding [37]. So in prior work, either electrochemical analysis or structural analysis has been reported. Here, we will study the effects of compression on both GDE structure and electrochemical activity.

Figure 3.3 and 3.4 show combined electrochemical and structural analysis of the effects of hot-pressing on acidic fuel cell cathode performance. Cathode performance typically limits the overall acidic fuel cell performance due to sluggish oxygen reduction reaction (ORR) kinetics and insufficient removal of water generated by the ORR, which leads to flooding. Thus cathode performance is dependent on the ability of the electrode to efficiently deliver oxygen to the catalyst sites and to effectively remove excess water from the porous electrode structure. One electrode is subjected repeatedly to a 3-step cycle (Figure 3.3a), namely hot-pressing (compression), microtomography (3D structural analysis), and microfluidic fuel cell testing (electrochemical performance). To start the process, a freshly-prepared electrode (0 lb) is
analyzed in the MicroCT by securing the whole electrode in the rotating sample holder such that only a small marked corner was exposed to the X-ray beam between the source and detector. This enables multiple ex-situ analyses of the same electrode volume after being exposed to different experimental conditions. After MicroCT analysis, the electrode is removed from the holder and used as a cathode in an acidic microfluidic H$_2$/O$_2$ fuel cell. Three polarization tests are performed, after which the cell is disassembled. The electrode is then hot-pressed at $P = 1 \times 10^3$ lb$_f$ and $T = 125 \pm 10$ °C, followed by MicroCT analysis and electrochemical analysis. This cycle is repeated 3 more times, after applying increasing mechanical compressions ($2 \times 10^3$, $5 \times 10^3$, and $10 \times 10^3$ lb$_f$, respectively). Whereas only one electrode was used to collect the specific dataset reported in Figures 3.3, 3.4, 3.5, and 3.6, we analyzed multiple electrodes in a similar way, which all provided similar results. Figure 3b shows a representative series of through-plane (XZ-plane) images of the same electrode as a function of mechanical compression force. While both the MPL and carbon fiber layer are compressed with increasing force, the majority of the compression is observed, as predicted, in the highly porous carbon fiber layer.

Figure 3.4 shows the effects of hot-pressing on the electrochemical performance of the cathode within the acidic fuel cell. The fuel cell polarization curve (Figure 3.4a) and power density curve (Figure 3.4b) as a function of hot-pressing pressure indicate that the overall fuel cell performance decreases with increasing compression. The corresponding individual electrode polarization curves show that these changes in overall fuel cell performance can be attributed to decreases in cathode performance (Figure 3.4c). As the cathode compresses, the onset potential decreases indicating reduced availability of catalytic sites, and ohmic losses increase indicating reduced reactant transport to the catalyst layer and, to a lesser extent, damaged carbon fiber connectivity in the macroporous layer (higher resistivity). As expected,
the anode performance does not change, because the same, un-compressed anode was used for all experiments.

Next, we related electrochemical performance data to structural characteristics. Figure 3.5a correlates bulk porosity of the cathode carbon fiber layer, obtained via MicroCT imaging, and fuel cell performance (normalized peak power density). Prior to compression, the bulk porosity of the carbon fiber layer is $70.6 \pm 0.9\%$ which is in good agreement with previous reports [38]. The subsequent reductions in porosity of the carbon fiber layer of the cathode (as a result of hot pressing) follow the same trend as the observed decreases in fuel cell performance. Only when going from no compression to a compression of $1 \times 10^3$ lb, the drop fuel cell peak power density appears to be more than the drop observed at higher pressures. At low compression, shifts in MPL and catalyst layer structures are likely responsible for a reduction in electrode performance, which we are presently studying in more detail. Figure 3.5b, 3.5c, and 3.5d show the correlation of fuel cell performance and bulk tortuosity, relative diffusivity, and permeability of the cathode carbon fiber layer, respectively, as a function of compression. As the compression increases, the reduction in porosity of the carbon fiber layer results in increases in tortuosity and in decreases in relative diffusivity as well as permeability.

Next we investigated the effects of hot-pressing on the local physical structure of the cathode (Figure 3.6). By segmenting the carbon fiber layer into 10 normalized regions in both the through-plane (Figure 3.6a) and in-plane (not shown) directions, the effects of compression on local porosity can be analyzed. Figure 3.6b shows the change in through-plane porosity distribution as a function of mechanical compression. The increase in porosity towards the center of the macroporous layer structure indicates that the carbon fiber layer was constructed by pressing two thinner carbon fiber layers via ply molding manufacturing [39]. The porosity drops
at the edges due to the uneven distribution of PTFE throughout the sample including the formation of a PTFE “skin” on outer edges of the backing layer, as has been reported by Fluckiger et al.[33] as well as Fishman et al.[40] and independently observed here (Figure 3.1a2). Initially, when going from no compression to a compression pressure of 1x10^3 lbf, the porosity distribution shifts and reduces slightly as the MPL compacts into the carbon fiber layer (Figure 3.6b). Between compressions of 1×10^3 and 5×10^3 lbf, the porosity distribution remained constant (curves all have the same shape) while the bulk porosity reduces substantially (curves shift down). At compressions greater than 5x10^3 lbf the porosity appears to approach a minimum value which is likely due to the formation of solid stacks of carbon fiber which cannot be compressed further easily, as observed in Figure 3.3b. While the porosity varies significantly in the through-plane directions, the in-plane porosity (both in the YZ- and XY-plane) varies only slightly (Figure 3.6c), with these slight variations probably due to in-plane anisotropy of the carbon paper. Interestingly, both in- and through-plane porosity distributions remains constant independent of the amount of mechanical compression applied.

Based on the through-plane porosity distribution data shown in Figure 3.6b, the corresponding through-plane distribution of physical properties such as tortuosity (Figure 3.6d), relative diffusivity (Figure 3.6e), and permeability (Figure 3.6f) can be calculated as a function of cathode compression using equations 3, 4, and 6, respectively. In general, tortuosity decreases with an increase of porosity whereas relative diffusivity and permeability increase with an increase of porosity. The through-plane heterogeneity of these transport properties observed here is in good agreement with previous reports [24]. The heterogeneity of these physical properties, which significantly affect transport through the electrode, should be considered for future development of multiphase transport models, especially for numerical water management.
models since the heterogeneous pore structure of GDLs is likely to cause liquid water retention in certain regions within GDLs [41].

In summary, the data reported above indicates that fuel cell electrode performance is very sensitive to changes in structure due to compression. In specific, both subtle shifts in structure in the MPL and catalyst layers at low compression pressures (< 1x10^3 lb) and more drastic structural densification of the macroporous carbon fiber layer at moderate compression pressures (≥ 1x10^3 lb) affect electrode performance. Mechanical compression during electrode preparation and within the stack after assembly should be minimized to prevent permanent changes to the electrode structure to avoid loss in performance.

3.5 Conclusions

In this study we demonstrated the utility of MicroCT for the detailed characterization of the 3D architecture of fuel cell electrodes, specifically the structure of the different layers and the interfaces between those layers, in a non-destructive fashion. Comprehensive information about layer thickness, internal architecture, and material distribution can be obtained from 2D radiographic cross-sectional image stacks and 3D tomographic virtual models of the GDE. The quality of these analyses depends on the thoroughness of the protocols used for post-image processing. Here we applied for the first time a filament tracing segmentation method to the characterization of fuel cell electrodes. This method utilizes structural connectivity in combination with grayscale thresholding, whereas existing methods use grayscale thresholding only. The use of structural connectivity information better differentiates fibrous masses within the electrode structure from void space, leading to a more accurate segmentation, and thus more accurate structural information.
Changes in electrochemical performance, as measured \textit{in-situ} using a microfluidic H\textsubscript{2}/O\textsubscript{2} fuel cell, can be correlated directly to changes in physical structure (\textit{i.e.}, porosity), as determined \textit{ex-situ} using MicroCT. We observed that fuel cell electrode performance is very sensitive to changes in structure due to compression. Both subtle shifts in structure in the MPL and catalyst layers at low compression pressures (<\(1\times10^{3}\) lb\textsubscript{f}) and more drastic structural densification of the macroporous carbon fiber layer at moderate compression pressures (\(\geq1\times10^{3}\) lb\textsubscript{f}) affect electrode performance. While hot-pressing is typically used in the assembly of fuel cell electrodes to enhance interlayer bonding, our study shows that mechanical compression during electrode preparation and within the stack after assembly should be minimized to prevent changes to the electrode structure that are detrimental to their electrochemical performance. For the GDL studied here, we concluded that a pressure less than \(1\times10^{3}\) lb\textsubscript{f} should be applied. However, this value is likely to be highly-dependent on the nature of the exact composition of the components (\textit{i.e.}, GDL type, membrane, catalyst layer) used. The MicroCT-based imaging and filament tracing post-processing methods presented here can also be used to probe for changes in the catalyst layer and the MPL (\textit{e.g.}, the effect of PTFE treatment) as a function of processing parameters. More generally, this study shows that systematic investigation of structure-activity relationships as enabled by the capabilities of MicroCT-analytical methods will benefit the rational design of novel highly active and durable electrodes, be it for fuel cells or for other energy conversion applications.
3.6 Figures

**Figure 3.1.** Cross-sectional view (a1) and top view (a2) SEM micrographs of a gas diffusion electrode (GDE) with an air-brushed Pt/C catalyst layer. (b) Setup for MicroCT imaging of a GDL with an air-brushed Pt/C catalyst layer, resulting in an initial reconstruction of the MicroCT data to generate 2D radiographic cross-sectional images in the YZ-plane (b1, through-plane), XZ-plane (b2, in-plane), and XY-plane (also through-plane, not shown) as well as a 3D tomographic virtual model (b3). The colored lines in the 2D images represent the corresponding YZ-plane (red line), XZ-plane (green line), and XY-plane (blue line).
Figure 3.2. (a) A flow-chart of the quantitative analysis procedure used to characterize GDE microstructure. Here, a volume section of 862 µm × 658 µm × 345 µm (x×y×z) of the macroporous layer is analyzed. From the the 2D image stack, each 2D grayscale image is segmented to result in a 2D binary image, which in turn helps to identify and separate voxels as predominantly filled with material (white) from those predominantly void (black). Next a 3D volume is reconstructed from the binary images, showing carbon fibers (green, false color) and void space (black), for subsequent quantitative analysis. (b) A side-by-side comparison of the raw grayscale image (left) and material voxel overlay of the binary images generated with each of the two segmentation methods (right): in red and white material voxels identified using the thresholding and the filament tracing method, respectively. Material voxels identified by both methods are pink.
Figure 3.3. (a) Experimental protocol for investigating the relationship between electrode structure (via MicroCT imaging) and performance (via testing in an acidic fuel cell) as a function of hot-pressing the cathode at different pressures. (b) 2D through-plane radiographic images of the same cathode consecutively hot-pressed at different pressures.
Figure 3.4. (a) Fuel cell polarization curve, (b) power density curve, and (c) corresponding individual electrode polarization curves, of the same cathode after hot-pressing at different pressures. Room temperature data; reactant streams: 10 sccm H₂/O₂; electrolyte: 1.0 M HClO₄ flowing at 0.6 mL/min.
Figure 3.5. Normalized acidic fuel cell peak power density and related (a) bulk porosity, (b) bulk tortuosity, (c) bulk relative diffusivity, and (d) bulk permeability of the cathode as a function of compression.
Figure 3.6. Local in-plane and through-plane porosity distribution and related physical properties of the carbon fiber layer of a cathode hot-pressed at different pressures: (a) Segmentation of the carbon fiber layer into 10 normalized regions in the through-plane direction (XZ-plane, not drawn to scale). (b) Local through-plane porosity distribution as a function of cathode compression (YZ-plane). (c) Comparison of local porosity distribution of a non-hot pressed and hot-pressed ($10^4$ lb$_f$) cathode for all three possible planes. Local through-plane distribution of (d) tortuosity, (e) relative diffusivity, and (f) permeability as a function of cathode compression.
3.7 References


Chapter 4
The Effects of Catalyst Layer Deposition Methodology on Electrode Performance*

4.1 Chapter Overview

The catalyst layer of the cathode is arguably the most critical component of low-temperature fuel cells and carbon dioxide (CO$_2$) electrolysis cells because their performance is typically limited by slow oxygen (O$_2$) and CO$_2$ reduction kinetics. While significant efforts have focused on developing cathode catalysts with improved activity and stability, fewer efforts have focused on engineering the catalyst layer structure to maximize catalyst utilization and overall electrode and system performance. Here, we study the performance of cathodes for O$_2$ reduction and CO$_2$ reduction as a function of three common catalyst layer preparation methods: hand-painting, air-brushing, and screen-printing. We employed *ex-situ* X-ray micro-computed tomography (MicroCT) to visualize the catalyst layer structure and established data processing procedures to quantify catalyst uniformity. By coupling structural analysis with *in-situ* electrochemical characterization, we directly correlate variation in catalyst layer morphology to electrode performance. MicroCT and SEM analyses indicate that, as expected, more uniform catalyst distribution and less particle agglomeration, lead to better performance. Most importantly, the analyses reported here allow for the observed differences over a large geometric volume as a function of preparation methods to be quantified and explained for the first time. Depositing catalyst layers via a fully-automated air-brushing method led to a 56% improvement in fuel cell performance and a significant reduction in electrode-to-electrode variability. Furthermore, air-

* This chapter has been adapted from the following publications:
brushing catalyst layers for CO₂ reduction led to a 3-fold increase in partial CO current density and enhanced product selectivity (94% CO) at similar cathode potential but a 10-fold decrease in catalyst loading as compared to previous reports.

4.2. Introduction

Electrodes play a vital role in all devices based on heterogeneous electrochemical reactions for energy conversion, energy storage, and chemical synthesis. The performance and durability of these devices is largely determined by the processes that occur at the catalyst layer-electrolyte interface. For example, the widespread commercialization of polymer-electrolyte membrane fuel cells (PEMFCs) has been limited by the cathodic oxygen reduction reaction (ORR) which requires high loadings of expensive platinum (Pt) catalyst to achieve performance benchmarks [1]. Furthermore, the development of economically-feasible electrochemical reactors to convert carbon dioxide (CO₂) to value-added compounds requires the advent of catalytic material with high activity and selectivity [2]. While significant research efforts have focused on catalyst discovery and development, considerably fewer efforts have focused on the study of these catalysts after immobilization on gas diffusion electrodes (GDEs). Developing an improved understanding of how different catalyst layer deposition methods impact the electrode performance is often key to enhancing overall performance of the electrochemical process.

Micro-computed X-ray tomography (MicroCT) is an emerging analytical technique that measures variations in X-ray attenuation upon rotating samples, to generate three-dimensional (3D) maps of samples with high spatial resolution (1-10 μm) in a non-destructive fashion over large geometric volumes (on the order of 1 mm³) [3]. Furthermore, variations in X-ray absorption enable identification of different phases/elements, and their distribution, within the sample. Typical GDEs, used for fuel cell and CO₂ electroreduction applications, consist of a 5-
20 μm thick catalyst layer deposited on a 200-500 μm thick gas diffusion layer (GDL). Though quite thin, the catalyst layers primarily consist of clusters of metallic particles that exhibit high X-ray absorption, enabling identification of small amounts of materials over a broad geometric area (1 mm × 1 mm). While MicroCT enables visualization of catalyst layer structure (down to a voxel size of 1 μm³) and uniformity across the carbonaceous GDL surface, analysis of the nanoscale materials within the catalyst layer requires the use of complimentary techniques with higher spatial resolution such as SEM, TEM, or nano-computed X-ray tomography (NanoCT). To date, most MicroCT investigations of materials for energy conversion have focused on the structural analysis of porous electrode architectures with a goal of providing more accurate parameters for numerical models [4-6]. Previously, we have developed a method of coupling the physical properties of porous electrodes to their electrochemical performance using ex-situ MicroCT measurements and in-situ single electrode measurements using a microfluidic H₂/O₂ fuel cell as an electro-analytical platform [7]. In addition to highlighting the adverse effect of excessive compression on the porous GDEs, we observed non-uniform distribution in the hand-painted catalyst layer which was not visible to the naked eye or to surface SEM characterization. Building on this earlier work, we now employ MicroCT to characterize catalyst layer structure and uniformity as a function of the catalyst layer deposition methodology. By coupling physical analysis with in-situ electrochemical measurements, using a microfluidic platform, we can directly correlate variation in catalyst layer morphology and electrode performance. To perform comparative analysis of cathode performance as a function of catalyst layer deposition methodology requires analytical platforms that are capable of isolating individual electrode (cathode and anode) performance such that any changes in overall cell performance can unambiguously be attributed to differences in cathode performance when the same anode is used.
for all experiments (identical anode polarizations). Deconvoluting individual electrode performance to obtain single electrode polarizations, however, is difficult in conventional membrane-based cells. To this end, we have developed a microfluidic \( \text{H}_2/\text{O}_2 \) fuel cell with a flowing electrolyte stream instead of a stationary membrane as an electro-analytical platform (Figure 1a) [8,9]. The flowing electrolyte (i) minimizes adverse fuel cell system limitations, \( i.e., \) water management, (ii) enables independent control of electrolyte parameters (\( i.e., \) pH, composition), and, more importantly, (iii) allows for \textit{in-situ} studies of single electrode performance via an external reference electrode. Here, we use this platform to systematically probe the key structural factors of the catalyst layer that govern the cathode performance within an operating fuel cell.

A variety of catalyst layer deposition methods has been reported to prepare electrodes for fuel cell and water electrolysis reactions. Catalyst ink-based methods including decal transfer [10], hand painting [11,12], spray deposition (\( e.g., \) air-brush [13-15], ultrasonic-spray [16], electro-spray [17]), and screen printing [18] processes are commonly used. Moreover, electrodeposition [19], sputter deposition [20], and dual ion-beam assisted deposition [21] (particularly for catalyst loadings down to 0.04 mg/cm\(^2\)) have also been studied. Recently Saha \textit{et al.} provided an excellent overview of the advantages and disadvantages of those deposition methods [21]. These focused efforts have resulted in loadings of ca. 0.4 mg Pt/cm\(^2\) for state-of-the-art fuel cell cathodes, compared to 4-10 mg/cm\(^2\) in the first generation of PEMFCs in the 1990s [1,22]. Though this represents a significant improvement, an approximately 4-fold further reduction is needed to meet the United States Department of Energy 2017 targets for large-scale automotive applications (\( i.e., \) a total (anode + cathode) loading of 0.125 mg Pt/cm\(^2\)) [23].
To date no efforts have focused on studying the effects of catalyst layer deposition methodology on performance of cathodes for CO₂ reduction. Silver (Ag) is known to be a very selective catalyst for electroreduction of CO₂ to CO over H₂ formation [24]. When operating the CO₂ electrolyzer with cathode materials that favor syngas production (e.g., Ag, Au, Zn [24]), optimizing the cell for CO production is likely more energy-efficient because H₂ evolution has a less negative theoretical reduction potential than CO evolution, and thus other technologies such as water electrolyzers may be more efficient for H₂ production. Typical energy efficiencies for commercial water electrolyzers are in the 56-73% range, with alkaline electrolyzers running at 110-300 mA/cm² and acidic PEM electrolyzers running at 800-1600 mA/cm² [2]. Hori et al. extensively studied the CO₂ reduction reaction on planar Ag electrodes (a thin Ag layer electrodeposited on a Cu substrate), and reported Faradaic efficiencies for CO, H₂, and HCOO⁻ of 81.5%, 12.4%, and 0.8%, respectively, at a current density of 5 mA/cm² in 0.1 M KHCO₃ using an H-type glass cell [24]. Such planar Ag electrodes suffer from low CO₂ concentration at the electrode surface due to the limited CO₂ solubility in aqueous electrolytes [25]. Yano et al. proposed the use of a Ag mesh as the cathode for CO₂ reduction in a modified H cell in which gaseous CO₂ was effectively delivered to the electrode-electrolyte interface from a gas chamber [26]. The Ag mesh allows for the reaction to take place at the three-phase gas/solid/liquid interface, which is expected to reduce CO₂ solubility issues as well as mass-transport limitations in aqueous electrolytes. They reported Faradaic efficiencies for CO and H₂ of ~90% and ~10%, respectively, at a cathode potential of -2 V vs. Ag/AgCl. Unfortunately, no current density data was provided, so it is unclear to what extent the three-phase gas/solid/liquid interface enhances performance. More recently, Delacourt et al. applied Ag catalyst inks on gas diffusion layers (GDLs) via hand-painting or spraying to generate cathodes with a Ag loading of 8-10 mg/cm² in
an ion-exchange membrane-based CO₂ electrolysis cell (similar to PEMFC configuration) [27]. They reported Faradaic efficiencies for CO and H₂ of 82% and 10%, respectively, when operating the cell at 20 mA/cm², at a cathode potential of -1.55 V vs. SCE (ca. -1.51 V vs. Ag/AgCl). While this last study shows that GDEs have the potential to increase the current density, to date very few efforts have focused on improving cathode performance for CO₂ reduction, let alone studying the effects of catalyst layer deposition methodology on performance.

Here, we investigate electrodes for two key reactions, the ORR in acidic low-temperature fuel cells (Figure 4.1a) and the CO₂ reduction reaction in CO₂ electrolysis cells (Figure 4.1b). The sluggish kinetics associated with both reactions lead to poor performance in actual systems limiting the competitiveness of both technologies. Developing a better understanding of how the method of deposition impacts catalyst layer structure and performance, and more importantly, quantifying the observed differences in catalyst layer structure in 3D and over a large geometric area, will enable electrode optimization, including improved catalyst utilization, and may provide broadly applicable guidelines for other processes relying on electrocatalytic conversion.

4.3 Experimental

4.3.1 Preparation of GDEs for H₂/O₂ Fuel Cells

*Hand-painted GDEs:* ELAT 1400 carbon cloth (NuVant Systems Inc.) was used as the GDL in this study. This GDL consists of a 5 wt% polytetrafluoroethylene (PTFE)-treated carbon cloth with a teflonized microporous layer on one side. Catalyst inks were prepared by mixing 4.71 mg Pt/C catalyst (50 wt% Pt, E-Tek) and 3.60 μL Nafion solution (5 wt%, Solution Technology, 30:1 catalyst-to-Nafion ratio), and adding the carrier solvents: 200 μL of Millipore water (18.2 MΩ), and 200 μL of isopropyl alcohol (Sigma-Aldrich). All catalyst inks were sonicated (Vibra-Cell ultrasonic processor, Sonics & Materials, Inc.) for 20 minutes to ensure uniform mixing and
were hand-painted using a paintbrush on the teflonized carbon side of the GDL to create a GDE covered with catalyst over a geometric area of 4 cm$^2$. Note that the mass of catalysts and Nafion weighed in the catalyst inks has accounted in 15% weight loss during the painting process. Thus the actual catalyst loading was verified to be 1.0 mg Pt/C/cm$^2$ (50 wt% Pt).

*Air-brushed GDEs*: ELAT 1400 carbon cloth was used as the GDL. Catalyst inks were prepared by mixing 6.67 mg Pt/C catalyst and 5.11 μL Nafion solution, and adding the carrier solvents: 200 μL of Millipore water, and 200 μL of isopropyl alcohol. All catalyst inks were sonicated for 20 minutes to ensure uniform mixing and were air-brushed using the automated air-brushing deposition machine (*Figure 4.2*) on the teflonized carbon side of the GDL to create a GDE covered with catalyst over a geometric area of 4 cm$^2$. More details of the airbrushing deposition process are described in the *Supporting Information*. Note that the mass of catalysts and Nafion weighed in the catalyst inks has accounted in 40% weight loss during the airbrushing process. Thus the actual catalyst loading was verified to be 1.0 mg Pt/C/cm$^2$ (50 wt% Pt).

*Screen-printed GDEs*: The screen-printed cathodes were purchased from a commercial vendor (Fuel Cell Store, USA) and are carbon cloth-based GDEs with a catalyst loading of 1.0 mg Pt/C/cm$^2$ (50 wt% Pt).

### 4.3.2 Preparation of GDEs for CO$_2$ Electrolysis Cells

Sigracet 35 BC GDLs (Ion Power, Inc.) were used as the GDL in this study. This GDL consists of a 5 wt% polytetrafluoroethylene (PTFE)-treated carbon paper with a teflonized microporous layer on one side. The cathodes were either hand-painted or air-brushed whereas the anode was hand-painted. For the hand-painted cathodes, catalyst inks were prepared by mixing 2.09 mg Ag catalyst (unsupported Ag nanoparticles, < 100 nm particle size, 99.5% trace metals basis, Sigma-Aldrich) and 1.60 μL Nafion solution, and adding the carrier solvents: 200 μL of Millipore water,
and 200 μL of isopropyl alcohol. For the air-brushed cathodes, catalyst inks were prepared by mixing 2.42 mg Ag catalyst and 1.85 μL Nafion solution, and adding the carrier solvents: 200 μL of Millipore water, and 200 μL of isopropyl alcohol. For the hand-painted anodes, catalyst inks were prepared by mixing 10 mg Pt black (Alfa Aesar) and 6.9 μL Nafion solution, and adding the carrier solvents: 400 μL of Millipore water, and 400 μL of isopropyl alcohol. Similar to the fuel cell electrodes, the weight loss was accounted and found to be 28%, 38%, and 15% for the hand-painted cathodes, air-brushed cathodes, and hand-painted anodes, respectively. All inks were sonicated for 20 minutes to ensure uniform mixing and were either hand-painted using a paintbrush or air-brushed using the automated air-brushing deposition machine on the teflonized carbon side of the GDL to create a GDE covered with catalyst over a geometric area of 2 cm². Thus, the cathodes consisted of 0.75 mg Ag/cm². The same anode that was used for all measurements consisted of 4.25 mg/cm² Pt black.

4.3.3 Cell Assembly and Electrochemical Testing

\textit{H}_2/\textit{O}_2 fuel cell: The microfluidic \textit{H}_2/\textit{O}_2 fuel cell was used in this study and has been described previously (Figure 4.1a) [9,28,29]. In short, two GDEs, an anode and a cathode, were placed on opposite sides of a 0.15-cm thick polycarbonate sheet with the 3-cm long and 0.33-cm wide window such that the catalyst layers interfaced with the flowing liquid electrolyte. The geometric surface area used to calculate current and power density is 1 cm². Two graphite current collectors with access windows and two precision-machined polycarbonate gas flow chambers were placed outside the GDEs. The multilayer assembly was held together using binder clips. Fuel cell experiments were conducted using a potentiostat (Autolab PGSTAT-302N, EcoChemie) at room temperature and ambient pressure. \textit{H}_2 and \textit{O}_2 gas (laboratory grade, S.J. Smith) are each fed at a flow rate of 10 sccm. Electrolyte flow rate was 0.6 mL/min.
controlled by a syringe pump (2200 PHD, Harvard Apparatus). 1.0 M perchloric acid (HClO$_4$, Sigma-Aldrich, 99.999%) in Millipore water was used as aqueous electrolyte. After exiting the fuel cell, the electrolyte stream travels through a plastic tube and into a collection beaker which contains a reference electrode (Ag/AgCl in saturated NaCl, BaSi). The tubing serves to ionically connect the reference electrode to the anode and the cathode. No ohmic losses are observed along the length of the tubing. Multimeters, in voltmeter mode, are connected to the reference electrode and each individual electrode to enable single electrode polarization measurements.

**CO$_2$ electrolysis cell:** In short, two catalyst-coated GDEs, an anode and a cathode, were placed on opposite sides of a 0.15-cm thick poly(methyl methacrylate) (PMMA) sheet with 0.5-cm wide by 2.0-cm long channel such that the catalyst layer interfaced with the flowing liquid electrolyte. The geometric surface area used to calculate current density is 1 cm$^2$. Two aluminum current collectors with access windows were placed outside the two GDEs. On the cathode side an aluminum gas flow chamber supplied CO$_2$ while the anode was open to the atmosphere for O$_2$ to escape. The assembly was held together with 4 bolts with Teflon washers to maintain electric isolation between electrodes. CO$_2$ electrolysis experiments were conducted using a potentiostat at room temperature and ambient pressure. CO$_2$ gas (S.J. Smith, 100%) was fed at a rate of 7 sccm. Electrolyte flow rate was 0.5 mL/min controlled by a syringe pump. 1.0 M potassium chloride (KCl, Sigma-Aldrich, $\geq$ 99.0% pure) in Millipore water was used as aqueous electrolyte. Electrolysis cell polarization curves were obtained by steady-state chronoamperometric measurements at which time gaseous products, as well as unreacted CO$_2$, were collected and injected into a gas chromatograph (Trace GC, ThermoFisher Scientific) equipped with a thermal conductivity detector for quantitative determination of product composition. As with the fuel cell configuration, individual anode and cathode polarization curves were independently
measured using an external Ag/AgCl reference electrode which was ionically connected to the electrolyzer.

The Faradaic efficiency ($FE_k$) of a gaseous product $k$ was calculated using the following equation:

$$FE_k = \frac{n_k F x_k F_m}{I}$$

Where $n_k$ is the number of electrons exchanged ($n_k = 2$ for reduction of CO$_2$ to CO), $F$ the Faraday’s constant ($F = 96485$ C/mol), $x_k$ the mole fraction of the gaseous product $k$ in the gaseous mixture (also equal to the volume fraction if gases are assumed to be ideal), $F_m$ the molar flow rate (mol/s), and $I$ the total current (A). Specifically, we calculated $x_k$ and $F_m$ using the following equations:

$$x_k = \frac{F_{v,CO}}{F_{v,CO} + F_{v,CO_2}} = \frac{F_{v,CO} / F_{v,CO_2}}{1 + F_{v,CO} / F_{v,CO_2}}$$

$$F_m = \frac{p F_v}{RT}$$

Where $F_{v,CO}$ and $F_{v,CO_2}$ are the volumetric flow rates (cm$^3$/s) of CO and CO$_2$, respectively. $P$ is the atmospheric pressure ($P = 1$ atm), $R$ the gas constant ($R = 82.06$ cm$^3$ atm K$^{-1}$ mol$^{-1}$), and $T$ the temperature ($T = 293$ K).

The energetic efficiency ($EE_k$) for the gaseous product $k$ was calculated using the following equation:

$$EE_k(\%) = \frac{E^o}{V_{cell}} \times FE_k(\%)$$
Where $E^\circ$ is the equilibrium cell potential ($E^\circ = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} = -0.10$ V - 1.23 V = -1.33 V for CO$_2$ reduction to CO and $E^\circ = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} = 0$ V - 1.23 V = -1.23 V for H$_2$ evolution), $V_{cell}$ is the applied cell potential, and $FE_k$ is the Faradaic efficiency of the gaseous product $k$. The overall cell energetic efficiency is the sum of the energetic efficiencies for CO and H$_2$.

### 4.3.4 MicroCT and SEM Imaging of GDEs

*Acquisition and Reconstruction of MicroCT Data:* We used the same acquisition and reconstruction procedures reported in our prior work [7]. In short, the whole GDE was clamped in a rotating sample holder and a corner was exposed to the X-ray beam field. During MicroCT imaging (Micro-XCT 400, Xradia), the sample was scanned using an X-ray source at 40 kV and 200 μA, and 745 projections were collected as the sample was rotated stepwise over 180° with a 10 second exposure time for each projection. The projection images were then processed to reconstruct 2D radiographic cross-sectional image stacks and 3D tomographic virtual models of the GDE. The initial reconstruction of MicroCT data was conducted using the *TXM Reconstructor* reconstruction software (Xradia), which accompanies the MicroCT hardware. The distances of the sample to the X-ray source (76 mm) and the X-ray detector (28 mm) resulted in a voxel (volume pixel) size of 1 μm$^3$. The field of view (FOV) was approximately 1000 μm × 1000 μm.

*Segmentation and Analytical Methodologies:* The *Amira* visualization software package (Version 5.3, Visage Imaging) was used to quantitatively analyze the catalyst layer structure. First, the 2D cross-sectional image stack was cropped to a discrete volume that is of analytical interest, here a 910 μm × 965 μm × 60 μm section of the catalyst layer. The analytical volume is selected based on criteria that the analytical volume is the majority of the total image volume of the catalyst layer (925 μm × 965 μm × 60 μm). Second, each 2D grayscale image (*e.g.*, Figure 3a1-a3) is
segmented to a 2D binary image to help identify and separate voxels predominantly filled with materials from those that are predominantly void. As with our prior work, segmentation was performed using the filament tracing method, available in Amira v5.3 visualization software [7]. After segmentation, a 3D reconstructed volume of these binary images was rendered for subsequent quantitative analysis (Figure 3b1-b3). We measured the uniformity of catalyst distribution by segmenting each of the catalyst layers into 25 normalized volume elements (each 182 μm × 193 μm × 60 μm). The catalyst fraction of the total amount of catalyst in each volume element was measured and is defined as: catalyst fraction = (catalyst_{vox, local}) / (catalyst_{vox, total}), where catalyst_{vox, local} is the number of catalyst voxels in each volume element and catalyst_{vox, total} is the number of catalyst voxels in the entire analytical volume of the catalyst layer. Catalyst layer thickness measurements were performed using a modified version of a previously reported protocol [28]. In detail, to determine the average layer thickness (Z-direction) of each sample, the through-plane (YZ-plane) cross-sectional images were analyzed. The thickness (Y-direction) of each of these images is one pixel which corresponds to the image resolution (1 μm). Each layer thickness measurement was taken across a 2D YZ-plane grid with 8 evenly spaced points. Same procedure was repeated for eight evenly spaced 2D YZ-planes along the X-direction, so thickness measurements were conducted on these 64 data points across each catalyst layer. Cross-sectional SEM imaging via nitrogen-cracking was employed to verify the accuracy of the thickness measurements.

**SEM Imaging of GDEs:** Morphology of catalyst particles within the catalyst layer of each sample was characterized using SEM (Philips XL30 ESEM-FEG). Images were acquired using an acceleration voltage of 7.5 kV, a spot size of 3.0 nm, and a working distance of 5.0 mm, resulting in a magnification of 100,000.
4.4 Results and Discussion

4.4.1 Linking Structure with Performance of Fuel Cell Cathodes

Effect of Deposition Method

Combined ex-situ MicroCT imaging and in-situ fuel cell analysis can be used to probe the impact of the catalyst layer structure and distribution to its electrochemical performance. To demonstrate the utility of such investigations, we studied the effects of three catalyst layer deposition methodologies (hand painting, air brushing, and screen printing) on fuel cell cathode performance in an acidic H₂/O₂ fuel cell (Figure 4.1a). Specifically, we studied how the differences in structure of the catalyst layers generated by each technique impact electrode performance. Hand painting using a paint brush is often used because it does not require sophisticated apparatus and procedures, and is an efficient way to make small batches of electrodes. Hwang et al. reported that air-brushing by hand results in mostly uniform catalyst layers provided the catalyst ink is not too concentrated [18]. For example, in this work we avoided agglomerate formation in the catalyst layer (which occurs if the concentration is too high) by dispersing 4-7 mg of catalyst in 400 μL of solvent. Koraishy et al. have shown that automated airbrushing leads to more uniform catalyst layers and better performance by studying the effects of a number of parameters on the performance of direct methanol fuel cell cathodes [13]. Screen printing can lead to catalyst layers with cracks due to slow evaporation rate of solvent from the catalyst ink slurry [18], but it is still used for commercial fabrication of electrodes due to good electrode reproducibility [30]. All of these prior studies used only SEM to characterize the catalyst layer structure for the different deposition methods. Here we will employ MicroCT in combination with SEM to visualize the structure of catalyst layers in 3D and over multiple length scales, ranging from several nanometers to the millimeter scale. To date,
such information has typically been obtained by analyzing the sample with SEM after sequential ion milling procedures (i.e., focused ion-beam-scanning electron microscopy, FIB-SEM) [31-36], or more recently by the use of NanoCT [32,37], which in some cases is combined with TEM [38]. Unfortunately, the utility of FIB-SEM is limited to small fields of view, 10 μm × 10 μm at most, and inherently involves destruction of the sample. The utility of NanoCT is limited to evaluating sub-millimeter size samples, so for the applications studied here a small section needs to be cut out of an electrode, which is non-trivial with respect to avoiding sample damage.

Here we prepared electrodes via automated airbrushing (Figure 4.2) and hand painting. The Experimental section describes both methods in more detail. For comparison, commercial screen-printed electrodes were also studied. To unambiguously compare the performance of these three catalyst layers generated by different deposition methods, these two in-house prepared electrodes and commercial screen-printed electrode consisted of identical catalyst loadings (1.0 mg Pt/C/cm² with 50 wt% Pt so 0.5 mg Pt/cm²) on the same GDL material (ELAT carbon cloth). We ensured the catalyst loading of each electrode generated by different catalyst deposition methods were identical so any changes in the ECSA can only be attributed to differences in catalyst layer deposition methods. Moreover, we chose the catalyst loading of 0.5 mg Pt/cm² to be consistent with the state-of-the-art cathode catalyst loading (0.4 mg Pt/cm²) [1,22] and, hopefully, to provide insights, using realistic loadings, on how optimizing catalyst layer structure can help achieve DOE 2017 targets (i.e., 4-fold further reduction in Pt loading) for large-scale automotive applications without sacrificing performance or durability [23]. The same anode that was prepared via air brushing with a loading of 1.0 mg Pt/C/cm² (50 wt% Pt) was used for all experiments.
Figures 4.3 shows the electrochemical performance of fuel cells operated with each cathode as a function of catalyst layer deposition. Figure 4.3a shows representative fuel cell polarization and power density curves of an acidic microfluidic \( \text{H}_2/\text{O}_2 \) fuel cell operated with an air-brushed (AB), hand-painted (HP), and screen-printed (SP) cathode while using the same anode for all experiments. These electrodes exhibited peak power densities of 167.1, 113.1, and 145.0 mW/cm\(^2\), respectively. The corresponding individual electrode polarization curves confirm that these differences in overall fuel cell performance indeed can be attributed to differences in cathode performance (Figure 4.3b). Furthermore, these cathode polarization curves show that the shifts in performance can be attributed to differences in kinetic losses (AB < SP < HP) and ohmic losses (AB ≈ SP < HP). Note that the larger than expected anode polarization is due to ohmic losses related to the relatively large electrolyte thickness (0.15 cm) in the microfluidic platform as compared to Nafion-based PEMFCs (e.g., ca. 50 µm for Nafion 212). While the increase cell resistance can reduce power performance, it does not hinder our ability to perform comparative analyses on the different cathodes.

Figure 4.4 shows the structural characterization of each cathode as a function of catalyst layer deposition method. After conversion of the raw MicroCT data into 2D radiographic cross-sectional image stacks and 3D tomographic virtual models of the GDE, detailed information regarding layer thickness, internal architecture, and material distribution is obtained for each of the three cathodes. In particular, Figures 4.4a1-a3 show through-plane (YZ-plane) 2D radiographic images of the three GDEs with different catalyst layers. In these images, the catalyst layer, the microporous layer (MPL), and the macroporous carbon fiber layer can be distinguished. We observed that the catalyst layer thickness of the HP cathode varies significantly (8 ± 6 µm excluding cracks in the MPL, but 23 to 49 µm thick in areas with cracks),
compared to the AB (8 ± 2 μm) and SP cathodes (7 ± 2 μm). Only the HP cathode shows catalyst distribution in the cracks from the MPL, which is probably due to high liquid content of the catalyst ink when it is deposited via paintbrush, allowing the catalyst particles to seep into cracks. The thickness measurements were performed using a modified version of a previously-reported protocol [28], which is described in the Experimental section. In addition, the 3D tomographic GDE virtual models (Figure 4.4b1-b3) visualizes the internal architecture and organization in false color, and indicates that the uniformity of catalyst distribution and layer smoothness critically determine electrode performance. Our another previously-reported segmentation (i.e., filament tracing method) and analytical methodologies were used to post-process the 2D radiographic cross-sectional images to extract critical structural parameters [7]. We quantified the uniformity of catalyst distribution (Figure 4.4c1-c3) to better understand the extent to which changes in catalyst microstructure correlates to changes in electrochemical performance. Figure 4.4c1-c3 show that the HP cathode in particular has a non-uniform catalyst distribution, resulting in reduced performance in comparison with the AB and SP cathodes. Each of the catalyst layers was segmented into 25 normalized volume elements (each 182 μm × 193 μm × 60 μm). The percentage provided in each volume element in Figure 4.4c1-c3 indicates the catalyst fraction of the total amount of catalyst, information that is obtained by analysis of the 3D tomographic virtual model. The catalyst distribution of the HP, AB, and SP cathodes ranges from 0.88 to 6.54% (σ = 1.94%), from 3.22 to 4.76% (σ = 0.41%), and from 3.19 to 4.91% (σ = 0.53%), respectively. Clearly the catalyst distribution is more uniform (smaller standard deviations) in the AB and SP cathodes than in the HP cathode.

We also studied the extent of catalyst agglomeration using SEM imaging. The presence of agglomerates is much more profound in the HP catalyst layer than the AB catalyst layer (Figure
4.4d1-d2), so the AB catalyst layer likely has a larger electrochemically-active surface area (ECSA) than the HP catalyst layer. This hypothesis is verified by the ECSA measurements, as described in more detail in the Supporting Information. The ECSA of the HP, AB, and SP cathodes are 9, 16, and 10 m²/gPt respectively, which is in agreement with the previously-reported values [1]. We ensured the catalyst loading of each electrode generated by different catalyst deposition methods were identical so any changes in the ECSA can only be attributed to differences in catalyst layer deposition methods. This likely happens because the agglomerates are trapped and grow in the paintbrush bristles and when enough pressure is applied or the paintbrush is wet enough these agglomerates are deposited as solid chunks with limited accessibility in the HP catalyst layer. In addition to reducing ECSA (due to inaccessible catalyst material) and thus catalyst utilization, the agglomerates also result in larger ohmic or mass transport losses (due to limited accessibility to some portions of the agglomerates) and thus reducing catalyst layer effectiveness. The screen-printed cathode was a commercial product in which the catalyst layer is coated with a thin Nafion film, which prevented direct imaging of the catalyst particles via SEM (Figure 4.4d3).

After completing electrochemical analysis (Figure 4.3) and structural characterization (Figure 4.4) of the electrodes, (some of) the differences in performance can be linked to structural differences. The increased kinetic losses of hand-painted cathode, as compared to the air-brushed and screen-printed cathodes (so kinetic losses: AB < SP < HP), can be attributed to reduced electrochemically-active surface area due to uneven catalyst distribution where agglomerate formation can limit catalyst utilization (inaccessible catalyst material). Likewise, the reduced ohmic losses associated with the air-brushed and screen-printed cathodes, as compared to the hand-painted cathode (so ohmic losses: AB ≈ SP < HP), can be attributed to
improved catalyst layer uniformity (thickness) and material distribution. The agglomerates in
the HP catalyst layer lead to larger ohmic losses due to limited accessibility to catalytic materials
(not all the agglomerate is inaccessible). These results not only show that hand painting is a non-
optimal deposition technique but also explain the causes of this poor electrode performance via
combined electrochemical and imaging analysis.

**Performance Reproducibility of Electrodes**

To effectively develop improved ORR catalysts for PEMFCs, a catalyst layer deposition
method that can apply various catalysts on GDLs in a uniform and reproducible fashion is
needed to assure that the activity of newly proposed catalysts can be compared unambiguously to
known catalysts. Unfortunately, this is not always the case. Even for state-of-the-art Pt catalysts,
reported ORR activities can vary by an order of magnitude in fuel cell testing under identical
operating conditions.\[^1\] This ambiguity in catalyst evaluation hampers progress in catalyst
research. Electrode manufacturing reproducibility, which in turn impacts reported performance,
has not been discussed often in fuel cell literature, likely due to the difficulty of deconvoluting
individual electrode performance in conventional membrane-based fuel cells. Microfluidic fuel
cells are well-suited for such reproducibility measurements because the easy integration of an
external reference electrode enables characterization of individual electrode performance within
an operating cell [8,9]. Here we use this approach to investigate the influence of the HP and AB
catalyst layer deposition methods on electrode-to-electrode reproducibility with respect to
performance (*Figure 4.5*). Each deposition process was repeated four times to yield four air-
brushed cathodes (AB1-4) and four hand-painted cathodes (HP1-4). All cathodes have the same
actual catalyst loading (*i.e.*, 1.0 mg Pt/C/cm², 50 wt% Pt). Curve-fitting and statistical analyses
are performed on each data set and are described in detail in the Supporting Information. Figure 4.5a shows average power density curves along with standard deviations for fuel cells operated with each of the sets of AB and HP cathodes. The AB and HP cathodes exhibited average peak powder densities of 167.0 ± 5.8 and 107.1 ± 9.8 mW/cm², respectively, which were confirmed to be statistically significant differences[39]. Similarly, we observed drastic improvements in reproducibility with respect to peak power density: only 3.4% variation in peak power density when using the AB cathodes compared to 9.2% variation for the HP cathodes.

Comparison of the individual electrode polarization curves (Figure 4.5b) further confirms the above observations, namely, that the reduced variability in the overall cell performance is due to the improved AB cathode reproducibility. Differences in electrode performance mostly appear in the ohmic regime, suggesting that the thickness of the hand-painted catalyst layers varies more substantially than that of the air-brushed catalyst layers, in agreement with the MicroCT data (Figures 4.4a1-a2 and 4.4b1-b2).

In summary, employing a fully-automated air-brushing catalyst layer deposition method led to enhancement in electrode performance of up to 56% (based on average power densities), as well as drastic improvements in electrode-to-electrode (and cell-to-cell) reproducibility (≤ 3.4% variation in performance). Based on prior work, the finding that air-brushed cathodes outperform hand-painted cathodes is expected [13,18]. Furthermore, Zils et al. studied the structure of the catalyst layers generated by the layer-by-layer (LbL) fast spray coating and air-brushing (by hand) methods using FIB/SEM [33]. They quantified the porosity, pore size distribution, and tortuosity of the catalyst layer over a very small geometric volume (6.2 μm × 2.4 μm × 1.6 μm) because the strength of FIB/SEM is to probe nanometer-scale catalyst layer morphology. In contrast, we employed MicroCT to analyze a large geometric volume (925 μm ×
965 μm × 60 μm) in order to quantify catalyst distribution and layer thickness. Thus, to our knowledge our results reported above is the first quantitative analysis of how different catalyst deposition methods lead to different catalyst layer structures over a large geometric volume, which in turn lead to substantial differences in performance and reproducibility.

4.4.2 Linking Structure with Performance of CO2 Electrolysis Cathodes

Here we immobilized Ag nanoparticles GDEs via hand painting and automated air brushing, and, like above, we studied how different catalyst layer deposition methods impact electrode performance with respect to overall current density, partial current density of the desired (CO) and the less desired product (H₂), and product selectivity. Furthermore, like above for the fuel cell cathodes, we utilize ex-situ MicroCT imaging and in-situ electrochemical reactor analysis to study how the differences in catalyst layer structure impacts electrode performance. Similar to the in-situ fuel cell cathode studies, a microfluidic CO₂ electrochemical reactor with an external reference electrode was employed to characterize the performance of individual electrodes within an operating cell (Figure 4.1b) [40]. Unlike the H₂/O₂ fuel cell where the H₂ oxidation reaction is very fast, here both electrode reactions, CO₂ reduction and H₂O oxidation, are sluggish and contribute to the overall cell polarization. Thus, variations in the H₂O oxidation electrode polarization on the anode (e.g., electrode misalignment, bubble formation, flooding) can have a significant impact on the overall cell performance and the CO and H₂ production rates. Consequently, we report the results of the electrochemical analysis with respect to both overall applied cell potential and cathode potential versus the external Ag/AgCl reference electrode. The overall cell performance data can be used to determine engineering metrics such as reactor energetic efficiency whereas the single electrode polarization data provides useful information, which can be compared to previously-reported three-electrode cell or H-type cell data. Figure
4.6 and 4.7 show the performance characteristics of the electrochemical reactor operated with an air-brushed (AB) and hand-painted (HP) cathode. As with the fuel cell cathodes, both electrodes consisted of identical catalyst loadings (0.75 mg Ag/cm², unsupported Ag nanoparticles) on the same GDL material (Sigracet 35 BC).

The current densities measured for the electrochemical reactors with the AB and HP cathodes, respectively, are very similar (Figure 4.6a), suggesting that the catalyst layer deposition method does not influence overall current density. The negligible differences in cathode performances further confirm this (Figure 4.6b). Also, the anode polarization curves are nearly identical; not surprising because the same anode was used for all experiments. We also analyzed the product yield (Figure 4.7). The measured partial current densities for CO (Figure 4.7a) and H₂ formation (Figure 4.7b) indicate that the cell with the AB cathode produced a larger amount of CO (desired reaction) than H₂ (undesired reaction). Consequently, the Faradaic efficiencies (Figure 4.7c), the fractions of the current that goes to the CO formation reaction and the competing H₂ evolution reaction, show that the AB cathode produces more CO and less H₂ than the HP cathode. In detail, the AB cathode generates 87 ± 2%, 95 ± 5%, 94 ± 2% CO at more negative cathode potentials (-1.38 V, -1.56 V, and -1.68 V vs. AgAgCl, respectively), whereas the HP cathode makes 79 ± 9%, 83 ± 14%, 82 ± 10% at more negative cathode potentials (-1.38 V, -1.56 V, and -1.72 V vs. Ag/AgCl, respectively). Furthermore, the cell energetic efficiencies, the fraction of energy supplied to the reactor that is contained in the desired product stream, are 46 ± 1% and 42 ± 3% with the AB cathode and the HP cathode, respectively at a cathode potential of -1.38 V vs. Ag/AgCl (-2.5 V cell potential). More details in energetic efficiency calculations are described in the Experimental section. Note that, although this reactor is intended for electroanalysis rather than performance, the observed current densities,
efficiencies, and product distribution compare favorably to previously reported results [27,41,42] despite the 10-fold lower Ag loading. Dufek et al. sought to overcome mass-transport limitations, which in turn, lead to less favorable product distribution at high current densities, by increasing reactor temperature and pressure [41,42]. In contrast, our results show that engineering the catalyst layer structure can reduce mass-transport limitations enabling higher partial current densities, enhanced product selectivity at similar cathode potential and this is accomplished with significantly lower catalyst loadings. Such results are encouraging as they may lead to reduced system-level costs and improved balance of plant.

To understand the differences in product yield between the AB and HP cathodes, we characterized the physical structure of the electrodes (Figure 4.8). Much like with the fuel cell cathodes, MicroCT data showed dramatic differences between the catalyst layers of the AB and HP electrodes (Figures 4.8a1-a2 and 4.8b1-b2). In the HP electrode, the catalyst appears to have permeated through the cracks in the microporous layer of the GDL, ending up being distributed throughout the GDE. This is likely due to the high liquid content of the catalyst ink which carried the catalyst materials into the bulk of the GDL. Only a fraction of the catalyst materials remains at the interface between the electrode and the flowing electrolyte stream. In contrast, the air-brushed catalyst layer is uniformly distributed across the GDL surface with no material deposition in the bulk. This is likely due to the drier nature of the deposition where the carrier solvents are evaporated both during the atomization process at the air-brush nozzle and at GDL surface which is held at an elevated temperature. Also, like the fuel cell cathodes, surface SEM images of the catalyst particles show agglomeration and unevenness in the catalyst layer of the HP electrode whereas the deposition on the AB electrode appears to be more uniform (Figure 4.8c1-c2).
Interestingly, despite the marked differences between the cathodes, the total current densities are quite similar which may suggest that the catalyst in the bulk of the hand-painted electrode may participate in electrochemical reaction (possibly via electrolyte permeation into the GDL through the hydrophilic holes created by the catalyst layer seepage), resulting in a higher than expected current density. While the total current densities generated by each electrode are quite similar, the product yields are different indicating that the amount of exposed carbon from the MPL of the GDE plays a role in the electrocatalysis, specifically catalyzing H$_2$ evolution. This hypothesis is verified by control experiments using a bare GDL with no catalyst as a cathode (Figure 4.6a-b and Figure 4.7a-b). The bare GDL produces a high current density of H$_2$ but does not produces CO until cathode potential < -1.65 V vs. Ag/AgCl. This indicates that non-uniform catalyst deposition which leads to the exposure of the carbonaceous MPL to the electrolyte can lead to increased H$_2$ evolution which reduces the CO production efficiency and may also lead to inaccurate conclusions about the performance/selectivity of novel catalyst materials. In addition, these side-reactions may damage the MPL (e.g., loss of hydrophobicity) and adversely impact electrode durability.

4.5 Conclusions

By coupling in-situ electrochemical characterization using microfluidic electroanalytical platforms and ex-situ MicroCT imaging, we have been able to directly correlate changes in electrode performance to differences in catalyst layer structure. We have employed this combined approach to study O$_2$ and CO$_2$ reduction reactions in low temperature fuel cells and CO$_2$ electrolyzers, respectively. Fuel cell studies revealed that air-brushed cathodes outperformed both hand-painted and screen-printed cathodes with identical catalyst loadings due to a more uniformly distributed agglomerate-free catalyst layer of even thickness. Furthermore,
the automated nature of the air-brushing procedure led to significant improvements in electrode-to-electrode reproducibility. CO₂ electrolysis studies revealed that air-brushing cathodes can also have significant effects on product distribution at high current densities. Defects in the catalyst layer expose carbon in the microporous layer which leads to an increase in unwanted hydrogen evolution due to easy access of water to these carbonaceous catalytic sites. A uniform and defect free catalyst layer minimizes this site reaction. The optimization of the CO₂ reduction electrode catalyst layer structure enabled increased current densities and improved product yields at a catalyst loading an order of magnitude lower than in previous reports [27,41,42]. The combined approach of MicroCT-based visualization and microfluidic-based electrochemical analysis offers a framework for systematic investigations of electrode-based electrochemical processes. This, in turn, will benefit the rational development of new materials and improved processing methodologies for catalyst layer deposition and electrode preparation, which in turn may lead to economically-viable electrochemical systems.
4.6 Figures

(a) **Microfluidic H₂/O₂ Fuel Cell**

**Anode:** \(2H_2 \rightarrow 4H^+ + 4e^-\)

**Cathode:** \(O_2 + 4H^+ + 4e^- \rightarrow 2H_2O\)

**Overall:** \(O_2 + 2H_2 \rightarrow 2H_2O\)

(b) **CO₂ Electrolysis Cell**

**Cathode:** \(CO_2 + 2H^+ + 2e^- \rightarrow CO + H_2O\)

\[2H^+ + 2e^- \rightarrow H_2\]

**Anode:** \(H_2O \rightarrow \frac{1}{2}O_2 + 2H^+ + 2e^-\)

**Overall:** \(CO_2 \rightarrow CO + \frac{1}{2}O_2\)

**Figure 4.1.** Schematic representations of (a) the microfluidic H₂/O₂ fuel cell and (b) the CO₂ electrolysis cell used in this study.
Figure 4.2. Schematic of the fully automated air-brushing deposition machine.
Figure 4.3. (a) Representative fuel cell polarization and power density curves and (b) corresponding individual electrode polarization curves, of air-brushed, screen-printed, and hand-painted cathodes with the same catalyst loading of 1.0 mg Pt/C/cm$^2$ (50 wt% Pt). The same anode, prepared by the air-brushing deposition method with the catalyst loading of 1.0 mg Pt/C/cm$^2$ (50 wt% Pt), was used for all experiments. Reactant streams: 10 sccm H$_2$/O$_2$; electrolyte: 1.0 M HClO$_4$ flowing at 0.6 mL/min; data collected at room temperature.
Figure 4.4. Structural analysis of fuel cell Pt/C cathodes (hand-painted vs. air-brushed vs. screen-printed). (a1, a2, a3) MicroCT 2D radiographic cross-sectional images in the YZ-plane (through-plane). (b1, b2, b3) MicroCT 3D tomographic virtual models. (c1, c2, c3) 3D reconstructed volume of the catalyst layer. The percentages indicate the volume occupied by catalyst. (d1, d2, d3) SEM top view micrographs of the catalyst layer. Note that the contrast and brightness of (d3) was adjusted for clear presentation as the catalyst layer was coated with a Nafion ionomer ink.
Figure 4.5. Electrode-to-electrode repeatability of air-brushed and hand-painted cathodes. (a) Average power density curves of air-brushed (AB1-4) and hand-painted (HP1-4) cathodes where N=4 for error bars. (b) Corresponding individual electrode polarization curves, of four different air-brushed cathodes (AB1-4) and four different hand-painted cathodes (HP1-4), with the same catalyst loading of 1.0 mg Pt/C/cm² (50 wt% Pt). The same anode, prepared by the air-brushing deposition method with the catalyst loading of 1.0 mg Pt/C/cm² (50 wt% Pt), was used for all experiments. Reactant streams: 10 sccm H₂/O₂; electrolyte: 1.0 M HClO₄ flowing at 0.6 mL/min; data collected at room temperature.
Figure 4.6. Electrochemical reduction of CO\(_2\) to CO using the flow reactor. (a) Current densities as a function of applied cell potential, and (b) corresponding individual electrode polarization curves of the flow reactor operated with an air-brushed, hand-painted, and bare GDL (no catalyst) cathode. Cathode catalyst: 0.75 mg/cm\(^2\) unsupported Ag nanoparticles; anode catalyst: 4.25 mg/cm\(^2\) unsupported Pt black; reactant streams: 7 sccm CO\(_2\); electrolyte: 1.0 M KCl flowing at 0.5 mL/min; data collected at room temperature and ambient pressure.
Figure 4.7. Results of electrochemical reduction of CO$_2$ to CO using the flow reactor. Partial current density of (a) the desired product CO and (b) the undesired product H$_2$, and (c) Faradaic efficiency for CO and H$_2$ as a function of cathode potential (V) vs. Ag/AgCl. N=3 for error bars.
Cathode catalyst: 0.75 mg/cm$^2$ unsupported Ag nanoparticles; anode catalyst: 4.25 mg/cm$^2$ unsupported Pt black; reactant streams: 7 sccm CO$_2$; electrolyte: 1.0 M KCl flowing at 0.5 mL/min; data collected at room temperature and ambient pressure.

**Figure 4.8.** Structural analysis of the hand-painted and air-brushed Ag cathode for CO$_2$ reduction. MicroCT 2D radiographic cross-sectional images in the YZ-plane (through-plane) (a1,a2), MicroCT 3D tomographic virtual models (b1, b2), and SEM top view micrographs (c1,c2) of the hand-painted and air-brushed cathode, respectively. Cathode catalyst: 0.75 mg/cm$^2$ unsupported Ag nanoparticles.
4.7 Supporting Information

**Electrochemically-Active Surface Area Measurements**

Figure 4.9 shows the cyclic voltammograms (CVs) of the electrochemically-active surface area (ECSA) measurements for the fuel cell cathodes. The fuel cell cathodes were tested in the microfluidic H₂/O₂ fuel cell (Figure 4.3) and were imaged using MicroCT and SEM (Figure 4.4). A small section (1.8 cm²) was cut out of each cathode to perform ECSA measurements using the three-electrode cell in which the small section of the GDE acted as the working electrode, the counter electrode was a Pt mesh, and the reference electrode was Ag/AgCl. Prior to measurements, Ar was purged for 10 minutes to remove any dissolved oxygen in the electrolyte (0.1 M HClO₄). Data were taken at room temperature at the scan rate of 50 mV/s. Note that the currents on Figure 4.9 have been geometric area-normalized (i.e., measured currents divided by the geometric area of the GDE (1.8 cm²)). ECSA was then calculated based on the H adsorption region assuming 210 μC/cm² Pt.[43]

![Figure 4.9](image.png)

**Figure 4.9.** CVs of hand-painted, screen-printed, and air-brushed Pt/C cathodes in 0.1 M HClO₄, recorded at 50 mV/s. Ar was purged for 10 minutes prior to measurements.
Statistical Analysis of Hand-Painted and Air-Brushed Cathode Performances

In Figure 4.5, we show that air-brushing deposition method drastically improves electrode to electrode reproducibility of performance. In detail, we investigated the variations in power density (Figure 4.5a) and in cathode polarization curve (Figure 4.5b) of 4 different hand-painted (HP1-4) and 4 different air-brushed cathodes (AB1-4). To assure that these two data sets are statistically different, we performed the t-test as follows.

First, we conducted curve fitting on the power density curve for each cathode to obtain a polynomial function of power density (y) as a function of current density (x) as follows.

\[ y = f(x) = A + B_1 \cdot x + B_2 \cdot x^2 + B_3 \cdot x^3. \]

This allows us to calculate the power density at different current density. Here we chose current densities of 300 and 500 mA/cm\(^2\), both in the ohmic regime, to demonstrate the statistical significance of those two data sets. The fitted power densities are tabulated in Tables 4.1 and 4.2.

| Peak Power Density \( y_1 \) (mA/cm\(^2\)) |
|-----------------------------------|---|---|---|---|---|
| AB1  | AB2  | AB3  | AB4  | \( y_1 \) | \( s_1^2 \) |
| 153.45 | 148.47 | 158.56 | 154.48 | 153.74 | 17.22 |

| Peak Power Density \( y_1 \) (mA/cm\(^2\)) |
|-----------------------------------|---|---|---|---|---|
| HP1  | HP2  | HP3  | HP4  | \( y_2 \) | \( s_2^2 \) |
| 120.52 | 98.36 | 97.69 | 114.87 | 107.86 | 134.41 |

Table 4.1. Fitted power densities of AB1-4 and HP1-4 at a current density of 300 mA/cm\(^2\).
Table 4.2. Fitted power densities of AB1-4 and HP1-4 at a current density of 500 mA/cm$^2$

<table>
<thead>
<tr>
<th></th>
<th>AB1</th>
<th>AB2</th>
<th>AB3</th>
<th>AB4</th>
<th>$\bar{y}_1$</th>
<th>$s^2_1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Peak Power Density ($y_i$ (mA/cm$^2$))</td>
<td>164.91</td>
<td>154.02</td>
<td>171.54</td>
<td>158.86</td>
<td>162.33</td>
<td>57.47</td>
</tr>
<tr>
<td></td>
<td>HP1</td>
<td>HP2</td>
<td>HP3</td>
<td>HP4</td>
<td>$\bar{y}_2$</td>
<td>$s^2_2$</td>
</tr>
<tr>
<td>Peak Power Density ($y_i$ (mA/cm$^2$))</td>
<td>84.98</td>
<td>30.56</td>
<td>48.00</td>
<td>77.86</td>
<td>60.35</td>
<td>651.20</td>
</tr>
</tbody>
</table>

Second, we calculated the mean ($\bar{y}$) and standard deviation ($s$) for each data set using the following equations.

$$
\bar{y} = \frac{\sum y_i}{n}
$$

$$
s^2 = \frac{1}{n-1} \sum (y_i - \bar{y})^2
$$

Where $n$ is the number of samples ($n = n_1 = n_2 = 4$ for both data sets). We then calculated the pooled variance ($s_{\bar{y}_1 - \bar{y}_2}$).

$$
s_{\bar{y}_1 - \bar{y}_2} = s_p \times \sqrt{\frac{1}{n_1} + \frac{1}{n_2}}
$$

$$
s_p = \sqrt{\frac{s^2_1 + s^2_2}{2}}
$$

Now, we can calculate the $t$ value ($t_{\text{calculated}}$).

$$
t_{\text{calculated}} = \frac{(\bar{y}_1 - \bar{y}_2)}{s_{\bar{y}_1 - \bar{y}_2}}
$$

Thus, $t_{\text{calculated}} = 8.21$ and $t_{\text{calculated}} = 7.66$ for current densities of 300 and 500 mA/cm$^2$, respectively.
Next, we determined our test statistic. The most common is a p-value of 0.05. Additionally, our degrees of freedom are $\text{df} = n_1 + n_2 - 2 = 6$. This value can be found in the $t$ table.[39] For $\text{df} = 6$ and p-value = 0.05 (one-tail t-test should work fine) the $t$ value is 1.943. Since $t_{\text{calculated}} > t_{\text{table}}$ we then conclude that with a 95% confidence interval the two data sets are significantly different. In other words, the results obtained with the hand-painting and air-brushing deposition methods are statistically different.
4.8 References


Chapter 5
Nanoparticle Silver Catalysts that Show Enhanced Activity for Electrochemical Reduction of CO$_2$ to CO$^*$

5.1 Chapter Overview

Electrochemical conversion of CO$_2$ has been proposed both as a way to reduce CO$_2$ emissions and as a source of renewable fuels and chemicals but conversion rates need improvement before the process will be practical. In this chapter we show that the rate of CO$_2$ conversion per unit surface area is about 10 times higher on 5 nm silver nanoparticles than on bulk silver even though measurements on single crystal catalysts show much smaller variations in rate. The enhancement disappears on 1 nm particles. We attribute this effect to the changes of the binding energy of key intermediates as the particle size decreases. These results demonstrate that nanoparticle catalysts have unique properties for CO$_2$ conversion.

5.2 Introduction

The discovery and development of efficient catalysts for CO$_2$ electroreduction is one of the grand challenges identified in the DOE report, catalysis for energy [1]. For electrochemical reduction of CO$_2$ to become a feasible process, catalysts are needed that exhibit both high energetic efficiency and high conversion rates [2]. Recently Rosen et al. discovered that the combination of two catalysts, a silver metal and ionic liquid 1-ethyl-3-methylimidazolium tetrafluoroborate (EMIM-BF$_4$) would lower the overpotential for CO$_2$ reduction by almost a volt [3,4]. Unfortunately, rates were lower than needed. The objective of this paper is to determine whether the rate would be enhanced by lowering the particle size of the silver catalysts. A

$^*$ This chapter has been adapted from the following publications:
previous paper reported a higher rate for CO$_2$ conversion on Ag(110) than on Ag(111) or Ag(100), but the effect was not large enough to have a significant effect on practical supported catalysts [5]. Small variations are also seen on platinum single crystals but again the effects are too small to have a significant effect on practical catalysts [6,7]. Still, previous workers had shown that gold nanoparticles have unique properties for a number of reactions. Therefore, we decided to determine whether silver nanoparticles have unique properties for CO$_2$ conversion in ionic liquids.

### 5.3 Experimental

The 5 nm catalyst was a custom made sample from a local supplier. The 1 nm sample was prepared from Mesosilver manufactured by Colloids For Life. The 200, 70, and 40 nm samples were purchased from Sigma Aldrich. Sigma-Aldrich labels its samples <500, <100, and 40 nm. The nomenclature of 200, 70, 40, 5 and 1 nm represents the actual average particle size of the samples as measured by dynamic light scattering and confirmed by TEM.

In the electrochemical experiments each catalyst sample was deposited onto a clean silver substrate, baked to remove organic impurities, and then soaked in acid or ionic liquid solution to remove metallic impurities. X-ray photoelectron spectroscopy (XPS) of similar samples on a silicon substrate showed the samples to be clean, except for small amounts of carbon and oxygen from the vacuum system. The samples were loaded into a standard 3 electrode cell for the measurements. In each plot the current was normalized by the electrochemical surface area of each electrode, measured by underpotential deposition lead stripping. Details of all procedures are given in the Supporting Information (Section 5.7).

The Ultraviolet photoelectron spectroscopy (UPS) data was taken after depositing the catalyst materials onto silicon substrates heating and soaking in acid, using a Physical
Electronics PHI 5400 photoelectron spectrometer that uses He I (21.2 eV) ultraviolet radiation and a pass energy of 8.95 eV. To separate the signal arising from secondary electron emission from the detector from the secondary electron emission from the sample, a -9 V bias was applied to the sample using a battery. The reported binding energies are the measured binding energy plus the 9 V.

In the flow apparatus described previously, catalysts were painted onto carbon paper, and mounted in a 2 compartment cell [8]. Dried ionic liquid flowed through the cathode compartment while 0.5 M sulfuric acid flowed into the anode. Voltage was applied to the cell, and the CO and hydrogen production were measured with a gas chromatograph.

5.4 Results and Discussion

In this study, we used different silver nanoparticle sizes ranging from 1 nm to 200 nm. Figure 5.1A-H shows the scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images of the nanoparticles. Figure 5.1N-K shows the results of dynamic light scattering (DLS) analysis which are in a good agreement with TEM results. To investigate the electronic properties of silver nanoparticles, X-ray photoelectron spectroscopy (XPS) was carried out (Figure 1(P-R)). Prior to measurements, the samples were immersed in 0.1 M sulfuric acid overnight and rinsed with DI water to remove impurities. XPS spectra were collected using a Kratos Axis ULTRA X-ray photoelectron spectrometer with monochromatic Al Kα excitation, 120 W (120 kV, 10 mA). Survey spectra were collected at a pass energy of 160 eV and high resolution spectra were collected using a pass energy of 40 eV. XPS results show that samples are clean, except for small amounts of carbon and oxygen from the vacuum system.

Figure 5.2 shows the result of a cyclic voltammetry (CV) experiment where nanoparticle silver was coated onto a silver rotating disk electrode, the electrode was loaded into an EMIM-
BF₄ solution containing about 75 ppm of water, the sample was rotated at 1000 rpm, and the potential was cycled from -1.14 V to 0.77 V with respect to SHE (see the Supporting Information (Section 5.7) for experimental details). Figure 5.2A shows how the CV of water varies with particle size under the conditions of the experiment. The plot shows how the current per unit surface area (i.e., the measured current divided by the measured surface area) varies with the particle size. Notice that all of the curves lie on top of each other, demonstrating that the rate per unit surface area of water electrolysis to produce hydrogen is independent of particle size, as would be expected from previous literature [9].

Figure 5.2 also shows similar experiments except that we bubbled CO₂ through the solution. In this case we observe a peak centered at about -0.75 V vs. SHE that is not seen in the absence of CO₂. This peak is associated with CO₂ conversion. Note that the peak grows as the particle size decreases from 200 to 5 nm, and then shrinks again as the particle size decreases to 1 nm. In other words, the results in Figures 5.2B-G show that the rate of CO₂ electrolysis depends strongly on the particle size.

Figure 5.2H illustrates the effect more clearly. Specifically, the peak current densities for CO formation (i.e., current densities at -0.75 V vs. SHE) in Figure 5.2B-G were plotted with respect to particle size to quantitatively show how the rate of CO₂ reduction changes as a function of particle size. Notice that the rate of CO₂ electrolysis is about a factor of 10 higher on 5 nm silver particles than on bulk silver surfaces or on catalysts comprised of 1 nm particles. Clearly this is a significant effect.

Figure 5.3 show steady state data taken using the flow apparatus described previously [3,8,10]. Briefly, the dual-electrolyte electrochemical reactor used in this study consists of two 1.5 mm thick poly(methyl methacrylate) (PMMA) sheets with 0.5-cm wide by 2.0-cm long
channels to provide the electrolyte flow channels for the catholyte (liquid stream in contact with the cathode; pure EMIM BF$_4$) and analyte (liquid stream in contact with the anode; 0.5 M sulfuric acid). Between the two electrolyte channels was a 0.8-cm wide and 2.5-cm long piece of Nafion 212 membrane (DuPont) used to separate the catholyte and anolyte while maintaining ionic conductivity. The cathode and anode that were made of gas diffusion electrodes (GDEs) were put on each PMMA sheet. Each electrode was backed by aluminum current collectors. The aluminum current collector that backed the cathode also served as a gas flow chamber to supply CO$_2$, while the anode was open to the atmosphere for oxygen to escape. At cell voltages of 3 V or less the CO current increases by a factor of 3 in changing from 200 to 40 nm particles (Figure 5.3). This is very similar to the change seen in Figure 5.2H. The particle size dependence disappears at higher applied voltages, however.

It is interesting to compare the results in Figures 5.2 and 5.3 to previous results for CO$_2$ conversion on single crystal catalysts. Hoshi et al.[5] previously examined CO$_2$ conversion on Ag(111), Ag(100) and Ag(110) and found that the rate of CO$_2$ reduction was about a factor of 2 higher on Ag(110) than on Ag(111) or Ag(100). If one assumes that the flat surface was mainly (111) or (100) orientated, while (110) facets and related steps cover that 20% of the surface of 5 nm particle, then based on the single crystal results, would only expect the rate to go up by about 20% i.e. 20%*(2-1). By comparison Figure 5.2 shows an order of magnitude change in rate. Further the 1 nm particles are the most irregular, yet they show a decreased activity compared to the single crystal results [5]. Thus, the nanoparticle catalysts used here clearly exhibit much different variations in rate as a function of structure than what would be expected from the single crystal results reported previously.
The explanation for these different effects is not obvious. Variations in rate with particle size can be caused by (i) variation in the number of step sites, kink sites, and other special geometries with particle size, (ii) variation in the electronic structure or work function of the particles with particle size, or (iii) variations in the binding energy of key intermediates with particle size [11]. Experimentally, we observe much larger variations in rate with particle size than was expected from work on single crystals [5,7] so variations in the concentration of steps, kinks and other structures, do not seem to explain our data.

We have considered changes in rate due to variations in the bulk electronic properties of the particles such as the work function or d-band position, but our UPS data (see Supporting Information (Section 5.7) for details of experiments) shown in Figure 5.4 indicate that the variations in the work function and the position of the center of the d-bands is insufficient to explain the observed variations in rate. Notice that the general shape of UPS spectrum of the particles does not vary significantly with particle size at particle sizes down to 5 nm. Importantly, the center of the d-band is not shifting significantly with particle size. We do observe variations in the work function of the particles with particle size as indicated in Table 5.1. Still, the work function is almost the same in bulk samples and in 40 nm particles, even though the rate varies significantly. Similarly, the measured work function is almost the same on 5 nm and 1 nm particles, even though the rate changes significantly. In each of these two cases, the variations in work function with particle size are smaller than the variations in work function with crystal face reported previously [12,13]. Thus, the variations in the work function and the electronic structure of our particles does not explain why we observe variations in rate with particle size that are larger than those seen on single crystal catalysts.
That leaves variations in the binding energy of intermediates as the explanation for the observed variation in rate. To see if the binding energy of intermediates would vary with particle size we performed cyclic voltammetry (CV) to determine the binding energy of hydroxyls and sulfates (or bisulfates) as a function of particle size. Specifically, the overpotential of hydroxyl / sulfate adsorption is considered a measure of binding strength of intermediates on silver nanoparticles; smaller overpotential indicates larger binding energy (stronger binding) of intermediates. **Figure 5.5** shows voltammograms of the sulfate and hydroxyl adsorption and desorption peaks on different diameter silver particles in 0.1 M sulfuric acid or 0.1 M NaOH. In this experiment, hydroxide adsorption scans swept between -0.1 and 0.6 V and sulfate scans between -0.1 and 0.9 V vs. Ag/AgCl. All scans were taken at 10 mV/s. The current was normalized by the electrochemical surface area of each electrode, measured by underpotential deposition lead stripping.

For the hydroxide peaks, we observe a shift in the overpotential required to drive the adsorption and desorption. At a current density of +2.5 mA/cm$^2$, the overpotential required to drive the adsorption at this rate is lowest on the 1 nm silver particles, and increases by about 100 mV with increasing particle size. Desorption of the hydroxide anion at the same rate (-2.5 mA/cm$^2$) follows the same trend. The overpotential is lowest using the 1 nm silver particles and increases with increasing particle size. This was also observed for the adsorption and desorption of the sulfate anion. This implies that the binding energy of sulfates and hydroxyls varies significantly with particle size, with the smallest particles showing higher binding than bulk samples. Importantly, this effect is larger than that observed in single crystals [14-17]. In summary, these data suggest that differences in the binding energy of intermediates with
particles of different size is large enough to explain why we observe larger increases in rate than has been observed in single crystals.

It is interesting to ask how the variations in binding energy could cause changes in rate. Assume for the moment that the conversion of CO$_2$ to CO under acidic conditions in the presence of EMIM$^+$ (EMIM-BF$_4$ is acidic) followed the mechanism proposed by Rosen et al. [3,4]:

\[
\text{EMIM}^+(l) + \text{CO}_2(g) + e^- \rightarrow \text{Complex}^{\text{ad}}(l) \tag{2}
\]

\[
\text{H}^+(l) + \text{Complex}^{\text{ad}}(l) \rightarrow \text{CO}(g) + \text{OH}^{\text{ad}} + \text{EMIM}^+(l) \tag{3}
\]

\[
\text{OH}^{\text{ad}} + \text{H}^+(l) + e^- \rightarrow \text{H}_2\text{O}(l) \tag{4}
\]

If the binding energy of the intermediates increased with shrinking particle size, the thermodynamic driving force for reaction 2 and 3 should increase, while the thermodynamic driving force for reaction 4 should decrease. Therefore, one would expect the rate of reactions 2 and 3 to increase, and the rate of reaction 4 to decrease. In the previous work of Rosen et al. [3,4] we suggested that during CO$_2$ conversion on 100-200 nm silver particles, reactions 2 and 3 are rate determining. In that case one could increase the rate by increasing the binding energy of intermediates by for example, making the particle sizes smaller. On the other hand, if we increased the binding energy of the intermediates enough, reaction 4 would become rate determining. In that case the rate of reaction would decrease, since the OH cannot be rapidly removed from the surface. Consequently, one would expect classic volcano behavior as seen in Figure 5.2H.

This model would also explain why the variations in rate with particle size are larger than those seen with single crystals. Previous data with single crystal catalysts show that sulfate [14,15] and hydroxyl binding [16,17] is only weakly affected by crystal face. Sulfate binds more
strongly on Ag(111) than on Ag(100) or Ag(110) [14,15], while the literature disagrees whether the (111) or (100) face of silver binds oxygen most strongly. In all cases the effects are 50 mV or less. By comparison, we observe almost 100 mV variations in binding energy. Thus, we observe larger variations in rate with nanoparticles than with single crystals because the binding energy of intermediates varies more strongly with geometry on nanoparticles than on single crystals.

Of course, we still have to explain why the variations in binding energy occur. One needs calculations to do so, and we have not done them yet. Still, recent calculations of Pozen et al. [18] show that the binding energy of ethylene varies more strongly on silver nanoparticles than expected from data on single crystal samples. Thus, there is precedent in the literature.

5.5 Conclusions

In summary, we have studied the effect of Ag nanoparticle size on its catalytic performance in the conversion of CO$_2$ into CO. We found that the catalytic activity increases with decreasing particle size until a certain particle size, here 5 nm, and that the activity drops when going to even smaller nanoparticle size (1 nm). Through XPS measurements (work function) and further electrochemical analysis (binding strengths) we were able to conclude that some reaction intermediates bind too strongly to the nanoparticles once they are too small, here < 5 nm. We expect that other metal nanoparticles will exhibit similar size-dependent effects, but further studies would be needed to confirm.
### 5.6 Figures and Tables

**Table 5.1.** Measured work functions of the particles

<table>
<thead>
<tr>
<th>Particle Size</th>
<th>Measured Work Function (eV)</th>
<th>Work Function Variation Expected From Wood's Model[19] (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>bulk</td>
<td>4.38 ± 0.022</td>
<td>4.37</td>
</tr>
<tr>
<td>70 nm</td>
<td>4.38 ± 0.023</td>
<td>4.38</td>
</tr>
<tr>
<td>40 nm</td>
<td>4.35 ± 0.026</td>
<td>4.38</td>
</tr>
<tr>
<td>5 nm</td>
<td>4.78 ± 0.019</td>
<td>4.48</td>
</tr>
<tr>
<td>1 nm</td>
<td>4.76 ± 0.050</td>
<td>4.91</td>
</tr>
</tbody>
</table>
Figure 5.1. (A-D) show SEM images of 1 nm, 5 nm, 70 nm and 200 nm silver nanoparticles, respectively. (E-H) TEM images of 5 nm, 40 nm, 70 nm and 200 nm silver nanoparticles, respectively. (K-N) show DLS results for 1 nm, 40 nm, 70 nm and 200 nm particles, respectively.
Figure 5.2. (A) cyclic voltammetry with argon in EMIM-BF$_4$ on bulk, 200 nm, and 5 nm silver nanoparticle catalysts (see Figure S3 for the expanded results). (B-G) cyclic voltammetry with CO$_2$ in EMIM-BF$_4$ on bulk, 200 nm, 70 nm, 40 nm, 5 nm and 1 nm silver nanoparticle catalysts, respectively. (H) Current density for CO and H$_2$ formation as a function of particle size (the numbers of current density for CO and H$_2$ formation are obtained from the peak current densities at -0.75 V vs. SHE (from B-G) and -1.14 V (from A) vs. SHE, respectively.) The maximum current density for CO peak occurs at 5 nm.
Figure 5.3. (A) Current density of CO as a function of silver particle size at different cell voltage (-2.75, 3.00, 3.25 V) measured in a flow cell. (B) -2.75 V data on an expanded scale. These data were taken with EMIM solutions containing about 75 μM water. Previous work[3] used 88% water on the cathode, resulting in much higher currents.
Figure 5.4. UPS spectra of 1 nm, 5 nm, and 70 nm of clean silver nanoparticles as well as of bulk silver. To allow for easy comparison of curve shape, the data has been re-scaled on the Y-axis so that the maximum intensities of all of the UPS peaks are the same.
Figure 5.5. Adsorption and desorption of (A) sulfate and (B) hydroxide on 1 nm, 5 nm, and 70 nm silver nanoparticles. The overpotential for both hydroxide and sulfate goes down as the particle size decreases.
5.7 Supporting Information

Scanning Electron Microscopy (SEM):
Physical morphology of the catalyst layer on gas diffusion electrodes (GDEs) was imaged using SEM (Philips XL30 ESEM-FEG). The GDEs were prepared as previously described using Sigracet 35 BC gas diffusion layers (GDLs) (Ion Power, Inc.). A suspension of catalyst (i.e., Ag nanoparticles) and Nafion binder (5 wt% Nafion ionomer in water, Solution Technology) was made by soninating with a 50/50 vol% mixture of water and isopropyl alcohol (Sigma-Aldrich), which was then air-brushed on the GDL using a fully-automated air-brushing catalyst deposition machine. The GDEs consisted of 1 mg/cm² Ag (five different particle sizes: 1 nm, 5 nm, 40 nm, 70 nm, and 200 nm) and 0.03 mg/cm² Nafion binder.

Transmission Electron Microscopy (TEM):
Morphological characterization of Ag nanoparticles was conducted using TEM (Philips CM200). Ag nanoparticles were suspended in isopropyl alcohol (Sigma-Aldrich) and sonicated for 30 minutes to ensure good particle dispersion. A very dilute concentration was needed to acquire TEM images. TEM grids were prepared by putting a few droplets of dilute nanoparticle suspensions on copper grids and dried overnight.

Dynamic light Scattering (DLS) Particle Size Analyzer:
DLS particle size measurements were carried out using the NiComp ZLS 380 system at 25°C. The instrument includes a 35 mW semiconductor laser with 670 nm emissions and a thermoelectric temperature control for samples. The 1 nm, 40 nm, 70 nm, and 200 nm silver particles were dispersed in water and the 5 nm sample was dispersed in toluene; all samples were sonicated for 30 minutes to ensure homogeneous particle dispersion. The typical error in DLS data is on the order of 5-10%.
**XPS Measurements of Silver Nanoparticles:**

To investigate the electronic properties of silver nanoparticles, X-ray photoelectron spectroscopy (XPS) was carried out. The XPS samples were prepared as follows. A suspension of Ag nanoparticles was made by sonication with a 50/50 vol% mixture of water and isopropyl alcohol (Sigma-Aldrich), which was then air-brushed on the silicon wafer using a fully-automated air-brushing catalyst deposition machine. A silver plate was used to represent bulk silver, and it was cleaned using Ar+ at 3V for 2 minutes. Prior to measurements, the samples were immersed in 0.1 M sulfuric acid overnight and rinsed with DI water to remove impurities. XPS spectra were collected using a Kratos Axis ULTRA X-ray photoelectron spectrometer with monochromatic Al Kα excitation, 120 W (120 kV, 10 mA). Data were collected using the hybrid lens setting with the slot aperture (300 x 700 mm2 analytical area) and charge neutralizer settings of 2.1 A filament current, 2.1 V charge balance and 2V filament bias. Survey spectra were collected as a pass energy of 160 eV and high resolution spectra were collected using a pass energy of 40 eV. The data were fitted with Gaussian-Lorentzian line shapes. The binding energy scale was referenced to the aliphatic C1s line at 285.0 eV.
Figure 5.6. XPS survey spectra of (A) 1 nm, (B) 5 nm, (C) 40 nm, and (D) 70 nm clean silver particles coated on silicon wafers.
UPS Measurements of Silver Nanoparticles:

Surface work function measurements were made using ultraviolet photoelectron spectroscopy (UPS). First the samples were cleaned as described in the XPS section loaded into the spectrometer, and an XPS spectrum was taken to insure sample cleanliness. Next UPS data were acquired with a Physical Electronics PHI 5400 photoelectron spectrometer using He I (21.2 eV) ultraviolet radiation and a pass energy of 8.95 eV. To separate the signal arising from secondary electron emission from the detector from the secondary electron emission from the sample, a -9 V bias was applied to the sample using a battery. The work function was calculated using the equation as follows.

\[
\text{work function} = \text{photon energy} - (\text{peak position} + \text{battery voltage} + 0.5\text{FWHM})
\]

Where FWHM is the full width at half-maximum.

Note that the UPS measurements were carried out immediately after the XPS using the exact same samples, and thus the samples stayed clean in the vacuum chamber.

3-Electrode Electrochemical Cell:

Experiments were carried out in a custom-made 150 mL, three-electrode electrochemical glass cell. 40, <100, and <500 nm silver nanoparticle samples were purchased from Sigma-Aldrich. The 5 nm ink was custom manufactured by a local supplier. The 1 nm electrode was made by evaporation deposition of a Mesosilver® silver colloid from Colloids for Life and treating with sulfuric acid to remove the metallic impurities in the sample. The catalyst metal black ink is prepared by mixing 5.6mg of nanoparticles with 1 ml deoxygenated Millipore water. These actual particle sizes in these samples measured as with DLS were 1, 5, 40, 70, and 200 nm, respectively. After 12.5 µL of the ink was placed on the surface of silver rotating disk, the drops were dried under ambient condition for 6 hours. The 5nm sample was placed in an oven at 100°C.
for 4 days in order to evaporate off the conjugating solvent. All of the samples were soaked in an acid or EMIM solution prior to use. The size of the nanoparticles was verified by DLS and SEM, and the cleanliness was verified by XPS. The counter electrodes used in this experiment is platinum catalyst. The counter electrode is made by attaching a 25x25 mm platinum mesh (size 52) to a 5 inch platinum wire (99.9%, 0.004 inch diameter). The reference electrode is a silver wire.

The electrolytes were first loaded into the glass cell and then purged with dry argon (99.99%) for two hours in order to remove oxygen from the electrolytes. Prior to all experiments, a 20-40 linear sweep cyclic voltammograms at 75 mV.s⁻¹ was taken between -1.5 V and +1 V vs. SHE in order to conditioning the electrodes, removing oxides from the surfaces. After, several cycles were performed at 10 mV.s⁻¹ before the final cycle to insure that the CV had stabilized (i.e., any contaminations or other material is removed from the surfaces). Finally, cleaning and stabilizing CV cycles were performed at 10 mV.s⁻¹ within the range of -1.25 V to 1 V vs. SHE. Then CO₂ was bubbled in the solution at 1 atm pressure for 20 minutes. Cyclic voltammetry was conducted again at a sweep rate of 10 mV/s in the same range.

**Cathodic Surface Area Measurements:**

The electrochemical surface area was performed without removal of oxygen in a 15 mL flask containing 5.00 mM Pb(NO₃)₂, 10 mM HNO₃ and 10 mM KCl. A cyclic voltammogram was recorded at 10mV/s between -0.10 and -0.55V vs. a Ag/AgCl electrode. The counter electrode was a 25x25 platinum mesh (size 52). An example of the UPD lead stripping peak is shown in Figure S2. According to Brand et al. [20] the area under this peak at Pb²⁺ concentrations of 5 mM or higher corresponds to a charge of 1.67 x 10⁻³ cm²/µC silver. The surface area measured by this experiment for all samples was very similar; around 0.25 cm². This is expected since high
density of nanoparticles used in our experiments produces a dense film of nanoparticles which produces a similar surface area.

**Figure 5.7.** Cyclic voltammogram showing the UPD and bulk deposition of Pb onto a silver cathode of 1nm particles (scan rate 10mV/s).

**Effect of Adsorption of OH\(^-\) and SO\(_4^{2-}\) on Binding Energy of Key Intermediates:**

The adsorption of sulfate and hydroxide was measured on 70 nm, 5 nm, and 1 nm silver nanoparticles. The hydroxide solution was 0.1 M potassium hydroxide, and the sulfate solution was 0.1 M sulfuric acid. The counter electrode was a 25x25 mm piece of platinum mesh (size 52), and the reference electrode was an Ag/AgCl electrode. Silver nanoparticles for the working electrode were put on a 1nm flat silver support by evaporation deposition. The 70 nm ink was a 10 mg/ml H\(_2\)O suspension of silver nanoparticles purchased from Sigma-Aldrich. After 10 \(\mu\)L of the ink was placed on the silver support, the drop was dried under an IR lamp for 20 minutes. The 5 nm ink was custom manufactured by a local supplier. After painting the support surface, the electrode was placed in an oven at 100°C for 4 days in order to evaporate off the conjugating solvent. The 1 nm electrode was made by evaporation deposition of a Mesosilver\(^\circledR\) silver colloid.
under an IR lamp. The size of the nanoparticles on the support was verified by DLS and SEM. All of the samples were soaked in an acid or EMIM solution prior to use.

The adsorption and desorption of hydroxide and sulfate on the silver surface was observed by cyclic voltammetry. Hydroxide adsorption scans swept between -0.1 and 0.6 V and sulfate scans between -0.1 and 0.9 V vs. Ag/AgCl. All scans were taken at 10 mV/s. The current was normalized by the electrochemical surface area of each electrode, measured by underpotential deposition lead stripping.

**Electrochemical Flow Cell Experiments:**

The dual-electrolyte electrochemical reactor was used in this study and has been described previously [21,22]. Two 1.5 mm thick poly(methyl methacrylate) (PMMA) sheets with 0.5-cm wide by 2.0-cm long channels were used to provide the electrolyte flow channels for the catholyte (liquid stream in contact with the cathode; pure EMIM BF₄) and anolyte (liquid stream in contact with the anode; 0.5 M sulfuric acid). Between the two electrolyte channels was a 0.8-cm wide and 2.5-cm long piece of Nafion 212 membrane (DuPont) used to separate the catholyte and anolyte while maintaining ionic conductivity. The cathode and anode that were made of gas diffusion electrodes (GDEs) were put on each PMMA sheet. Each electrode was backed by aluminum current collectors. Notice that the aluminum current collector that backed the cathode also served as a gas flow chamber to supply CO₂, while the anode was open to the atmosphere for oxygen to escape. The assembly was held together with 4 bolts using Teflon washers to maintain electric isolation between electrodes.

The electrodes were prepared as previously reported² using Sigracet 35 BC gas diffusion layers (GDLs) (Ion Power, Inc.). In short, a suspension of catalyst and Nafion binder (5 wt% Nafion ionomer in water, Solution Technology) was made by sonicating with a 50/50 vol% mixture of
water and isopropyl alcohol (Sigma-Aldrich), which was then painted on the GDL using a paint brush. The cathodes consisted of 5 mg/cm² Ag (three different particle sizes: 40 nm, 70 nm, and 200 nm) and 0.15 mg/cm² Nafion. The same anode that consisted of 5 mg/cm² Pt black (Alfa Aesar) and 0.15 mg/cm² Nafion was used for all of the cathodes.

The cell testing procedures are as follows. An Autolab Potentiostat (PGSTAT-30, EcoChemie) was used to control the cell potential and measure the resulting current. At each cell potential, the cell was allowed to reach steady state for 200 s, after which the gaseous products as well as unreacted CO₂ were collected and injected into the gas chromatography (GC) instrument (Trace GC, ThermoFisher Scientific) for quantitative determination of the composition of products. A mass flow controller (32907-80 Cole Palmer) was used to flow CO₂ (100%, S.J Smith) from a cylinder at a flow rate of 7 sccm and at 25°C, and a syringe pump supplied both electrolytes at 0.5 mL/min. The catholyte was pure EMIM BF₄ (≥98%, Sigma-Aldrich) and the anolyte was 0.5 M sulfuric acid (95-98%, Sigma-Aldrich).
5.8 References


Chapter 6

Gold Nanoparticles on Polymer-Wrapped Multiwall Carbon Nanotubes: An Efficient and Selective Catalyst for CO₂ Reduction*

6.1 Chapter Overview

Current, and still rising, atmospheric CO₂ levels have been linked to climate change, necessitating multifaceted approaches to curb further undesired effects. CO₂ capture followed by electrochemical reduction utilizing excess renewable energy from intermittent renewable sources may provide a way to reduce CO₂ emissions while producing building blocks for chemicals. Current performance levels, however, are insufficient for commercialization, in part due to the unavailability of catalysts with adequate activity and selectivity. Here we report the structural and electrochemical characterization of a catalyst system for the electrochemical reduction of CO₂ to CO: Au nanoparticles supported on polymer-wrapped multiwall carbon nanotubes. This catalyst exhibits a high selectivity for CO over H₂: 80-92% CO, as well as a high activity: a maximum partial current density for CO exceeding the performance of state-of-the-art Ag nanoparticle catalyst (160 vs. 90 mA/cm²). The observed high activity, originating from a high electrochemically-active surface area (23 m²/g Au), in combination with the low loading (0.17 mg/cm²) of the highly dispersed Au nanoparticles underscores this catalyst’s promise for efficient electrochemical reduction of CO₂.

6.2 Introduction

The continuous, steady increase in atmospheric CO₂ levels has been linked to climate change, leading to, for example, erratic weather patterns and rising ocean temperatures.[1]

* This chapter has been adapted from the following publications:
Slowing down, and eventually curbing, the increase in atmospheric CO₂ levels will require concurrent implementation of multiple approaches, including switching from fossil fuel-burning power plants to renewable energy sources; increasing the energy efficiency of buildings; increasing the fuel efficiency of vehicles or switching to electric vehicles; and carbon capture and sequestration.[2, 3] Also, addressing the main challenge of implementing renewable sources such as wind and solar, their intermittency, will require development of a scalable and broadly deployable means for storage of electricity.

One option to both reduce CO₂ emissions and to provide a potential means for energy storage at scale is the electrochemical reduction of CO₂ into chemicals that can be stored and transported at scale, and used upon demand.[4-6] Technically, electrochemical reduction of CO₂ is analogous to running a fuel cell in reverse. The CO₂ reduction reaction takes place at the cathode, while typically the water oxidation reaction or chlorine evolution reaction take place at the anode. Over the past few decades, research has mostly focused on the half-reaction of the cathode (i.e., the CO₂ reduction reaction). Prior work by Hori et al. has shown that use of different metal catalysts lead to different predominant products.[7] For example, group 1 metals such as Au and Ag lead to carbon monoxide (CO), group 2 metals such as Pb and Sn lead predominantly to formic acid, group 3 metals such as Pt and Fe lead to H₂, whereas group 4 metals such as Cu lead to mixtures of short hydrocarbons.[7] Here we focus on catalysts for selective production of CO because CO is a key building block for chemical synthesis, for example through the Fischer-Tropsch process which can produce higher hydrocarbons. To date, the best performance for electrochemical reduction of CO₂ to CO has been achieved with precious metal catalysts such as silver (Ag) and gold (Au).[4, 8-10] Previously we have reported that under ambient conditions a partial current density for CO as high as 91 mA/cm² in
combination with a Faradaic efficiency of 94% for CO at energy efficiencies as high as 46% can be achieved using a gas diffusion electrode (GDE) covered with a catalyst layer of Ag nanoparticles.[8] Dufek et al. have reported improved reactor performance at elevated temperature and/or pressure, specifically current densities as high as 350 mA/cm$^2$ in combination with a Faradaic efficiency of 82% for CO, but at an energetic efficiency of less than 30%.[11, 12] This performance, especially the low energy efficiency, is insufficient for this approach to become an economically viable process, which probably would require an energy efficiency of >50%.[13] Currently no catalysts are known that exhibit sufficient activity (i.e., >250 mA/cm$^2$) at a sufficiently low overpotential to ensure an energy efficiency exceeding 50%. Prior experimental and computational studies suggest that Au might be a better catalyst than the frequently studied Ag.[7, 9, 14] For example, Au nanoparticles have been shown to exhibit a higher activity and a lower onset for reduction of CO$_2$ to CO.[9] However, Au nanoparticles are known to lack stability due to aggregation.[9]

A common approach to lower the loading of precious metal catalyst is the use of high-surface-area catalyst support such as carbon black, titanium dioxide, or carbon nanotubes.[15] This approach may also improve catalyst stability (e.g., prevent particle aggregation). Among these various catalyst supports, carbon nanotubes (CNTs) provide high electrical conductivity, good electrochemical durability, and high surface area to support catalyst particles. Catalyst nanoparticles can be deposited on CNTs using a variety of deposition methods, including impregnation, ultrasound, sputter deposition, precipitation, and electrochemical deposition.[15] To overcome their chemically inert nature, CNTs are often oxidized using a strong acid solution (mixture of H$_2$SO$_4$ and HNO$_3$) to introduce COOH and OH groups on the surface to make the surface more hydrophilic, thus enhancing the binding of metal nanoparticles to CNTs.[15, 16]
However, treatment with strong acid also affects the durability of CNT-based electrocatalysts.[16] An alternative approach to enhance nanoparticle adhesion that does not involve oxidation with strong acid involves wrapping multi-wall carbon nanotubes (MWNTs) with polymers.[16-19] The polymer (e.g., polybenzimidazole (PBI) and pyridine-containing polybenzimidazole (PyPBI)) provides nucleation sites for in-situ growth of Pt nanoparticles. In prior work, some of us have used the resulting polymer-wrapped MWNTs covered with Pt nanoparticles as catalyst for the oxygen reduction reaction (ORR) in both acidic and alkaline fuel cells.[16-19] Compared to Pt on carbon black or Pt on oxidized MWNTs, the highly dispersed Pt nanoparticles (particle size: 3.2 ± 0.78 nm) on polymer-wrapped MWNTs exhibit increased catalyst activity as a result of a higher electrochemically active surface area (ECSA) while still providing high catalyst stability at low Pt loadings (0.45 mg/cm²).

Here we adopt this strategy to obtain a highly active and stable catalyst for CO₂ reduction: Au nanoparticles on polymer wrapped MWNTs (MWNT/PyPBI/Au, Figure 1). As for the prior work on Pt supported on polymer wrapped MWNTs, we expect this approach (i) to ensure a low loading of Au; (ii) to yield surface-bound Au nanoparticles in a size range that provides a high electrochemically active surface area and thus high activity; and (iii) to prevent Au nanoparticle aggregation typically observed when they are supported via other methods. For comparison we also created a similar catalyst supported on polymer-wrapped carbon black (CB/PyPBI/Au).

6.3 Experimental

6.3.1 Preparation of the MWNT/PyPBI/Au catalyst

The pyridine-containing polybenzimidazole (Poly[2,2'-(2,6-pyridyl)-5,5'-bibenzimidazole]), PyPBI, was prepared using the previously described method.[18] To wrap the MWNTs (Nikkiso
Co) with the PyPBI, 4 mg of the as-prepared PyPBI was dissolved in 20 mL of \( N,N \)-dimethylacetamide (DMAc), followed by addition of 20 mg of the MWNT. The resulting mixture of MWNT and PyPBI in DMAc was then sonicated for 4 hours to ensure uniform wrapping of the MWNTs with the PyPBI. After sonication, the mixture was filtered using the PTFE filter paper (0.2 µm pore size, Millipore) and rinsed with DMAc twice to remove residual PyPBI, followed by drying under vacuum overnight. The resulting black powder is herein referred to as MWNT/PyPBI.

The synthesis of Au NPs on the MWNT/PyPBI is described as follows. First, 5 mg of MWNT/PyPBI powder was dispersed in 10 mL of an ethylene glycol/water mixture \((v/v=6/4)\) via sonication for 1 hour. Second, 0.946 mL of 1.4 mM HAuCl\(_4\) in water purchased from Wako (4.5 mg Au) was diluted with 15 mL of an ethylene glycol/water mixture \((v/v=4/1)\). Next, the MWNT/PyPBI suspension was added into the dilute HAuCl\(_4\) solution. After stirring for 5 minutes, 3 mL of 0.1 mM NaBH\(_4\) in water was added in. The mixture of MWNT/PyPBI, HAuCl\(_4\) and NaBH\(_4\), ethylene glycol and water was continually stirred for 24 hours at room temperature under N\(_2\). The mixture was then filtered using a PTFE filter paper (0.1 µm pore size, Millipore) and dried under vacuum overnight. The resulting black powder is herein referred to as MWNT/PyPBI/Au. The MWNT/PyPBI/Au consists of 50 wt.% Au and 50 wt.% MWNT/PyPBI as measured using the thermal gravimetric analysis (TGA).

### 6.3.2 Three-electrode cell operation

High purity water (18 MΩ) was obtained from a Millipore water purification system. All reagents were analytical grade and used as received. The three-electrode cell experiments were carried out using a CH Instruments bipotentiostat. The electrochemical cell consisted of a Au wire counter electrode and a “no-leak” Ag/AgCl reference electrode (Cypress), separated from
the working electrode by means of a Luggin capillary. Electrochemical measurements were all recorded and reported versus the Ag/AgCl electrode. The catalysts for the three electrode cell experiments were prepared as follows: catalyst inks containing the powder catalyst (enough to contain 1.0 mg Au) and Nafion (5 wt%, Aldrich) in a mass ratio of catalyst to Nafion of 30/1 were prepared in 1 mL of an isopropyl alcohol/H₂O mixture (v/v = 4/1) and sonicated prior to electrode preparation. A 10 μL drop of the catalyst ink was deposited and dried under flowing Ar on a rotating ring-disk electrode (Pine Instruments), comprised of a polished (0.05 micron alumina) glassy carbon disk electrode (0.196 cm²) with a Pt ring.

Prior to measurements of reduction activity as well as the ECSA measurements, the electrochemical cell was purged with Ar gas. Gas flow was then redirected to maintain Ar flow over the top of the 1 M KCl (≥99.9995% Sigma Aldrich) or 0.5 M H₂SO₄ (J. T. Baker) electrolyte solution. Data collection under CO₂ first involved purging the electrolyte solution, followed by the reduction of gas flow into the electrolyte solution prior to data collection.

**6.3.3 Electrochemical testing procedures in a flow cell**

CO₂ electrolysis experiments were conducted using a potentiostat (Autolab PG30) at room temperature and ambient pressure. CO₂ gas (S.J. Smith, 100%) was fed at a rate of 7 sccm. In all experiments, the electrolyte flow rate was 0.5 mL/min controlled by a syringe pump (Harvard Appartus PhD 2000). The electrolyte was 1 M potassium chloride (KCl, Sigma-Aldrich, ≥99.9995% pure) in water. Millipore water was used for all electrolytes. Electrolysis cell polarization curves were obtained by steady-state chronoamperometric measurements in which gaseous products, as well as unreacted CO₂, were collected and injected into a gas chromatograph (Trace GC, ThermoFisher Scientific) equipped with a thermal conductivity detector for quantitative determination of product composition. Individual anode and cathode
polarization curves were independently measured using an external Ag/AgCl reference electrode which was ionically connected to the electrolyzer.

6.4 Results and Discussion

The synthesis procedures of the MWNT/PyPBI/Au and CB/PyPBI/Au catalysts as well as the corresponding TEM images are shown in Figure 6.2. First the MWNT/PyPBI (or CB/PyPBI) catalyst support is prepared by suspending the MWNTs (or CB) in a PyPBI solution in \( N, N\)-dimethylacetamide (DMAc). The mixture was sonicated for 4 hours to ensure uniform wrapping of the PyPBI. After sonication, the mixture was filtered, rinsed, and dried under vacuum to yield either the MWNT/PyPBI or the CB/PyPBI catalyst support. Second, Au nanoparticles were grown \textit{in-situ} on the surface of the these two catalyst supports. Specifically, the MWNT/PyPBI (or CB/PyPBI) powder was re-suspended in an ethylene glycol/water mixture (v/v = 3/2) and chloroauric acid (HAuCl\(_4\)) was dissolved in the same solvent. Then the two solutions were mixed in a certain ratio, and upon the addition of sodium borohydride (NaBH\(_4\)) reduction of Au\(^{III}\) to Au\(^0\) is induced on the MWNT/PyPBI (or CB/PyPBI) support, leading to nanoparticle nucleation and growth. The two products are obtained after extensive stirring and filtration. Further details are provided in the \textit{Methods} section and in the \textit{Supplementary Information}.

We characterized the MWNT/PyPBI/Au and CB/PyPBI/Au catalysts using TEM (Figure 6.2c and 2d), XRD (Supplementary Figure S1), and thermal gravimetric analysis (TGA). Figure 6.2c and 6.2d show that 1-20 nm Au nanoparticles are uniformly embedded on the surface of the MWNT/PyPBI and CB/PyPBI supports. The XRD diffraction patterns show that the Au nanoparticles in all Au-based samples are polycrystalline. TGA measurements show that the Au content of the MWNT/PyPBI/Au and CB/PyPBI/Au samples is 50 and 45 wt.\%, respectively.
Electrochemical characterization revealed that MWNT/PyPBI/Au outperformed CB/PyPBI/Au as well as unsupported Ag, unsupported Au, and Au supported on carbon black (CB/Au) for the reduction of CO₂. We performed these tests in a previously-reported microfluidic CO₂ electrolysis cell, using gas diffusion electrodes (GDEs) that were covered with the different catalysts, all at identical metal loading (0.17 mg Au/cm²), deposited using an automated airbrush method. Details on cell assembly, testing procedures, and data analysis can be found in the Supplementary Information. The results show that under ambient conditions the different Au-based catalysts yield different partial current densities for CO production. The lowest current densities for CO are found with Au particles deposited directly onto the GDE surface. Increasingly higher partial current densities for CO are achieved for the Au-based catalysts supported on CB (CB/Au), supported on polymer-wrapped CB (CB/PyPBI/Au), and supported on polymer-wrapped MWNTs (MWNT/PyPBI/Au). To our knowledge, the 160 mA/cm² partial current density for CO production observed for MWNT/PyPBI/Au at a potential of -1.78 V vs. Ag/AgCl under ambient conditions is the highest performance observed to date. In comparison, CB/PyPBI/Au and CB/Au reach a partial current density for CO of 90-100 mA/cm² at similar cathode potentials, while all other catalyst and control samples exhibit significantly lower current densities.

We also characterized the different catalysts using a standard 3-electrode electrochemical cell, specifically to determine their ECSA by comparing the area of the cathodic Au oxide stripping peak observed for each sample. These measurements, summarized in Table 6.1, demonstrate that the MWNT/PyPBI/Au catalyst exhibits the highest ECSA (23 m²/g Au), about 25% higher than the ECSA found for CB/PyPBI/Au, at least twice as high as the ECSA found for CB/Au, and about 8 times higher than the ECSA of unsupported Au
particles (unsupported Au < CB/Au < CB/PyPBI/Au < MWNT/PyPBI/Au). These increases in ECSA for the different catalysts correspond qualitatively with the trends in the observed relative partial current densities for CO. This suggests that the catalytic performance enhancements observed can be attributed largely to the increase in ECSA when the catalytically active nanoparticles are deposited in unsupported fashion or on different support materials.

Figure 6.3c and 6.3d show the Faradaic efficiencies for CO and H₂, respectively, for the various catalyst samples and controls deposited on the electrodes that were tested in the microfluidic flow cell. Up to a cathode potential of -1.5 vs. Ag/AgCl, exhibit selectivity similar to what has been observed previously for unsupported Au and Ag: After the onset region (approximately -1.0 to -1.1 V), the Faradaic efficiency for CO rapidly climbs to stable levels of 80-100%. The electrodes with MWNT/PyPBI/Au as well as with unsupported Ag exhibit the best selectivity for CO, exceeding 90%. At cathode potentials exceeding -1.5 V, a drop in the selectivity for CO is apparent for all Au-based samples. In part this can be explained by the increased evolution of H₂, whose production is known to be catalyzed by carbon supports at these potentials.[8] Also, at these cathode potentials large amounts of gaseous CO and H₂ are produced leading to the formation of bubbles in the flow cell, which possibly lowers the amount of reaction products that are actually recorded in GC analysis of the product mixture. In general, one would not want to operate an electrolyzer for electrochemical reduction of CO₂ to CO at cathode potentials exceeding -1.5 V, in order to retain an energy efficiency exceeding 50%. For example, the energy efficiency for MWNT/PyPBI/Au at -1.39 V equals 55%, whereas it drops to 39% at -1.78V.

This platform of polymer-wrapped CNTs has proven to be successful in leading to the higher utilization efficiency of Pt nanoparticles with respect to their subsequent activity as a fuel cell
electrocatalysts.[16-19, 21] Because of this increased utilization, reduction of total metal loading is possible without sacrificing overall activity and selectivity. Similar to our previously-reported Pt-based catalysts for polymer electrolyte membrane fuel cells (PEMFCs) such as the MWNT/PyPBI/Pt and MWNT/PBI/Pt, these hybrid materials comprising of Au particles on polymer-wrapped catalyst supports (MWNT/PyPBI/Au) may provide an ideal three-phase boundary for CO₂ reduction at which effective transport of electrons, protons, and gaseous CO₂ and CO can occur. The MWNT/PyPBI/Au catalyst exhibits a high selectivity for CO over H₂: 80-92% CO, as well as a high activity: a maximum partial current density for CO exceeding the performance of state-of-the-art Ag nanoparticle catalyst (160 vs. 90 mA/cm²), in combination with the low loading (0.17 mg/cm²) of the highly dispersed Au nanoparticles. This low Au loading is similar to targets set for precious metal content of electrodes for similar electrocatalytic processes such as fuel cells.[22] We also tested the stability of this catalyst in a 3-electrode cell by holding the cell potential at -1.6V over 26 hours. During this time the electrode actually slowly improved in performance, by about 12% (See SI for details).

6.5 Conclusions

In conclusion, these studies demonstrate that MWNT/PyPBI platform is a promising material to serve as a support for Au nanoparticles, small particles, no aggregation, stable performance. The maximum current density of 160 mA/cm² exceeds the performance levels of 90-100 mA/cm² typically obtained with Ag nanoparticles, the best catalyst for electroreduction of CO₂ to CO reported to date.

Wrapping MWNTs with a polymer again showed to be an excellent approach as a support material to stabilize highly active precious metal catalyst for electrocatalysis. Indeed, this approach may also beneficial for other metal nanoparticle catalysts for the electroreduction of
CO2 to other products. Moreover, the polymer-wrapped MWNT-supported Au catalyst reported here may be promising for a variety of other catalytic reactions known to be catalyzed by Au, for example for low-temperature water gas shift reactions and NO reduction with hydrocarbons, both of industrial relevance.
6.6 Figures and Tables

Figure 6.1. Schematic representation of the microfluidic electrolysis cell used in this study for electroreduction of CO\textsubscript{2} to CO. Top-right: Schematic representation of the Au catalyst supported on polymer wrapped multiwall nanotubes (MWNT/PyPBI/Au) studied here. Top-left: Reconstructed 3D view (obtained from MicroCT data) of a gas diffusion electrode coated with a MWNT/PyPBI/Au catalyst layer (0.17 mg Au/cm\textsuperscript{2}), deposited via automated airbrushing.
Figure 6.2. Synthesis procedure and TEM images of the as-produced catalysts. Schematic representation of the preparation of (a) MWNT/PyPBI/Au and (b) CB/PyPBI/Au used in this study. TEM images of the as-synthesized catalysts: (c) MWNT/PyPBI/Au (50 wt.% Au) and (d) CB/PyPBI/Au catalyst (45 wt.% Au).
Figure 6.3. Results of electrochemical reduction of CO\textsubscript{2} in a flow reactor. Partial current density of (a) CO and (b) H\textsubscript{2} as well as Faradaic efficiency for (c) CO and (d) H\textsubscript{2} as a function of cathode potential (V) vs. Ag/AgCl. The error bars represent the standard deviation of the average of three experiments (N=3). Cathode catalyst: 0.34 mg/cm\textsuperscript{2} MWNT/PyPBI/Au (50 wt% Au, ca. 0.17 mg Au/cm\textsuperscript{2}); 0.38 mg/cm\textsuperscript{2} CB/PyPBI/Au (45 wt% Au, ca. 0.17 mg Au/cm\textsuperscript{2}); 0.28 mg/cm\textsuperscript{2} CB/Au (60 wt% Au, ca. 0.17 mg Au/cm\textsuperscript{2}); 0.16 mg/cm\textsuperscript{2} Au; 0.19 mg/cm\textsuperscript{2} MWNT/PyPBI; 0.19 mg/cm\textsuperscript{2} CB/PyPBI. Anode catalyst: 4.25 mg/cm\textsuperscript{2} Pt black. Reactant streams: 7 sccm CO\textsubscript{2}. Electrolyte: 1.0 M KCl flowing at 0.5 mL/min. Data collected at room temperature and ambient pressure.
Table 6.1. Summary of results obtained from cyclic voltammetry of samples with Au content. Estimation of Au electroactive surface area using charge associated with stripping of the Au surface oxide (420 μC cm\(^{-2}\)) [23] and electrical charge associated with the integration of the oxide peak between the potential limits of 0.9 V to 0.5 V [20, 24]. Three independent trials, each with recast electrodes, are factored into each average value reported.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Electrical charge (μC)</th>
<th>Specific electrochemically active surface area (m²/g Au)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au</td>
<td>110 ± 40</td>
<td>3 ± 1</td>
</tr>
<tr>
<td>CB/Au</td>
<td>410 ± 80</td>
<td>10 ± 2</td>
</tr>
<tr>
<td>CB/PyPBI/Au</td>
<td>740 ± 100</td>
<td>18 ± 3</td>
</tr>
<tr>
<td>MWNT/PyPBI/Au</td>
<td>950 ± 50</td>
<td>23 ± 1</td>
</tr>
</tbody>
</table>
6.7 Supporting Information

CATALYST PREPARATION

Preparation of the MWNT/PyPBI/Au catalyst

(1) Synthesis of the polymer-wrapped catalyst support, MWNT/PyPBI

The MWNTs were supplied by Nikkiso Co. The pyridine-containing polybenzimidazole (Poly[2,2’-(2,6-pyridyl)-5,5’-bibenzimidazole]), PyPBI, was prepared using the previously described method.[Fujigaya, Okamoto, Nakashima, Carbon, 2009] To wrap the MWNTs with the PyPBI, 4 mg of the as-prepared PyPBI was dissolved in 20 mL of N, N-dimethylacetamide (DMAc), followed by addition of 20 mg of the MWNT. The resulting mixture of MWNT and PyPBI in DMAc was then sonicated for 4 hours to ensure uniform wrapping of the MWNTs with the PyPBI. After sonication, the mixture was filtered using the PTFE filter paper (0.2 µm pore size, Millipore) and rinsed with DMAc twice to remove residual PyPBI, followed by drying under vacuum overnight. The resulting black powder is herein referred to as MWNT/PyPBI.

(2) Deposition of Au nanoparticles on the MWNT/PyPBI to form the MWNT/PyPBI/Au

The deposition of Au nanoparticles on the MWNT/PyPBI catalyst support was carried out via an in-situ surface growth method. Specifically, chloroauric acid (HAuCl₄) in an ethylene glycol/water mixture (v/v=3/2) was used as the Au precursor and the reduction of Au⁺ to Au° takes place upon the addition of the reducing agent, sodium borohydride (NaBH₄). The PyPBI on the surface of the MWNT/PyPBI support provides effective binding sites for the nucleation and growth of Au nanoparticles. Thus, Au nanoparticles tend to grow directly onto the catalyst support, MWNT/PyPBI, as opposed to forming Au agglomerates in the bulk solution. We have observed that the reaction temperature, concentration of the chloroauric acid, amount of the reducing agent and uniform mixing are crucial to the formation of uniformly-distributed Au nanoparticles on the MWNT/PyPBI support. Therefore, we have optimized the synthesis procedures and the details are described as follows:

First, 5 mg of MWNT/PyPBI powder was dispersed in 10 mL of an ethylene glycol/water mixture (v/v=6/4) via sonication for 1 hour. Second, 0.946 mL of 1.4 mM HAuCl₄ in water (4.5 mg Au) was diluted with 15 mL of an ethylene glycol/water mixture (v/v=4/1). Next, the MWNT/PyPBI suspension was added into the dilute HAuCl₄ solution. After stirring for 5
minutes, 3 mL of 0.1 mM NaBH₄ in water was added in. The mixture of MWNT/PyPBI, HAuCl₄ and NaBH₄, ethylene glycol and water was continually stirred for 24 hours at room temperature under N₂. The mixture was then filtered using a PTFE filter paper (0.1 µm pore size, Millipore) and dried under vacuum overnight. *The resulting black powder is herein referred to as MWNT/PyPBI/Au.* The MWNT/PyPBI/Au consists of 50 wt.% Au and 50 wt.% MWNT/PyPBI as measured using the thermal gravimetric analysis (TGA).

**Sources of other commercial samples (CB/Au, Au, Ag)**

Detailed information of the commercial samples used in this study is described in Table 6.2. Average particle sizes of the metal (Ag or Au) nanoparticles were measured using TEM.

**Table 6.2. Sources and average particle size of the commercial samples used in this study**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Vendor</th>
<th>Sample description on the vendor’s webpage</th>
<th>Average particle size</th>
</tr>
</thead>
<tbody>
<tr>
<td>CB/Au</td>
<td>E-Tek</td>
<td>60 wt.% Au on carbon black</td>
<td>Mainly ~5-10 nm Au; large Au agglomerates of ~20-35 nm are also observed</td>
</tr>
<tr>
<td>Au</td>
<td>Sigma Aldrich</td>
<td>Au nanopowder, &lt;100 nm particle size</td>
<td>~70 nm Au</td>
</tr>
<tr>
<td>Ag</td>
<td>Sigma Aldrich</td>
<td>Ag nanopowder, &lt;100 nm particle size</td>
<td>~70 nm Ag</td>
</tr>
</tbody>
</table>

**CATALYST CHARACTERIZATION**

**Transmission electron microscopy (TEM)**

TEM was used to determine the morphology of the catalysts (JEOL, JEM2010), operated at 200 kV. The catalyst powder was suspended in isopropyl alcohol (Sigma-Aldrich) and sonicated for 30 minutes to ensure good catalyst dispersion. A very dilute concentration was needed to acquire TEM images. TEM grids were prepared by putting a few droplets of the dilute suspension on copper grids and dried overnight.

**Wide-angle X-ray diffraction (WAXD / XRD)**
XRD measurements were carried out to study the crystal structure of the Au nanoparticles on all Au-containing samples. The catalyst powder was suspended in paratone oil for XRD measurements. All spectra are background corrected to take out the paratone oil scattering peak as well as the amorphous contribution from the sample. Figure 6.4 shows the XRD results.

![XRD Diffraction Patterns](image)

**Figure 6.4.** XRD diffraction patterns of the four Au-containing samples (MWNT/PyPBI/Au, CB/PyPBI/Au, CB/Au, and Au) as well as one of the control samples (MWNT/PyPBI). The other control sample, CB/PyPBI, only shows amorphous scattering in the diffraction pattern and thus its background corrected XRD pattern is not shown here. All diffractograms of the Au-containing samples exhibit the same six characteristic diffraction peaks of polycrystalline Au. Also, the diffractograms of MWNT/PyPBI/Au and MWNT/PyPBI both exhibit the diffraction peak at ~27°, which can be attributed to the graphite structure (002) of MWNTs.

**Electrochemical measurements in a three-electrode electrochemical cell**

**Three-electrode cell operation**
High purity water (18 MΩ) was obtained from a Millipore water purification system. All reagents were analytical grade and used as received. The three-electrode cell experiments were carried out using a CH Instruments bipotentiostat. The electrochemical cell consisted of a Au wire counter electrode and a “no-leak” Ag/AgCl reference electrode (Cypress), separated from the working electrode by means of a Luggin capillary. Electrochemical measurements were all recorded and reported versus the Ag/AgCl electrode. The catalysts for the three electrode cell experiments were prepared as follows: catalyst inks containing the powder catalyst (enough to contain 1.0 mg Au) and Nafion (5 wt%, Aldrich) in a mass ratio of catalyst to Nafion of 30/1 were prepared in 1 mL of an isopropyl alcohol/H₂O mixture (v/v = 4/1) and sonicated prior to electrode preparation. A 10 μL drop of the catalyst ink was deposited and dried under flowing Ar on a rotating ring-disk electrode (Pine Instruments), comprised of a polished (0.05 micron alumina) glassy carbon disk electrode (0.196 cm²) with a Pt ring.

Prior to measurements of reduction activity as well as the ECSA measurements, the electrochemical cell was purged with Ar gas. Gas flow was then redirected to maintain Ar flow over the top of the 1 M KCl (≥99.9995% Sigma Aldrich) or 0.5 M H₂SO₄ (J. T. Baker) electrolyte solution. Data collection under CO₂ first involved purging the electrolyte solution, followed by the reduction of gas flow into the electrolyte solution prior to data collection.

Cyclic voltammetric measurements of reduction activity

Supplementary Figure S2 shows the reduction activity of samples with a CO₂ feed compared their respective activity under Ar.
Figure 6.5. Cyclic voltammetric measurements of reduction activity of (a, b) control samples as well as (c-f) Au catalysts with a CO$_2$ feed compared to their respective activity under Ar. Data was recorded in 1M KCl at 50 mV/s.
Electrochemically-active surface area (ECSA) measurements

Supplementary Figure S3 shows the results of the measurements of the ECSA of Au on all Au catalysts.

**Figure 6.6.** Cyclic voltammetric measurements of Au samples deposited on a glassy carbon RDE in a 3-electrode cell (0.5 M H$_2$SO$_4$, 0.1 V/s), where each trial demonstrates a new ink deposition. A peak associated with the reduction of Au oxide appears between 0.9 and 0.5 V in the negative-going scans for each sample.
ELECTROCHEMICAL MEASUREMENTS IN A FLOW CELL

Preparation of GDEs

Previously we have reported the preparation of GDEs for use in a CO₂ electrolysis cell. In short, Sigracet 35 BC gas diffusion layers (GDLs, Ion Power) were used, which consist of 5 wt% poly-tetrafluoroethylene (PTFE)-treated carbon paper that has a teflonized microporous layer on one side. The cathodes were air-brushed whereas the anode was hand-painted using previously described methods. The preparation of catalyst inks for cathodes is as follows:

(1) Au catalysts (MWNT/PyPBI/Au, CB/PyPBI/Au, CB/Au, Au)

The catalyst inks were prepared as follows: catalyst inks containing the powder catalyst (enough to contain 0.17 mg/cm² Au) and Nafion (5wt.% Nafion solution, Aldrich) in a mass ratio of catalyst to Nation of 30/1 were prepared in 1 mL of an isopropyl alcohol/H₂O mixture (v/v = 4/1) as the carrier solvent and sonicated for 30 minutes prior to deposition onto the GDE. Note that the actual amounts of catalyst powder added to the vial varied from sample to sample to account for the difference in Au content as well as losses of catalyst during the deposition.

(2) Ag catalysts (Ag)

The catalyst inks were prepared as follows: catalyst inks containing the powder Ag catalyst (enough to contain 0.75 mg/cm² Ag) and Nafion (5wt.% Nafion solution, Aldrich) in a mass ratio of catalyst to Nation of 30/1 were prepared in 0.4 mL of an isopropyl alcohol/H₂O mixture (v/v = 1/1) as the carrier solvents.

(3) Control samples (MWNT/PyPBI, CB/PyPBI)

The catalyst inks were prepared as follows: catalyst inks containing the polymer-wrapped supports (enough to contain 0.19 mg/cm² MWNT/PyPBI or CB/PyPBI) and Nafion (5wt.% Nafion solution, Aldrich) in a mass ratio of catalyst to Nation of 30/1 were prepared in 1 mL of an isopropyl alcohol/H₂O mixture (v/v = 4/1) as the carrier solvents.
For the hand-painted anodes, catalyst inks were prepared by mixing 10 mg Pt black (Alfa Aesar) and 6.9 μL Nafion solution, and adding 400 μL of Millipore water and 400 μL isopropyl alcohol as the carrier solvents. The same anode that was used for all measurements had a catalyst loading of 4.25 mg/cm² Pt black.

All inks were sonicated for 30 minutes to ensure uniform mixing and were either hand-painted using a paintbrush or air-brushed using an automated air-brushing deposition setup onto the teflonized carbon side of the GDL to create a GDE covered with catalyst over a geometric area of 2 cm². Importantly, the actual catalyst loading of the GDEs (to account for losses during the deposition) was determined by weighing the GDE before and after deposition and was indicated in all figure captions in the paper.

### Table 6.3. Catalyst ink formulations of Au samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Au content of the catalyst (wt.%)</th>
<th>Target Au loading on the GDE (mg/cm²)</th>
<th>Target amount of catalyst powder on the GDE (mg)</th>
<th>Amount of catalyst powder to add to vial (mg)*</th>
<th>Amount of Nafion solution to add to vial (μL)</th>
<th>Amount of carrier solvent to add to vial (mL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MWNT/PyPBI/Au</td>
<td>50</td>
<td>0.17</td>
<td>0.650</td>
<td>1.625</td>
<td>1.243</td>
<td>1</td>
</tr>
<tr>
<td>CB/PyPBI/Au</td>
<td>45</td>
<td>0.17</td>
<td>0.722</td>
<td>1.806</td>
<td>1.381</td>
<td>1</td>
</tr>
<tr>
<td>CB/Au</td>
<td>60</td>
<td>0.17</td>
<td>0.542</td>
<td>1.354</td>
<td>1.036</td>
<td>1</td>
</tr>
<tr>
<td>Au</td>
<td>100</td>
<td>0.17</td>
<td>0.325</td>
<td>0.813</td>
<td>0.622</td>
<td>1</td>
</tr>
</tbody>
</table>

- It has accounted for 60% losses of catalysts during the deposition.

### Cell assembly

Two catalyst-coated GDEs, an anode and a cathode, were placed on opposite sides of a 0.15-cm thick poly(methyl methacrylate) (PMMA) sheet with 0.5-cm wide by 2.0-cm long window (1 cm²) such that the catalyst layers faced the flowing liquid electrolyte. The geometric surface area used to calculate current density is 1 cm². This three-layer assembly was clamped between two aluminum current collectors with access windows. On the cathode side an aluminum gas flow chamber supplied CO₂ while the anode was open to the atmosphere so formed O₂ can
escape. The assembly was held together with 4 bolts with Teflon washers to maintain electric isolation between electrodes.

**Electrochemical testing procedures**

CO₂ electrolysis experiments were conducted using a potentiostat (Autolab PG30) at room temperature and ambient pressure. CO₂ gas (S.J. Smith, 100%) was fed at a rate of 7 sccm. In all experiments, the electrolyte flow rate was 0.5 mL/min controlled by a syringe pump (Harvard Appartus PhD 2000). The electrolyte was 1 M potassium chloride (KCl, Sigma-Aldrich, ≥99.9995% pure) in water. Millipore water was used for all electrolytes. Electrolysis cell polarization curves were obtained by steady-state chronoamperometric measurements in which gaseous products, as well as unreacted CO₂, were collected and injected into a gas chromatograph (Trace GC, ThermoFisher Scientific) equipped with a thermal conductivity detector for quantitative determination of product composition. Individual anode and cathode polarization curves were independently measured using an external Ag/AgCl reference electrode which was ionically connected to the electrolyzer.

**Electrochemical data analysis**

The Faradaic efficiency \( FE_k \) of a gaseous product \( k \) was calculated using the following equation:

\[
FE_k = \frac{n_k F x_k F_m}{I}
\]

Where \( n_k \) is the number of electrons exchanged (\( n_k = 2 \) for reduction of CO₂ to CO), \( F \) is Faraday’s constant (\( F = 96485 \) C/mol), \( x_k \) is the mole fraction of the gaseous product \( k \) in the gaseous mixture (also equal to the volume fraction if gases are assumed to be ideal), \( F_m \) is the molar flow rate (mol/s), and \( I \) is the total current (A). Specifically, we calculated \( x_k \) and \( F_m \) using the following equations:

\[
x_k = \frac{F_{v,CO}}{F_{v,CO} + F_{v,CO_2}} = \frac{F_{v,CO}}{F_{v,CO} / F_{v,CO_2}} \frac{1 + F_{v,CO} / F_{v,CO_2}}{I}
\]

\[
F_m = \frac{P F_v}{RT}
\]
Where $F_{v,CO}$ and $F_{v,CO_2}$ are the volumetric flow rates (cm$^3$/s) of CO and CO$_2$, respectively. $P$ is the atmospheric pressure ($P = 1$ atm), $R$ the gas constant ($R = 82.06$ cm$^3$ atm K$^{-1}$ mol$^{-1}$), and $T$ the temperature ($T = 293$ K).

The energetic efficiency ($EE_k$) for the gaseous product $k$ was calculated using the following equation:

$$EE_k(\%) = \frac{E^o}{V_{cell}} \times FE_k(\%)$$

Where $E^o$ is the equilibrium cell potential ($E^o = E^o_{cathode} - E^o_{anode} = -0.10$ V - 1.23 V = -1.33 V for CO$_2$ reduction to CO and $E^o = E^o_{cathode} - E^o_{anode} = 0$ V - 1.23 V = -1.23 V for H$_2$ evolution), $V_{cell}$ is the applied cell potential, and $FE_k$ is the Faradaic efficiency of the gaseous product $k$. The overall cell energetic efficiency is the sum of the energetic efficiencies for CO and H$_2$. 

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6.8 References


Chapter 7

A Nitrogen-Doped Carbon Catalyst for Electrochemical CO₂ Conversion to CO*

7.1 Chapter Overview

We report the structural and electrochemical characterization of a nitrogen-doped carbon catalyst system for the electrochemical reduction of CO₂ to CO; pyrolyzed carbon nitride supported on multiwall carbon nanotubes. This new class of catalyst exhibits a high selectivity for CO over H₂ (~98% CO and ~2% H₂), as well as high activity in an electrochemical flow cell. A maximum partial current density for CO of 90 mA/cm² was obtained, with up to 3.5x higher current density for CO at intermediate cathode potentials (V= -1.46 V vs. Ag/AgCl), as well as higher energy efficiencies (up to 52%) compared to the state-of-the-art silver nanoparticle-based catalysts, under identical experimental conditions. Moving away from precious metal catalysts without sacrificing activity and selectivity may significantly enhance the prospects of electrochemical CO₂ reduction as an approach to reduce atmospheric CO₂ emissions or as a method for load-leveling in relation to the use of intermittent renewable energy sources.

7.2 Introduction

Rising carbon dioxide levels, especially as a result of human activity over the last 100 years, have been linked to climate change, and its associated undesirable effects such as erratic weather patterns and rising ocean temperatures.[1] Multiple approaches, such as carbon sequestration, electrification of the transportation sector, and switching from fossil fuels to renewable energy sources, will need to be implemented to curb the increase in CO₂ levels.[2, 3] Addressing the

* This chapter has been adapted from the following publications:
main challenge of implementing renewable sources such as wind and solar, their intermittency,
will require development of a scalable and broadly deployable means for storage of electricity.
One option to both reduce CO₂ emissions, and providing a potential means for energy storage at
scale is the electrochemical reduction of CO₂ into chemicals that can be stored and transported at
scale, and used upon demand.[4-6] However, catalysts for electrochemical reduction of CO₂ into
product such as CO, formic acid, methanol, and small hydrocarbons currently do not exhibit
sufficient activity and selectivity for this application. Metals such as silver (Ag), and gold (Au),
exhibit best performance for conversion of CO₂ to CO,[4, 7-9] but high cost, sensitivity to
poisoning, difficulty of regeneration / reclamation, and insufficient activity hampers their utility.
Here we explore non-precious, carbon-based catalysts for the electrochemical reduction of CO₂
to CO, particularly a new nitrogen-doped carbon catalyst system, consisting of carbon nitride
supported on multiwall carbon nanotubes (MWCNTs) (CN/MWCNT, Figure 7.1a).

7.3 Experimental

7.3.1 Catalyst Preparation

The synthesis of this nitrogen-doped carbon-based catalyst for CO₂ reduction is
straightforward. Cyanuric chloride (1,3,5-trichlorotriazine; C₃N₃Cl₃), sodium azide (NaN₃),
benzene, and multiwall carbon nanotubes were added to a magnetically stirred, stainless-steel
high pressure reactor. All materials were used as-received without further purification. The
reactor was heated to 220°C for 22 hours, and the cyanuric chloride and sodium azide reacted
according to the scheme [10]

\[ \text{C}_3\text{N}_3\text{Cl}_3 + 3\text{NaN}_3 \rightarrow \text{g-C}_3\text{N}_4 + 3\text{NaCl} + 4\text{N}_2 \]

The products, graphitic carbon nitride (g-C₃N₄)-coated MWCNTs, were removed from the
reactor, washed with benzene and Millipore water and then heated overnight at 80°C under
vacuum. Subsequently the material was milled in silicon carbide pots, and then subjected to pyrolysis at 1000°C in flowing N₂. *The resulting black powder is herein referred to as CN/MWCNT.* Note that the as-produced material is referred to as CN/MWCNT as opposed to g-C₃N₄/MWCNT. This is because if the material has been subjected to heat treatment (pyrolysis at 1000°C) it is just nitrogen-doped carbon and most of these pyrolyzed materials are amorphous.

The control sample, Ag nanoparticles, was purchased from Sigma Aldrich (Sigma Aldrich labels its sample as <100 nm). The actual average particle size of this sample is 70 nm as measured by dynamic light scattering and confirmed by TEM.

### 7.3.2 Catalyst Characterization

*Transmission electron microscopy (TEM)*

TEM was used to determine the morphology of the CN/MWCNT catalyst (JEOL, JEM2010), operated at 200 kV. The CN/MWCNT powder was suspended in isopropyl alcohol (Sigma-Aldrich) and sonicated for 30 minutes to ensure good catalyst dispersion. A very dilute concentration was needed to acquire TEM images. TEM grids were prepared by putting a few droplets of the dilute suspension on copper grids and dried overnight.

*CHN elemental analysis*

A CHN elemental analyzer (Yanaco, CHN corder MT-6) was used to determine the nitrogen content of the CN/MWCNT sample.

*X-ray photoelectron spectroscopy (XPS)*

XPS was carried out to characterize the chemical composition and nitrogen types in the carbon matrix of CN/MWCNT. XPS spectra were collected using a Kratos Axis ULTRA X-ray photoelectron spectrometer with monochromatic Al Kα excitation, 120 W (120 kV, 10 mA).
Data were collected using the hybrid lens setting with the slot aperture (300 x 700 mm² analytical area) and charge neutralizer settings of 2.1 A filament current, 2.1 V charge balance and 2V filament bias. Survey spectra were collected as a pass energy of 160 eV and high resolution spectra were collected using a pass energy of 40 eV. The data were fitted with Gaussian-Lorentzian line shapes. The binding energy scale was referenced to the graphitic C1s line at 284.5 eV.

7.3.3 GDE Preparation

Previously we have reported the preparation of GDEs for use in a CO₂ electrolysis cell [11]. In short, Sigracet 35 BC gas diffusion layers (GDLs, Ion Power) were used, which consist of 5 wt% poly-tetrafluoroethylene (PTFE)-treated carbon paper that has a teflonized microporous layer on one side. The cathodes were air-brushed whereas the anode was hand-painted using previously described methods.[11] For the Ag cathodes, catalyst inks were prepared by mixing 2.42 mg Ag catalyst and 1.85 μL Nafion solution, and adding 200 μL Millipore water and 200 μL isopropyl alcohol as the carrier solvents. For the CN/MWCNT cathodes, catalyst inks were prepared by mixing 6.95 mg CN/MWCNT catalyst and 5.33 μL Nafion solution, and adding 200 μL Millipore water and 200 μL isopropyl alcohol as the carrier solvents. For the hand-painted anodes, catalyst inks were prepared by mixing 10 mg Pt black (Alfa Aesar) and 6.9 μL Nafion solution, and adding 400 μL of Millipore water and 400 μL isopropyl alcohol as the carrier solvents. The actual catalyst loading of the GDEs (to account for losses during the deposition) was determined by weighing the GDE before and after deposition. The Ag cathodes were covered with 0.75 mg Ag/cm² and the CN/MWCNT cathodes were covered with 2.39 mg CN/MWCNT/cm². The same anode that was used for all measurements had a catalyst loading of 4.25 mg/cm² Pt black. All inks were sonicated for 20 minutes to ensure uniform mixing and
were either hand-painted using a paintbrush or air-brushed using an automated air-brushing deposition setup onto the teflonized carbon side of the GDL to create a GDE covered with catalyst over a geometric area of 2 cm².

### 7.3.4 Electrochemical Measurements in a Flow Cell

**Cell assembly**

Two catalyst-coated GDEs, an anode and a cathode, were placed on opposite sides of a 0.15-cm thick poly(methyl methacrylate) (PMMA) sheet with a 0.5-cm wide by 2.0-cm long window (1 cm²) such that the catalyst layers faced the flowing liquid electrolyte. The geometric surface area used to calculate current density was 1 cm². This three-layer assembly was clamped between two aluminum current collectors with access windows. On the cathode side an aluminum gas flow chamber supplied CO₂ while the anode was open to the atmosphere so formed O₂ could escape. The assembly was held together with 4 bolts and Teflon washers to maintain electric isolation between electrodes.

**Electrochemical testing procedures**

CO₂ electrolysis experiments were conducted using a potentiostat (Autolab PG30) at room temperature and ambient pressure. CO₂ gas (S.J. Smith, 100%) was fed at a rate of 7 sccm. In all experiments, the electrolyte flow rate was 0.5 mL/min controlled by a syringe pump (Harvard Appartus PhD 2000). The electrolyte was 1 M potassium chloride (KCl, Sigma-Aldrich, ≥99.9995% pure) in water. Millipore water was used for all electrolytes. Electrolysis cell polarization curves were obtained by steady-state chronoamperometric measurements in which gaseous products, as well as unreacted CO₂, were collected and injected into a gas chromatograph (Trace GC, ThermoFisher Scientific) equipped with a thermal conductivity detector for quantitative determination of product composition. Individual anode and cathode
polarization curves were independently measured using an external Ag/AgCl reference electrode which was ionically connected to the electrolyzer.

**Electrochemical data analysis**

The Faradaic efficiency ($FE_k$) of a gaseous product $k$ was calculated using the following equation:

$$FE_k = \frac{n_k F x_k F_m}{I}$$

Where $n_k$ is the number of electrons exchanged ($n_k = 2$ for reduction of CO$_2$ to CO), $F$ is Faraday’s constant ($F = 96485$ C/mol), $x_k$ is the mole fraction of the gaseous product $k$ in the gaseous mixture (also equal to the volume fraction if gases are assumed to be ideal), $F_m$ is the molar flow rate (mol/s), and $I$ is the total current (A). Specifically, we calculated $x_k$ and $F_m$ using the following equations:

$$x_k = \frac{F_{v,CO}}{F_{v,CO} + F_{v,CO_2}} = \frac{F_{v,CO} / F_{v,CO_2}}{1 + F_{v,CO} / F_{v,CO_2}}$$

$$F_m = \frac{P F_v}{RT}$$

Where $F_{v,CO}$ and $F_{v,CO_2}$ are the volumetric flow rates (cm$^3$/s) of CO and CO$_2$, respectively. $P$ is the atmospheric pressure ($P = 1$ atm), $R$ the gas constant ($R = 82.06$ cm$^3$ atm K$^{-1}$ mol$^{-1}$), and $T$ the temperature ($T = 293$ K).

The energetic efficiency ($EE_k$) for the gaseous product $k$ was calculated using the following equation:

$$EE_k(\%) = \frac{E^o}{V_{cell}} \times FE_k(\%)$$
Where $E^\circ$ is the equilibrium cell potential ($E^\circ = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} = -0.10 \text{ V} - 1.23 \text{ V} = -1.33 \text{ V}$ for CO$_2$ reduction to CO and $E^\circ = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} = 0 \text{ V} - 1.23 \text{ V} = -1.23 \text{ V}$ for H$_2$ evolution), $V_{\text{cell}}$ is the applied cell potential, and $FE_k$ is the Faradaic efficiency of the gaseous product $k$. The overall cell energetic efficiency is the sum of the energetic efficiencies for CO and H$_2$.

### 7.4 Results and Discussion

Cost, durability, and poisoning concerns have also spurred extensive research towards catalysts with low or no precious metal content for the oxygen reduction reaction (ORR) in fuel cells. Involving materials, such as Pt-alloys, nitrogen-coordinated iron (Fe) or cobalt (Co) in a carbon matrix (i.e., Fe/N/C, Co/N/C), and metal-free nitrogen-doped carbon catalysts.[12] Nitrogen-doped carbons (nanotubes,[13] nanotube arrays,[14] graphene,[15, 16] nanocages[17]) and carbon nitrides,[18-23] have been intensively studied in recent years for a variety of reactions, such as (i) in the ORR in PEMFCs[18-23]; (ii) in photocatalytic water splitting to produce hydrogen and oxygen[24, 25]; and (iii) in the photocatalytic reduction of CO$_2$, where the primary products include CO, methanol, and ethanol, although at low quantum yield.[26, 27] For example, we previously showed that carbon nitride or pyrolyzed nitrogen nitride supported on a carbon exhibiting high surface area and electrical conductivity enhances ORR activity.[20-23] We also showed that high temperature treatment (i.e., pyrolysis) plays a critical role in the ORR activity of carbon nitride supported on carbon supports, with the optimal activity found for samples pyrolyzed at 1000°C.[21, 22] These N-doped catalysts all contain only carbon and nitrogen along with small amounts of dopants / impurities and are synthesized by simple and scalable methods. The similarity of the CO$_2$ reduction reaction with the ORR, as well as our prior work on heterogeneous catalysts involving nitrogen-containing organic ligands,[28] suggests that nitrogen-doped carbon-based catalysts should also be explored for CO$_2$ reduction.
Indeed, Kumar et al. recently reported an N-containing carbon fiber catalyst, derived from pyrolysis of electrospun mats of polyacrylonitrile (PAN) polymer. The micron-scale fibers exhibited some activity for CO$_2$ reduction to CO, up to 5 mA/cm$^2$ in a standard 3-electrode cell.[29]

The CN/MWCNT catalyst is synthesized as follows. Cyanuric chloride (1,3,5-trichlorotriazine (C$_3$N$_3$Cl$_3$)) and sodium azide (NaN$_3$) are heated to 220°C for 22 hours in the presence of MWCNTs to yield MWCNTs coated with graphitic carbon nitride (g-C$_3$N$_4$, the most stable allotrope of carbon nitride[30-32]) (Scheme 7.1). After rinsing and milling, the product is pyrolyzed at 1000°C to yield carbon nitride supported on multiwall carbon nanotubes (CN/MWCNT). Prior work on similar ORR catalysts has revealed that pyrolysis increases catalyst surface area, and changes the distribution of C-N bond types.[21, 23] Further information on the synthesis of CN/MWCNT can be found in the Experimental section.

Characterization of the as-produced CN/MWCNT powder using TEM revealed information about its structure (Figure 7.1b). Short, defective, kinked MWCNTs were observed, with a diameter slightly larger than the nominal diameter. This difference is attributed to the pyrolyzed carbon-nitride coating. However the contrast between the MWCNT and the CN coating was insufficient for their interface to be observed, due to the similarity between the two materials. CHN elemental analysis yielded a nitrogen content of 0.39 at%. This low value is due to the fact that pyrolyzed carbon nitride only coats the very surface of the MWCNT, whilst the bulk is almost entirely carbon. Peaks observed in X-ray photoelectron spectroscopy (XPS) survey spectra (Figure 7.2a) are attributed to carbon, nitrogen and oxygen. The nitrogen content from XPS is 0.12 at.% (0.12 at.% N, 2.20 at.% O, 97.68 at.% C). Metal impurities (especially Fe) are absent within the detection limit (Figure S1 in the SI). Deconvolution of the high-resolution
XPS spectra peaks in the N1s region reveals the presence of different nitrogen bonds: pyridinic (~398.5 eV, 33.4%), pyrrolic (399.5 eV, 26.3%), tertiary/graphite-like (~400.5 eV, 27.6%), and amine (~401.7 eV, 12.7%) (Figure 7.2b).

Next we determined the activity of the CN/MWCNT catalyst for electroreduction of CO2. In cyclic voltammetry (CV) measurements in a 3-electrode cell the CN/MWCNT catalyst exhibits about a five times higher activity for CO2 conversion compared to the commonly used Ag nanoparticle (~70 nm) catalyst, although the Ag catalyst shows an earlier onset (Figure 7.3). This result suggests promise for application of the CN/MWCNT in CO2 electrolysis at high current densities.

Next, we tested the catalytic activity for electrochemical CO2 reduction on CN/MWCNT using a CO2 electrolysis cell.[7] The catalyst was deposited as a cathode catalyst onto a gas diffusion electrode (GDE) (carbon paper). Analysis via X-ray micro-computed tomography (MicroCT) reveals a uniform and crack free electrocatalyst layer (Figure 7.4a) supported on the highly porous GDE. Cross-sectional observation using scanning electron microscopy (SEM) confirms that the CN/MWCNT catalyst layer uniformly coats the GDE with a catalyst layer thickness of about 15 µm. SEM top-down images of the CN/MWCNT electrocatalyst layer reveal that the carbon nitride-coated MWCNTs form agglomerates of varying sizes at the micron-scale (Figure 7.4b). This microstructure may act to improve the accessible surface area and enhance mass diffusion through the layer.

Figure 7.5 shows the performance characteristics of the microfluidic CO2 electrolysis cell operated with the CN/MWCNT catalyst, compared with an Ag nanoparticle (~70 nm) catalyst. The CN/MWCNT cathode catalyst displays significantly higher CO partial current density than the Ag catalyst at cathode potentials of -1.2 ~ -1.6 V vs. Ag/AgCl, revealing that the
CN/MWCNT catalyst is highly active for the conversion of CO$_2$ to CO (Figure 7.5a). The CO$_2$ electrolysis cell produces a partial CO current density of up to 90 mA/cm$^2$ at a cathode potential of -1.62 V vs. Ag/AgCl, when operated with the CN/MWCNT cathode catalyst. Furthermore, an up to 3.5x higher current density for CO was observed for CN/MWCNT at intermediate cathode potential (V=-1.46 V vs. Ag/AgCl) compared to the state-of-the-art Ag nanoparticle-based catalyst (Figure 7.5a).

The CN/MWCNT catalyst also catalyzes hydrogen formation to a very small extent, whereas the Ag cathode produces nearly no hydrogen within the detection limit of GC (Figure 7.5a). Figure 7.5b indicates that the CN/MWCNT exhibits excellent selectivity for the desired product, CO, over H$_2$, i.e., ~98% CO and ~2% H$_2$. In summary, the CN/MWCNT catalyst exhibits high activity and selectivity for the electrochemical reduction of CO$_2$ to CO, with better performance than any other catalyst reported to date, including nitrogen-doped carbon fibers,[29] or state-of-the-art silver nanoparticle catalysts.[7]

The overall energetic efficiencies, the fraction of energy supplied to the reactor that is successfully transferred to chemical bonds in the desired product, are 52% and 48% at a cathode potential of -1.46 V vs. Ag/AgCl (-2.75 V cell potential) and -1.62 V vs. Ag/AgCl (-3.0 V cell potential), respectively, when the cell is operated with the CN/MWCNT catalyst. In comparison, the Ag catalyst exhibits an energetic efficiency of 46% at a cathode potential of -1.68 V vs. Ag/AgCl (-3.0 V cell potential). The slightly higher energy efficiency observed for CN/MWCNT can be attributed to the better selectivity for CO over H$_2$ (Figure 7.5b) So at similar cathode or cell potentials the CN/MWCNT catalyst provides higher current densities (up to 3.5x) and slightly higher energy efficiency.
To explain the origin of the activity of the non-precious CN/MWCNT catalyst reported here, we propose the following mechanism (Figure 7.6). CO$_2$ has no overall dipolar moment due to the symmetry of the molecule, despite the different electronegativity of oxygen and carbon atoms. However the electrostatic potential varies along the molecule.[33] Introducing nitrogen into a graphene sheet has a similar effect on the electrostatic potential, increasing the electron density in the region of the nitrogen atom, and reducing the electron density in the region of the neighboring carbon atoms.[34] These variations in electrostatic potential provide a low energy pathway for the approach of a CO$_2$ molecule to the carbon surface; the electronegative nitrogen atom attracts the electropositive carbon atom in the CO$_2$ molecule, and the electronegative oxygen atom on the CO$_2$ molecule is attracted to the electropositive carbon atom at the surface (Figure 7.6a). The C=O bond length in the CO$_2$ molecule is approximately 1.2 Å, compared with approximately 1.4 Å for the C-N bond at the surface. This mismatch is expected to put strain the C=O bond, weakening it. Hydrogen ions present in the surrounding water (e.g., as hydronium ions) would then be more likely to react with the CO$_2$ molecule, accepting electrons and cleaving the C=O bond (Figure 7.6b), forming carbon monoxide and water (Figure 7.6c), and leaving the active site unchanged. In addition, this side-on binding event is considered more likely due to the alignment of the P$_z$ molecular orbitals. In the nitrogen-doped carbon surface, 2P$_z$ orbitals protrude out-of-plane; and in the CO$_2$ molecule they are arranged perpendicular to the axis of the molecule (Figure 7.7 in the SI). By adopting the side-on configuration, the P$_z$ orbitals of the surface and the molecule can share electrons, thus minimizing the total energy of the system. The effect of nitrogen atom position and type (i.e., in-plane, edge or defect; pyridinic, graphitic or pyrrolic) is not yet clear. Further experimental and computational studies
will need to be performed to clarify the mechanism, and determine the most likely nitrogen configuration for this reaction pathway.

7.5 Conclusions

In summary, we report a new nitrogen-doped carbon catalyst system, composed of pyrolyzed carbon nitride supported on multiwall carbon nanotubes as a proof-of-concept non-precious catalyst for the electrochemical reduction of CO$_2$ to CO in an electrochemical flow cell. This class of nitrogen-doped carbon catalysts exhibits high activity and selectivity for the electrochemical CO$_2$ conversion to CO. The CN/MWCNT catalyst is low cost and can be synthesized in large, scalable quantities. Although this is a proof-of-concept metal-free catalyst system, it already outperforms the state-of-the-art silver catalysts under identical experimental conditions. Moving away from precious metal catalysts without sacrificing activity and selectivity offers hope for electrochemical CO$_2$ reduction to become an economically viable process, as it will largely reduce the capital cost.

Experimental and computational efforts will be needed to better understand the observed interesting catalytic activity, and to further improve the catalyst’s activity. For example, experimental efforts may focus on studying the effects of nitrogen bond types and nitrogen content on activity and selectivity. Moreover, different classes of nitrogen-doped carbons that are produced via different synthesis routes or using different starting materials should be explored. From the computational standpoint, in-depth modeling efforts using DFT methods, for example, will help provide insight in the reaction mechanism, including its ability to selectively produce CO, which in turn will assist the design and synthesis of novel non-precious catalysts.
Figure 7.1. (a) Schematic representation and (b) TEM image of the CN/MWCNT catalyst for the CO$_2$ reduction reaction.
Scheme 7.1. Synthesis of the CN/MWCNT catalyst.

I.  
\[
\begin{align*}
&C_3N_3Cl_3 \\
&3NaN_3 \\
&MWCNT \\
\xrightarrow{\Delta P} \\
&220^\circ C \\
&22 \text{ h} \\
\end{align*}
\]
\[\Rightarrow\]
\[
\begin{align*}
g-C_3N_4/MWCNT \\
&3NaCl \\
&4N_2
\end{align*}
\]

II.  
\[
\begin{align*}
g-C_3N_4/MWCNT \\
\xrightarrow{\text{pyrolysis}} \\
&1000^\circ C \\
\end{align*}
\]
\[\Rightarrow\]
\[
\begin{align*}
&CN/MWCNT
\end{align*}
\]
**Figure 7.2.** (a) Full XPS survey spectrum of the CN/MWCNT and (b) high resolution XPS spectrum of the N1s region.
Figure 7.3. Cyclic voltammetry measurements of reduction activity of the CN/MWCNT and Ag catalysts with a CO₂ feed in a standard 3-electrode cell. Data was recorded in 1M KCl at 25 mV/s.
Figure 7.4. Catalyst layer characterization: (a) Reconstructed 3D view obtained from MicroCT data and (b) SEM top-down images of the CN/MWCNT catalyst layer (loading 2.39 mg/cm²) coated on the GDE via automated airbrushing.
Figure 7.5. Electrochemical characterization of the CN/MWCNT and Ag catalysts: (a) Partial current densities vs. cathode potential for CO and H₂; (b) Faradaic efficiency vs. cathode potential for CO and H₂. The error bars represent the standard deviation of the average of three experiments (N=3). Cathode catalyst: 2.39 mg/cm² CN/MWCNT or 0.75 mg/cm² unsupported Ag nanoparticles. Anode catalyst: 4.25 mg/cm² unsupported Pt black. Reactant streams: 7 sccm CO₂; 1.0 M KCl electrolyte flowing at 0.5 mL/min. Data collected at room temperature and ambient pressure.
Figure 7.6. Proposed mechanism for the electrochemical reduction of CO$_2$ on a nitrogen-doped carbon surface. (a) CO$_2$ adsorbed to a C-N site reacts with a proton. (b) A second proton reacts with the adsorbed OCOH. (c) CO and H$_2$O products leave the surface.
Figure 7.7. Schematic representation of the Pz molecular orbital alignment (the electron probability density is shown here, for simplicity) between the CO$_2$ molecule and the nitrogen-doped carbon surface.
7.7 References

Chapter 8
Conclusions and Future Work

8.1 Conclusions and Future Work

The modern world faces immense challenges associated with meeting its energy needs, due to its current dependence on fossil fuels. At the same time, the world faces the threat of global climate change linked to CO$_2$ emissions. Indeed, global energy consumption has risen significantly since the industrial revolution and is expected to double again in the next 50 years. This is accelerating the depletion of conventional fossil fuels and has led to a steady increase in atmospheric CO$_2$ levels. Taken together, the dual challenges of finding alternative energy sources and curbing CO$_2$ emissions are daunting. Multifaceted approaches are needed to produce, store, and utilize energy in more efficient and environmentally sustainable ways. This thesis researches two energy conversion technologies that show promise to help address both challenges: fuel cells for efficient electrical power generation, and electrolysis of carbon dioxide into value-added intermediates for chemical production.

This thesis describes a suite of studies undertaken to better understand the structure-performance relationships of electrodes and the application of this knowledge to the design of new, supported catalysts to improve electrode performance. Chapter 2 discusses the current status and opportunities for catalyst design, electrolyte choice and electrode structure for electrochemical reduction of CO$_2$. Chapters 3 and 4 report on the proof-of-concept utilization of MicroCT for detailed characterization of the 3D structure of fuel cell electrodes in a non-destructive fashion. Coupled with electrochemical analysis in a microfluidic fuel cell, variations in electrode structure (catalyst layer uniformity, electrode compression) can be directly correlated to differences in electrode performance. Chapters 5-7 describe results on the synthesis,
characterization, and testing of catalysts, electrodes, and electrolysis cells for the electrochemical conversion of CO$_2$ to CO, an intermediate that can be used in subsequent Fischer-Tropsch processes for the synthesis of value-added chemicals such as diesel fuels. Together, these studies present the framework for developing catalytic materials to help CO$_2$ reduction become a more economically viable process.