ELECTROCATALYTIC CO₂ CONVERSION IN FLOW REACTORS

by

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A DISSERTATION SUBMITTED IN PARTIAL FULFILLMENT OF
THE REQUIREMENTS FOR THE DEGREE OF

DOCTOR OF PHILOSOPHY

in

THE FACULTY OF GRADUATE AND POSTDOCTORAL STUDIES

(Chemical and Biological Engineering)

THE UNIVERSITY OF BRITISH COLUMBIA

(Vancouver)

April 2020

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The following individuals certify that they have read, and recommend to the Faculty of Graduate and Postdoctoral Studies for acceptance, the dissertation entitled:

Electrocatalytic CO$_2$ Conversion in Flow Reactors

submitted by Danielle Salvatore in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemical and Biological Engineering

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Abstract

Electrochemical reduction of CO₂ to value-added liquid fuels and chemical feedstocks is a sustainable approach to off-peak electricity utilization. The propagation of a CO₂ value chain through capture-conversion technology is bottlenecked by a lack of systems capable of catalytic CO₂ conversion with the efficiency, selectivity, robustness, and economic viability relevant to industry. The design of a CO₂ electrolyzer that can operate at current densities \( J > 200 \text{ mA/cm}^2 \), Faradaic efficiencies (FE) > 85%, voltages < 3 V is germane to this challenge. Improving the efficiencies, selectivities and current densities of CO₂ electrocatalytic systems are of scientific, environmental, and economic importance.

In this thesis, I first demonstrate the development of a flow reactor that utilizes gas-phase CO₂ to achieve higher current densities \( J = 200 \text{ mA/cm}^2 \) than is possible with conventional aqueous-fed systems. I use a silver catalyst dispersed on a gas diffusion layer to produce CO with high selectivity ( > 50%). I deploy a bipolar membrane which allows the use of non-corrosive conditions on either electrode, thereby prolonging cell lifetime.

I then detail the design and use of an analytical device to compare the voltages for different CO₂ flow reactor architectures to identify which cell components should be optimized to most effectively lower the overall cell voltage. Analysis of the voltages across the components of three different flow reactor configurations highlights that the reactions at the anodes and cathodes are relatively efficient and that much of the voltage loss occurs at the membrane. These results illuminate that a better understanding of membranes and the membrane-catalyst interface is needed.

Finally, I demonstrate the incorporation of a molecular catalyst into a CO₂ flow reactor for efficient conversion of CO₂ to CO. Molecular catalysts are known to have high activity for the CO₂
reduction reaction but typically at low rates of conversion (i.e., < 30 mA/cm²). In this work, I show that a widely available molecular catalyst, cobalt phlalocyanine, can mediate CO₂ to CO formation in a flow reactor with high conversion rates commensurate with solid-state metal catalysts (i.e., > 150 mA/cm² and FE > 85%).
Lay Summary

Cost-competitive energy storage technologies are critical to enabling a renewable energy economy. Converting CO₂ to fuels and chemical feedstocks with renewable energy is an appealing storage strategy because the carbon products made are compatible with existing petrochemical and fossil fuel infrastructures. A key challenge associated with commercializing such technologies is that low conversion efficiencies need to be overcome. One method to address low conversion efficiencies is to feed the CO₂ as a gas instead of as a dissolved species in water in order to increase the CO₂ available at the catalyst surface. This thesis demonstrates the development of a CO₂ reactor that is capable of converting gaseous CO₂ at high efficiencies.
Preface

Chapter 2 is adapted from the paper “Electrolytic CO₂ Reduction in a Flow Cell”, *Accts. of Chem. Res.* 2018, 51, 910-910. The work was supervised by Prof. Berlinguette. The outline and background research were carried out by myself along with Dr. David Weekes in the Berlinguette group. The figures were constructed by me. The manuscript was written by Dr. David Weekes and myself with contributions from Angelica Reyes, Aoxue Huang, and Prof. Curtis Berlinguette.

Chapter 3 is adapted from the paper “Electrolysis of Gaseous CO₂ to CO in a Flow Cell with a Bipolar Membrane”, *ACS Energy Lett.* 2017, 3, 149-154. The project was designed and developed by myself. The work was supervised by Prof. Berlinguette. All experiments were carried out by myself with the exception of the scanning electron microscopy performed by Dr. Kevan Dettlebach in the Berlinguette group. The manuscript was written by myself with contributions from Dr. David Weekes and Prof. Curtis Berlinguette.

Chapter 4 is adapted from the paper “Voltage Matters When Reducing CO₂ in an Electrochemical Flow Cell”, *ACS Energy Lett.* 2020, 5, 215-220. The project was designed and developed by myself. The work was supervised by Prof. Curtis Berlinguette. I carried out all experiments and data analysis. The manuscript was written by myself with contributions from Prof. Curtis Berlinguette.

Chapter 5 is adapted from the paper “Molecular electrocatalysts can mediate fast, selective CO₂ reduction in a flow cell”, *Science.* 2019, 365, 367-369. The work was supervised by Prof. Curtis Berlinguette and Prof. Marc Robert. The experiments were carried out by myself, Shao Ren and Dorian Julie. The manuscript was written by myself, Shao Ren, Dorian Julie with contributions from Prof. Marc Robert and Prof. Curtis Berlinguette.
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<td>Diffusion length</td>
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<td>Anion exchange membrane</td>
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<td>Bipolar membrane</td>
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<td>RHE</td>
<td>Reversible hydrogen electrode</td>
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<tr>
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Acknowledgements

Thank you.

To my supervisor Dr. Curtis Berlinguette, your enthusiasm, drive and work ethic were strong contributors to the successful completion of this thesis and to my growth as a student.

To my committee members, Dr. Elod Gyange and Dr. Fariborz Thaghipour for their guidance and critical analysis of my work.

To all the excellent people at UBC who helped me with my research, with special mention to the chemistry department’s shops & services.

To the many Berlinguette group members, past and present, with whom I’ve had the pleasure of working alongside. These group members are not only wonderful scientists but also great people and have made every day spent in the lab enjoyable.

To my amazing friends, near and far, that have joined me on the roller coaster that is graduate school. Thank you for the incredible life I was able to build here, I am grateful for all of the adventures. With special mention to: FP, KR, DMW, MT, RG, AH, RD, CG, BPM, CK, RF, MG, EL, Plums & Vancity FC.

Lastly, to my family for your unwavering encouragement, love and support.
to my family.
Chapter 1: Motivation & Outline

1.1 Motivation

Scalable energy storage technologies are needed to deploy low-cost renewable energy on a global scale.\(^1\) Large scale energy storage is an appealing way to address the geographic and seasonal mismatch of electricity supply and demand.\(^2\) Carbon dioxide (CO\(_2\)) capture and utilization provide a means for simultaneously reducing greenhouse-gas emissions and displacing fossil-fuel-derived products. CO\(_2\) electrolyzers, which use electricity and water to produce carbon-based chemicals and fuels from CO\(_2\), provide an intriguing opportunity to store renewable electricity in chemical form.\(^3\) CO\(_2\) electrolysis offers the advantage over electrolytic hydrogen formation of producing chemicals for which large scale transportation, processing, and energy infrastructure already exists. The opportunity to leverage existing infrastructure and scientific knowledge to facilitate the deployment of carbon-neutral energy carriers has motivated academia and industry to design CO\(_2\) reduction reaction (CO\(_2\)RR) electrolyzers. These electrolyzers are capable of using electricity to convert CO\(_2\) into more energetic and commercially valuable chemicals (i.e., carbon monoxide, methane, ethylene, and propanol).\(^3\)

1.2 CO\(_2\)RR Product Selection

Electrochemical CO\(_2\) reduction is performed in an electrolytic reactor that requires four components; (i) a negative electrode (cathode) that can reduce CO\(_2\) into a carbon product, (ii) a positive electrode (anode) that mediates a counter-reaction to provide electrons and protons to the cathode [this reaction is typically the oxygen evolution reaction (OER), but can also be a variety of organic oxidation reactions],\(^4\) (iii) an electrolyte (solid or liquid) that can transport ions, and (iv) a voltage source that shuttles electrons from the anode surface through an external circuit to the
cathode surface. A major focus of catalytic CO$_2$RR research is selectively making a single product (e.g., carbon monoxide, formic acid, ethylene).$^{5-7}$ Hydrogen is a product of the parasitic hydrogen evolution reaction (HER) and is almost always formed alongside carbon-containing products. Since the CO$_2$RR and HER reactions both utilize protons/water as a reactant and occur at similar reduction potentials, these reactions are highly competitive. Table 1-1 summarizes some of the possible CO$_2$RR products and their standard reduction potentials.$^8$

**Table 1.1** Stoichiometric requirements and thermodynamic half-reaction potentials for CO$_2$ reduction reaction products at neutral conditions. The parasitic HER reaction is also shown.

<table>
<thead>
<tr>
<th>Reduction Product</th>
<th>Reaction</th>
<th>Number of electrons</th>
<th>E vs. SHE (pH 7.0)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon monoxide, CO</td>
<td>CO$_2$ + H$_2$O + 2e$^-$ → CO + 2OH$^-$</td>
<td>2</td>
<td>-0.52 V</td>
</tr>
<tr>
<td>Formic Acid, HCOOH</td>
<td>CO$_2$ + 2H$_2$O + 2e$^-$ → HCOOH + OH$^-$</td>
<td>2</td>
<td>-0.43 V</td>
</tr>
<tr>
<td>Ethylene, C$_2$H$_4$</td>
<td>2CO$_2$ + 8H$_2$O + 12e$^-$ → C$_2$H$_4$ + 12OH$^-$</td>
<td>12</td>
<td>0.064 V</td>
</tr>
<tr>
<td>Ethanol, EtOH</td>
<td>2CO$_2$ + 9H$_2$O + 12e$^-$ → C$_2$H$_5$OH + 12OH$^-$</td>
<td>12</td>
<td>-0.33 V</td>
</tr>
<tr>
<td>Propanol, C$_3$H$_7$OH</td>
<td>3CO$_2$ + 13H$_2$O + 18e$^-$ → C$_3$H$_7$OH + 18OH$^-$</td>
<td>18</td>
<td>0.095</td>
</tr>
<tr>
<td>Hydrogen, H$_2$</td>
<td>2H$_2$O + 2e$^-$ → H$_2$ + 2OH$^-$</td>
<td>2</td>
<td>-0.42 V</td>
</tr>
</tbody>
</table>

Recent techno-economic analyses have identified the key figures of merit and products worth targeting for CO$_2$RR electrolyzers. A gross margin model developed by Kenis and co-workers highlights the importance of high current densities ($J > 200$ mA/cm$^2$), long-term operation
(1 year), with high selectivity (i.e., Faradaic Efficiency, $FE >90\%$) and low cell potential (i.e., high overall energy efficiency, $< 3 \text{ V}$) figuring prominently in the analysis.\textsuperscript{9} A simple discounted cash-flow model developed by Jiao and co-workers compares the market price ($$/\text{kg}$) and annual global demand (Mtonne) of different target CO$_2$RR products for a CO$_2$RR electrolyzer (Figure 1.1, assumptions: $J = 200 \text{ mA/cm}^2$; $V_{\text{cell}} = 3 \text{ V}$; $FE = 90\%$; and lifetime = 10 years).\textsuperscript{10} The sizable global markets for methanol, methane, ethylene, and ethanol are appealing (Figure 1.1b). However, it is challenging for electrolysis to compare favorably because it typically costs $<1.5 \text{ USD/kg}$ to produce these products from conventional industrial methods (Figure 1.1a). The generation of hydrocarbons and alcohols from CO$_2$ involves challenging proton-coupled electron transfer (PCET) reactions ($>6\text{e}^- \text{ and } 6\text{H}^+$) that inherently require large applied voltages with currently known catalysts.\textsuperscript{11,12} In contrast, formic acid formation, which invokes a $2\text{e}^-/2\text{H}^+$ PCET reaction, can be produced with high $FE$s, but the size of the market is likely too small to make a meaningful contribution to global CO$_2$ emissions. A seemingly reasonable case can be made for producing CO from CO$_2$. There is a sizable global demand for syngas (and downstream products thereof) along with electrolytic production costs lower than the market price. Moreover, high $FE$ values (up to 99%) for CO$_2$ electroreduction to CO have been demonstrated.\textsuperscript{13–15} For these reasons, this thesis will focus on developing an electrolyzer that converts CO$_2$ into CO.
Figure 1.1 (a) The market price (blue) and electrolysis price (red) for CO₂ reduction products and (b) the current annual global demand (in Mtonne) for potential CO₂ reduction products. The electrolysis price is calculated by assuming a \( J = 200 \text{ mA/cm}^2 \), a \( V_{\text{cell}} = 3 \text{ V} \), \( FE = 90\% \), and a lifetime of 10 years. The electrolysis price of CO and CHOOH is lower than the market price, indicating economic viability.

1.3 CO₂RR Catalysts & Reaction Environment

The electrocatalyst is one of the most critical components of a CO₂ electrolyzer because it dictates both the product selectivity and energy efficiency of the CO₂RR. There are a large number of review articles elucidating the details of each catalytic reaction.⁵,⁸,¹²,¹⁶ Notably, Hori mapped out CO₂RR catalysis on different metal electrodes: Zn, Ag, and Au primarily catalyze the formation of carbon monoxide, while Sn, Pb, In, and Bi mediate the reduction of CO₂ to formic acid.⁵ Copper is the only metal that can facilitate CC coupling to give significant amounts of multi-carbon molecules.⁵ The local environment about the catalyst also plays a vital role in modulating the selectivity of the CO₂RR and the thermodynamic driving force of the competing HER, including local pH,¹⁶–²⁰ electrolytes²¹,²² and cations.²³–²⁶ When the CO₂RR occurs at a low pH regime, there is significantly more H⁺ available for the parasitic HER reaction. In a high pH regime, there is less available CO₂ due to the rapid equilibrium of CO₂ and OH⁻. Moreover, these factors are highly sensitive to current density and applied potential.²⁷
1.4 CO₂RR Testing at High Current Densities

Most investigations of CO₂RR electrocatalysts are typically performed in three-compartment batch-type aqueous “H-cells” that restrict $J$ to <100 mA cm⁻² due to mass transfer limitations and low CO₂ solubility (Figure 1.2a). Mass transport is limited in H-cells because these batch-type reactors are dependent on the diffusion of the reactant (i.e., CO₂) through the electrolyte to the reaction surface. Given that the applied current density affects the chemical environment of a catalyst and the catalytic activity, catalyst testing in an H-cell is generally not representative of commercial operating conditions that require current densities >200 mA cm⁻².

To test catalysts at higher current densities, studies must be performed in continuous flow reactors that enhance mass transfer relative to batch-type H-cell reactors by continuously circulating the reactants and products to and away from the electrodes (Figure 1.2b). The primary difference between these architectures is a roughly 3-order of magnitude reduction in the CO₂ diffusion pathway to the surface of the catalyst: from ~50 μm in an H-cell (Figure 1.2c) to 50 nm using a gas-diffusion layer (Figure 1.2d), which allows for the increased maximum current densities reported in literature. 1D reaction–diffusion models have been developed to approximate the similarities and differences in the local catalytic environments as a function of reaction rate for both cases. Because flow cell reactors are single reactor units of a typical electrolyzer, their designs can scale to the larger stacks that constitute a commercial electrolyzer unit. This approach has proven highly effective in the development of other commercial-scale electrochemical reactors such as fuel cells and water electrolyzers.
Figure 1.2 General schematics for a CO$_2$RR (a) H-cell reactor and a CO$_2$RR (b) flow reactor. Mass transport phenomena in (c) a planar electrode and (d) a gas diffusion electrode.

Despite the importance of the flow reactor to the translation of electrocatalysts to commercial products, there are strikingly few studies of CO$_2$RR electrocatalysts in continuous flow reactors. While flow reactors present an obvious next step to electrolyzer development, there are several challenges associated with assembling and testing them for the CO$_2$RR. The choice of
each component in CO$_2$ flow reactors affects the performance of the catalyst (i.e., each catalyst has different reaction conditions), wherein H-cell testing is much more straightforward to achieve (i.e., typical reaction conditions work for several catalysts). The goal of this thesis is to develop a flow reactor framework to advance the understanding of how different components of the flow reactor operate synergistically at commercially relevant efficiencies.

1.5 Outline of the Dissertation

The goals of this thesis are outlined in Figure 1.3. There are three main objectives: (i) to design a gas-fed CO$_2$ flow reactor (Chapter 3); (ii) to introduce reference electrodes into the flow reactor to quantify the energy losses for each component (Chapter 4); and (iii) to increase selectivity and decrease cell potential by incorporating an efficient molecular CO$_2$RR catalyst (Chapter 5).
Figure 1.3 Outline of thesis goals relating to a CO\textsubscript{2} flow reactor. I first designed a CO\textsubscript{2} gas-fed flow reactor (Chapter 3) followed by the design of an analytical flow reactor to measure voltage drops (Chapter 4). Finally, I incorporated a molecular catalyst in a CO\textsubscript{2} flow reactor (Chapter 5).

A literature review of electrocatalytic CO\textsubscript{2} in flow reactors is provided in Chapter 2. In this chapter, I will summarize some of the strategies that have been applied in flow reactors to optimize reactor components to improve electrocatalytic CO\textsubscript{2} reduction efficiency. The most efficient flow reactors that are used in CO\textsubscript{2} electrolysis schemes can be categorized into either membrane or hybrid architectures. Each architecture invokes different dynamic mechanisms for the delivery of gaseous CO\textsubscript{2} to electrocatalytic sites, and both have been demonstrated to achieve high current densities ($J > 200$ mA/cm\textsuperscript{2}) for CO\textsubscript{2} reduction. One strategy common to both reactor architectures for improving $J$ is the delivery of CO\textsubscript{2} to the cathode in the gas phase rather than dissolved in a liquid electrolyte. I will highlight how the judicious selection and modification of CO\textsubscript{2} feedstock, membranes, gas diffusion electrodes, and water management strategies in flow reactors can have a profound effect on electrocatalytic performance.

Chapter 3 describes the design and performance of a gas-fed CO\textsubscript{2} flow reactor for the conversion of CO\textsubscript{2} to CO at high current densities. The current densities of aqueous fed CO\textsubscript{2} flow reactors are inherently limited by the low solubility of CO\textsubscript{2} (~30 mM in H\textsubscript{2}O at atmospheric pressure) as well as the low diffusion coefficient of CO\textsubscript{2} in water (0.0016 mm\textsuperscript{2}/s).\textsuperscript{31} Gas-phase electrolysis has the potential to increase mass transport and achieve current densities several orders of magnitude higher than liquid phase electrolysis at atmospheric pressures. In this chapter, I demonstrate the ability to feed gaseous CO\textsubscript{2} at the cathode to overcome the diffusion limitations of CO\textsubscript{2} in aqueous solutions.
**Chapter 4** discusses the voltage losses in CO$_2$ flow reactors. An energy-efficient CO$_2$RR electrolyzer requires that we minimize the overall cell voltages in flow reactors (<3 V), yet empirical data to resolve where the voltage losses occur has not yet been reported. Accurate resolution of the sources of these voltage losses requires the inclusion of reference electrodes in the interior of the flow reactor. In this chapter, I demonstrate the design of an analytical flow reactor that experimentally measures the potential across each component of gas-phase CO$_2$ membrane reactors while the flow reactor is in operation. This testing platform can be utilized with any flow reactor architecture to compare the voltages and identify which cell components should be optimized to most effectively lower the overall cell voltage. My analysis of the voltages across the components of different flow reactor configurations highlights that much of the voltage loss occurs at the membrane while the reactions at the anodes and cathodes are relatively efficient.

**Chapter 5** presents the incorporation of a molecular catalyst into a CO$_2$ flow reactor for efficient conversion of CO$_2$ to CO. Solid-state electrocatalysts are capable of mediating the CO$_2$ reduction reaction at current densities ≥150 mA/cm$^2$, but maintaining high product selectivities at high current densities remains a challenge. Molecular CO$_2$RR catalysts are known to achieve high selectivities and low overpotentials, but have only been demonstrated in H-cells at current densities <10 mA/cm$^2$. Incorporating a molecular catalyst into a flow reactor can leverage the advantages of both technologies to achieve high selectivity at high current density. In this chapter, I show that a flow reactor employing the widely available molecular catalyst cobalt tris(phenanthroline) can mediate CO$_2$ to CO formation with >95% selectivity at current densities of 150 mA/cm$^2$ with an overall two-electrode cell voltage of 2.5 V. This value is 0.4 V lower – corresponding to a 7% gain in energy efficiency – than reported for a state-of-the-art solid-state silver catalyst at a similar CO partial current density.
A summary of the work is provided in **Chapter 6**. I also discuss the next steps to building larger-scale reactors for a more significant impact on electrolytic energy storage through the CO$_2$RR.
Chapter 2: Literature Review

This literature review first details the design and operation of the two primary flow reactor architectures (i.e., membrane and hybrid reactors) for the CO\textsubscript{2}RR. This review will then highlight different optimization strategies used for both CO\textsubscript{2} reactor types. Finally, I present a landscape of the state-of-the-art efficiencies and reaction rates for electrolytic conversion of CO\textsubscript{2} to CO in flow reactors.

2.1 CO\textsubscript{2} Flow Reactor Architectures

Electrochemical CO\textsubscript{2} reduction has been investigated for several decades in many different types of reactors including: H-cell reactors,\textsuperscript{5} microfluidic reactors,\textsuperscript{33} filter press reactors,\textsuperscript{34} trickle bed reactors,\textsuperscript{35} hybrid reactors\textsuperscript{36} and zero-gap membrane reactors.\textsuperscript{11,32,37} The two prominent reactor types that have emerged for the conversion of CO\textsubscript{2} to CO are zero-gap membrane reactors and hybrid reactors (Figure 2.1). Both of these reactors overcome the mass-transport limitations of an H-cell by continuously circulating the reactants and products to and away from the electrodes.\textsuperscript{36,38–46} The geometry and operational parameters of each of these reactors can vary significantly. However, both architectures employ several common features: cathode and anode flowplates/current collectors, cathode and anode gas diffusion electrodes (GDEs), and a membrane.
Figure 2.1 Schematics of two different types of CO\textsubscript{2} reactors: (a) a zero-gap membrane reactor is a continuous flow reactor that contains a membrane in direct contact with both the anode and cathode to form a membrane electrode assembly; (c) a hybrid reactor utilizes a conductive catholyte solution (e.g., KOH, NaOH) in-between the membrane and the cathode gas diffusion electrode (GDE). For each architecture, a 3D exploded view is shown on the left, and a cross-sectional view is shown on the right.

A cross-sectional schematic of a CO\textsubscript{2} flow reactor is depicted in Figure 2.2. The cathode and anode flowplates / current collectors enable reactant delivery to the gas diffusion electrodes (typically KOH on the anode and gaseous CO\textsubscript{2} on the cathode) through the machined flow channels while also providing electrical current through the conductive metal. A gas diffusion electrode [consisting of a gas diffusion layer (GDL), a microporous layer (MPL), and a catalyst layer] is used to increase the electrochemically active surface area and contact time between reactants and
active sites. The inclusion of a GDE at the cathode of CO₂ reactors is essential to achieving reasonable current densities (>100 mA/cm²) for the CO₂RR by decreasing the diffusion boundary layer thickness. The anode may also contain a GDL-supported electrocatalyst, but there are reports where freestanding gas diffusion materials active for OER (e.g., nickel foam) are used.³⁷ In a membrane reactor, the cathode GDE and anode GDE material are placed on either side of a polymer electrolyte membrane (PEM) to complete the membrane electrode assembly (MEA), which is sandwiched in between the anodic and cathodic flow plate / current collectors (Figure 2.1a). In a hybrid reactor, a thin layer between the cathode GDE and the membrane is used to continuously flow catholyte solution over the surface of the electrocatalyst (Figure 2.1b).

![Cross-sectional diagram of the components that mediate the flow of CO₂, water, and ions at the cathode side and the anode side of an electrolytic flow reactor fed with gaseous CO₂ on the cathode and KOH on the anode.](image)

**Figure 2.2** Cross-sectional diagram of the components that mediate the flow of CO₂, water, and ions at the cathode side and the anode side of an electrolytic flow reactor fed with gaseous CO₂ on the cathode and KOH on the anode.

### 2.1.1 Membrane Reactors

Zero-gap membrane reactor (denoted “membrane reactors” throughout this thesis) architectures are based on well-established low-temperature water electrolysis or fuel cell systems (Figure 2.1a).³⁹ A characteristic feature of this architecture is that the cathode and anode are
pressed tightly onto opposite sides of the polymer electrolyte membrane (PEM; <100 μm). This configuration serves to minimize ohmic losses by decreasing the distance between the electrodes while maintaining chemical isolation between the anode and cathode compartments. The choice of PEM modulates the pH on either side of the membrane, affecting reactant availability at the catalyst surface and the thermodynamic driving force of the cathodic and anodic reactions (described in detail in section 2.4.1). Porous GDEs situated between the flowplates and the membrane support the catalyst and are used to promote prolonged contact between CO₂ molecules and the electrocatalyst during electrolyte flow and remove byproducts. Using this reactor architecture, CO₂ can be delivered to the cathode as a dissolved species in a mildly basic electrolyte solution (e.g., aqueous bicarbonate) or directly in the gas phase.

2.1.2 Hybrid Reactors

Hybrid reactors are an alternative configuration based on a microfluidic cell pioneered by Kenis in 2010 (Figure 2.1b). This architecture relies on a thin (<1 mm) channel separating the membrane and the cathode between which catholyte is passed (e.g., KHCO₃, KOH, NaOH). Gaseous CO₂ supplied to the cathode side diffuses through a porous GDL and reacts at the catholyte/cathode interface to form the catalytic products (as opposed to the polymer-cathode interface encountered in membrane reactors). This configuration can also operate without a membrane separating the anode and cathode sides of the cell, relying instead on diffusion to separate reduction and oxidation products. The choice of liquid catholyte enables the CO₂RR to occur at a higher pH, suppressing HER, leading to high conversion efficiencies of carbon products. Sargent and coworkers demonstrated that by switching from a 1M KHCO₃ to 1M KOH catholyte, they were able to achieve a 150 mA/cm² increase in J at the same cathodic
potential (-0.7 V vs RHE). Kenis and coworkers demonstrate that there is also a cation effect, where larger catholyte cations (e.g. Cs) suppress H₂ evolution.⁵⁰ For example, almost double the partial current density for CO can be obtained with 1M CsOH (72 mA/cm²) in comparison to a small cation (1M NaOH; 49 mA/cm²). Although the liquid catholyte enables high conversion efficiencies, this layer is expected to be responsible for a significant ohmic drop across the cell.⁵³

2.2 Performance Metrics

Four figures of merit are often cited to measure the performance of a CO₂ flow reactor: current density (J), faradaic efficiency (FE), cell potential (V₉ₑₑ), and lifetime. Techno-economic analyses point to the need for high current densities (J >200 mA/cm²), CO₂RR faradaic efficiencies (FE >90%), stabilities (>1 year), and low cell potentials (<3 V) for commercial viability.¹⁰,⁵⁴ While no such system exists today, pilot CO₂ reactors are capable of competitive performance across one or two of these metrics, such as high current densities and FE’s, or moderate current densities for lifetimes of ~100 hours.⁴³,⁵⁵ The simultaneous achievement of all four of the figures of merit mentioned above, however, has yet to be demonstrated. The next section of this Chapter will highlight different optimization strategies for membrane and hybrid reactor architectures to achieve these figures of merit.

2.3 Flow Reactor Optimization

The optimal choice of gas diffusion electrode, catholyte, anolyte, and membrane will differ depending on the constraints of the selected CO₂ reactor architecture. Within the MEA, each component must work symbiotically to transport ions, electrons, and gases to and from the catalyst sites (Figure 2.2). Both reactors share several components that can inform the design of the other
despite relying on different fluid dynamic environments. The chemistry of PEMs, for example, has been almost exclusively studied in membrane reactors, yet hybrid reactors can also contain membranes.\textsuperscript{36,43,56} GDL materials are similarly common to both architectures, yet studies on the effects of manipulating GDL properties have primarily been carried out in hybrid devices.\textsuperscript{57} Research efforts focused on both membrane, and hybrid reactors are therefore synergistic in informing the fundamental science and engineering of CO\(_{2}\)RR technology. This section will focus on the different feedstocks (2.3.1), membranes (2.3.2), gas diffusion electrodes (2.3.3), and water management strategies (2.3.4) used for the optimization of both membrane and hybrid CO\(_{2}\) reactors.

\subsection*{2.3.1 CO\(_{2}\) Feedstock}

CO\(_{2}\) can reach the surface of the electrocatalyst on a GDL either in the gaseous phase or as a dissolved gas in an aqueous electrolyte. In the latter case, a mass transport limitation exists because the CO\(_{2}\) availability at the catalyst surface is low. This mass transport limiting current density \((J_L)\) can be calculated using a 1-dimensional mole balance on the diffusion boundary layer adjacent to the GDE surface by assuming the concentration of CO\(_{2}\) at the catalyst surface is 0 under steady-state conditions (equation 2.1).\textsuperscript{58}

\[
J_L = \frac{nFDC_{CO_2}}{\delta}
\]

(eq. 2.1)

In this calculation, a typical diffusion length of \(\delta = 1 \text{ \mu m}\) is used.\textsuperscript{58} The number of electrons (n) transferred in the CO\(_{2}\)RR is 2 for the case of CO production. Low diffusion coefficients \((D = 0.0016 \text{ mm}^2/\text{s})\) and solubility limits \((C_{CO_2} = 0.033 \text{ M})\) of CO\(_{2}\) exist in aqueous media at ambient temperature and pressure (Figure 2.3).\textsuperscript{59} This mass-transfer limitation restricts \(J\) for CO\(_{2}\)RR to \(-30\)
mA/cm² in liquid-fed systems. A \( J_L = 30 \text{ mA/cm}^2 \) represents a major disconnect between industrial chemical reactors (i.e., water electrolyzers typically operate at \( >500 \text{ mA/cm}^2 \); an order of magnitude larger). The mass transport limitations inherent to aqueous \( \text{CO}_2 \) electrolyzers can be overcome by delivering gaseous \( \text{CO}_2 \) to the cathode (Figure 2.3C). While the concentration of gaseous \( \text{CO}_2 \) is only 25% higher (0.041 M), the diffusion coefficient (\( D = 16 \text{ mm}^2/\text{s} \)) is four orders of magnitude higher than an aqueous \( \text{CO}_2 \) feed (\( D = 0.0016 \text{ mm}^2/\text{s} \)). Delivering \( \text{CO}_2 \) as a gaseous feed presents the opportunity to increase \( J_L \) values from 30 mA/cm² to >3000 mA/cm².

**Figure 2.3** Cartoon illustrating the relative saturated concentrations and diffusion coefficients (\( C \) and \( D \) from Equation 2.1, respectively) for (a) water, (b) \( \text{CO}_2 \) in aqueous solution,\(^{31}\) and (c) humidified gaseous \( \text{CO}_2 \).\(^{58}\) Values at room temperature and pressure are indicated.

While a 1-D diffusion model enables a qualitative prediction of limiting current densities, this model is typically only used for planar electrodes. Because flow reactor configurations and gas diffusion electrodes and/or porous electrodes are used to achieve high current densities for \( \text{CO}_2 \text{RR} \), the effective diffusion through the flowfields and porous mediums should be considered (Figure 2.4).\(^{61}\) The effective diffusion through the porous medium is a function of the properties of the GDL (i.e., tortuosity, porosity) and the diffusion coefficient of the diffusing species. While
the effective diffusion can be modulated by changing the properties of the porous medium, CO$_2$(g) has a diffusion coefficient that is four orders of magnitude higher than CO$_2$(aq) and will have less mass transport limitations. A 3-D mass transport model for aqueous or gaseous CO$_2$ flow reactors would be a useful tool for predictive effective diffusion and limiting current densities in flow reactors using porous diffusion medium. We can utilize models developed for fuel cells and water electrolyzers as a basis for prediction but these models invoke different reactions and reactive species and a 3-D model for CO$_2$RR has yet to be developed.$^{62-64}$

![Diagram](image)

**Figure 2.4** Structures and mass transport processes of the porous electrodes for two different CO$_2$ feedstocks: CO$_2$ dissolved in an aqueous solution & a gaseous humidified CO$_2$ feed.

There are currently very few reports that directly apply the strategy of using gaseous CO$_2$ in a membrane reactor as a means of increasing $J$.\textsuperscript{$11,32,34,37,55,65,66$} In Chapter 3, I substantiate the advantages of using a gaseous CO$_2$ feedstock in flow reactors by benchmarking a membrane reactor fed with a humidified gas-phase CO$_2$ cathode stream against a liquid electrolyte feed.$^{37}$ Cyclic voltammograms indicate $J$ values approximately two-fold higher for the gas-fed reactor than the liquid-fed reactor at -3.0 V (100 mA/cm$^2$ for a gas feed, 50 mA/cm$^2$ for liquid feed). Hybrid reactors overcome this diffusion limitation by supplying gaseous CO$_2$ through the back of
the GDL, while still utilizing an aqueous electrolyte on the catalyst side of the GDL.\textsuperscript{33,43,67}

2.3.2 Membrane

The PEM separates the anode and cathode of the cell and mediates the flow of ions from one half-cell reaction to another while simultaneously preventing product crossover. Three classes of membranes are used in CO\textsubscript{2} flow reactors: anion exchange membranes (AEMs);\textsuperscript{32,68,69} cation exchange membranes (CEMs);\textsuperscript{65,70,71} and bipolar membranes (BPMs).\textsuperscript{37,72–74} Each type of membrane transports a different set of ionic species depending on the charge of the functional groups present in the membrane. H\textsuperscript{+} and OH\textsuperscript{−} are the primary charge carriers in CO\textsubscript{2}RR membranes because they exhibit an order-of-magnitude higher ionic mobility than other ions present in aqueous electrolytes.\textsuperscript{75} The transport of H\textsuperscript{+} and OH\textsuperscript{−} defines the pH and electrochemical reactions that occur in the anode and cathode compartments (Figure 2.5). CEMs transport cations from an acidic anode to the cathode, AEMs mediate transport of anions from an alkaline cathode to the anode, and BPMs enable the dissociation of H\textsubscript{2}O under an applied potential and transport H\textsuperscript{+} to the cathode and OH\textsuperscript{−} to the anode. The efficiencies of these ion transport processes in the different types of membranes have been examined extensively for their effects on water electrolysis,\textsuperscript{76} but far less so in the context of CO\textsubscript{2}RR. The lack of understanding of how membrane properties affect CO\textsubscript{2}RR efficiency and selectivity motivates the need to explore relationships between, for example, concentrations of functional groups in a membrane, membrane thickness, water uptake, and conductivity.\textsuperscript{77}
Figure 2.5 Polymer exchange membranes and the respective reactions at the anode (A) and the cathode (C). (a) Cation exchange membranes (CEM) contain negatively-charged functional groups that mediate the movement of positive ions such as H⁺ from the anode to the cathode (Figure 2.5a). In

2.3.2.1 Cation Exchange Membrane (CEM)

CEMs, such as Nafion®, contain negatively-charged functional groups (e.g., SO₃⁻) that mediate the movement of positive ions such as H⁺ from the anode to the cathode (Figure 2.5a). In
2008, Newman and co-workers reported the first CEM-based flow-cell reactor for CO$_2$($g$) reduction to CO.$^{65}$ They reported that the incorporation of a solid-supported aqueous electrolyte buffer layer (1 M KHCO$_3$) between the membrane and cathode GDL was necessary to suppress H$_2$ formation. This initial reactor design was able to achieve current densities of 100 mA/cm$^2$ at an $FE$ of 20% for CO production. The reactor, however, suffered from poor stability, and the $FE$ for CO degraded quickly over 5 hours of electrolysis. Since the work by Newman, there have been efforts to increase the $J$ and $FE$ of CEM-based membrane reactors using a gaseous CO$_2$ feed, but none have been successful in achieving $Js > 20$ mA or $FEs > 15%$.$^{34,78,79}$ Although CEMs exhibit desirable properties for CO$_2$ flow reactors, such as good mechanical integrity and high ionic conductivity, the high H$^+$ concentration provided by the CEM to the cathode enhances HER and concurrently diminishes the $FEs$ for CO$_2$RR.

### 2.3.2.2 Anion Exchange Membrane (AEM)

In an AEM, positively-charged functional groups (e.g., C$_3$H$_5$N$_2^+$, NH$_3^+$) facilitate anion (e.g., OH$^-$, HCO$_3^-$ and CO$_3^{2-}$) transport from the cathode to the anode, enabling the CO$_2$RR to occur in a basic environment (Figure 2.5b). AEMs may be more suitable for CO$_2$ reduction than CEM systems because a basic environment decreases the thermodynamic driving force for the HER by decreasing the concentration of H$^+$ at the catalyst surface. In this basic environment, H$_2$O acts as a proton donor for the CO$_2$RR. In the desired pathway, AEMs selectively transport OH$^-$ from the cathode to the anode. The basic cathode conditions also enable OH$^-$ ions to react with CO$_2$ by acid-base equilibrium to form dissolved inorganic carbon species (HCO$_3^-$ and CO$_3^{2-}$) which can be readily transported through the AEM. This is detrimental because these dissolved inorganic carbon species have lower ionic mobilities than OH$^-$ (45 and 60 S mol$^{-1}$ cm$^2$ for HCO$_3^-$
and CO$_3^{2-}$, respectively, \textit{c.f.} 198 S mol$^{-1}$ cm$^2$ for OH$^-$) and can be oxidized to CO$_2$ at the anode upon transport through the membrane. The buildup of these larger ions can inhibit membrane ion transport and reduce CO$_2$ reduction efficiency.$^{75,80,81}$

Many of the best performing membrane-containing CO$_2$ reactors known today use AEMs. In 2017, Masel and co-workers presented a gas-fed CO$_2$ membrane reactor that could achieve high current densities (200 mA/cm$^2$) at 3.0 V and 98% \textit{FE} for CO production.$^{32}$ The authors were also able to demonstrate exceptional cell stability (4500 h continuous electrolysis at $J = 50$ mA/cm$^2$, 3.0 V, \textit{FE} for CO $\sim$90%) by using \textit{N}-methylimidazolium-substituted styrenic copolymers as the AEM material (now commercialized as Sustainion$^{\text{TM}}$) to facilitate the improved transport of HCO$_3^-$ ions (Figure 2.6a). There have been several follow up reports utilizing a Sustainion$^{\text{TM}}$ membrane for high conversion of CO$_2$ to carbon products,$^{11,82,83}$ including my own report in \textit{Chapter 5}.$^{66}$ Masel also incorporated a Sustainion$^{\text{TM}}$ membrane in a 3-compartment cell with a Sn catalyst for the conversion of CO$_2$ to formic acid.$^{82}$ Sinton and co-workers utilized a Sustainion$^{\text{TM}}$ membrane in both a hybrid reactor and membrane reactor with a Cu catalyst for conversion of CO$_2$ to C2+ products at $>50\%$ \textit{FE} and $>100$ mA/cm$^2$.$^{11}$ In \textit{Chapter 5}, I demonstrate the incorporation of a molecular catalyst in a membrane reactor utilizing a Sustainion$^{\text{TM}}$ membrane. I can achieve low cell voltages at high current densities (2.5 V at 150 mA/cm$^2$). A second type of AEM was introduced in 2019. Zhuang and co-workers tested a Au cathode interfaced with a quaternary ammonia poly(\textit{N}-methyl-piperidine-co-p-terphenyl) AEM at 3.0 V (Figure 2.6b). The membrane reactor reached current densities of 500 mA/cm$^2$ and a \textit{FE} for CO greater than 85%.$^{55}$ This increase to higher current densities was achieved while operating at an elevated temperature of 50 °C.
Figure 2.6 Schematic structures of (a) polystyrene tetramethyl imidazolium chloride (PSTMIM), commercialized as Sustainion™ and (b) quaternary ammonium poly(N-methyl-piperidine-co-terphenyl) (QAPPT) AEM membranes.

There are three major operational challenges encountered when utilizing AEMs in both membrane and hybrid reactors. The first major issue is product crossover from the cathode to the anode. Negatively charged CO$_2$RR products (i.e., HCOO$^-$) are easily transported across the positively charged AEM. Neutral products (i.e., MeOH, EtOH) are also able to crossover through diffusion mechanisms.$^{84}$ For example, Mallouk and co-workers demonstrated 30% HCOO$^-$ crossover at 200 mA/cm$^2$ with an AEM in a membrane reactor.$^{84}$

The second operational challenge involves acid-base equilibria between the CO$_2$ feed and CO$_2$RR byproducts (Figure 2.7). The reaction between the CO$_2$ feed and OH$^-$ to generate HCO$_3^-$ and CO$_3^{2-}$ reduces the amount of free CO$_2$ available to the catalyst.$^{85}$ The generated HCO$_3^-$ and
CO$_3^{2-}$ can then crossover the AEM to the anode electrolyte. Seger, Chorkendorff, and co-workers have recently demonstrated that CO$_2$ crossover across the AEM, in the form of CO$_3^{2-}$, exceeds the amount of CO$_2$ converted to the target product (60% of total CO$_2$ is neutralized). They demonstrated this finding in a zero-gap membrane reactor with a Sustainion$^\text{TM}$ membrane, an Ag electrode at $J = 200$ mA/cm$^2$, and $V_{\text{cell}} = 3.3$ V.

The third operational challenge that exists when HCO$_3^-$ and CO$_3^{2-}$ can readily react with K$^+$ by forming KHCO$_3$ and K$_2$CO$_3$ crystals on the electrode/membrane surfaces. In hybrid reactors, the HCO$_3^-$ and CO$_3^{2-}$ reacts with K$^+$ in the KOH catholyte solution. In membrane reactors, co-ion transport of K$^+$ from the anode to the cathode enables K$^+$ to react with HCO$_3^-$ and CO$_3^{2-}$ to form KHCO$_3$ and K$_2$CO$_3$. KHCO$_3$/K$_2$CO$_3$ crystal formation affects the operation of the reactor because the solid crystals fill the pores of the GDE and flow plates preventing reactant delivery. The use of pure H$_2$O as opposed to KOH at the anode reduces CO$_3^{2-}$ and HCO$_3^-$ crystal formation. However, this strategy lowers the ionic conductivity of the anode electrolyte and drives up the cell potential.
Figure 2.7 CO$_2$RR and equilibrium reactions occurring at the diffusion boundary layer/catalyst layer interface in an AEM based CO$_2$ reactor.
2.3.2.3 Bipolar membrane (BPM)

There is also a growing body of literature featuring membrane reactors that utilize a BPM for the CO$_2$RR. A BPM is a membrane that consists of an anion exchange layer (AEL) adjacent to a cation exchange layer (CEL) (Figure 2.5c). BPMs induce H$_2$O dissociation at the CEL-AEL interface under an applied potential and deliver H$^+$ and OH$^-$ to the cathode and anode, respectively. Under ideal operating conditions, these fluxes of ions maintain acidic and basic conditions at the anode and cathode, respectively, during electrolysis.\textsuperscript{89} A benefit of a BPM over a CEM is that inexpensive anode catalyst materials (e.g., Ni foam) can be used in the basic anolyte instead of the rare-earth metal catalysts (e.g., Ir, Ru)\textsuperscript{90} that are stable only under acidic conditions.\textsuperscript{91,92} BPMs have also been shown to inhibit product crossover, the parasitic process in AEM-based CO$_2$ flow reactors described above.\textsuperscript{84} Less than 1\% formate crossover is observed at 200 mA/cm$^2$ with a BPM-based membrane reactor.\textsuperscript{84} Our research group, in collaboration with Mallouk and co-workers, first demonstrated the use of a BPM in a liquid-phase CO$_2$ membrane reactor in 2016.\textsuperscript{72} Our BPM-containing reactor sustained electrolysis at high current densities (50 mA/cm$^2$) commensurate with an equivalent setup containing an AEM or CEM. In Chapter 3, I discuss gaseous CO$_2$ electrolysis in a BPM-based membrane reactor. The BPM configuration using gaseous CO$_2$ is capable of reaching a $\sim$65\% $F.E._{CO}$ at 100 mA/cm$^2$ and 3.4 V for 24 h.\textsuperscript{37} In a separate report, we showed BPMs can also be used to convert HCO$_3^-$ to electrochemically active CO$_2$ \textit{in-situ} to supply the reactant for the CO$_2$RR.\textsuperscript{93} While BPMs have shown promise in CO$_2$ reactor architectures, managing the H$^+$ flux to the cathode to reduce HER and minimizing the voltage consumption ($> 0.83$ V) required to induce water dissociation at the CEL-AEL interface are the most significant challenges BPM containing CO$_2$ electrolyzers.\textsuperscript{94}
2.3.3 Gas Diffusion Electrodes

A typical GDE is comprised of a GDL, MPL, and a catalyst layer (Figure 2.8). The GDL is a porous material typically composed of a dense array of conductive carbon fibers (carbon paper or carbon cloth). The MPL is a more densely-packed carbon microporous layer (typically carbon nanofibres or compressed carbon powder). The deposition of the electrocatalyst directly on the MPL, to make the catalyst layer, has the effect of increasing \( J \) for electrochemical reactions by increasing the catalytic surface area and enabling prolonged contact between the reactants and catalytic sites. Multiple deposition methods can be used to incorporate catalysts onto the GDL, including: drop-casting, airbrushing, electrodeposition, or compression.\textsuperscript{38,40,57} The catalyst layer typically includes the electrocatalyst material itself along with an ionomer additive as a binder to improve ion transport and catalyst layer adhesion to the GDL. There are several material properties of the GDL–including porosity, hydrophobicity, electrical conductivity, and physical robustness–that can be tailored through the judicious selection of material constituents and fabrication methods.\textsuperscript{95}
Figure 2.8 Cross-sectional diagram of the components (GDL, MPL, catalyst layer) that comprise a gas diffusion electrode (GDE).

A series of studies from Kenis and co-workers demonstrated the effect of manipulating certain GDL properties on electrochemical performance in a CO$_2$ reactor$^{38,40,57}$ In the earliest experiment, the method of catalyst deposition was correlated to the performance of the GDE for CO$_2$RR. By depositing catalyst layers using a fully-automated airbrushing method, a 56% improvement in CO$_2$RR performance was observed in comparison to hand-painted GDEs.$^{57}$ In the second report on electrode modification, multi-walled carbon nanotubes were incorporated into the Ag catalyst layer. In a configuration where the Ag catalyst and carbon nanotubes were homogeneously distributed, the hybrid reactor using 1 M KOH as the catholyte yielded $J_s$ of 350 mA/cm$^2$ at high $FE$ (>95% selective for CO).$^{40}$ In the most recent report, Kenis and co-workers also modulated the amount of PTFE that was incorporated in the MPL of the GDE.$^{38}$ They demonstrated that their custom made GDEs (i.e; 20 wt% PTFE) exhibited higher partial current density for CO production in comparison to a commercially available GDE.$^{38}$ It is worth noting
that all of these experiments were optimized for a membrane-free hybrid reactor architecture, but provide valuable insight into the influence of GDL properties on electrochemical CO$_2$ reactor performance.

In a more recent study by Sargent and co-workers, a new type of GDE was developed for a hybrid reactor.$^{52}$ This GDE employed a porous polytetrafluoroethylene (PTFE) membrane as a hydrophobic GDL in place of traditional carbon GDL. The catalyst was then deposited on the PTFE membrane, followed by a porous carbon layer for current collection. This new type of GDE exhibited more than 100 hours of stable operation at 150 mA/cm$^2$ total current density with >90% $FE$ for CO. It is believed that the hydrophobic PTFE membrane, which prevents electrolyte flooding, is responsible for long term performance. The mass transport and catalytic performance of GDEs are likely also affected by properties including porosity, permeability, and conductivity, factors that have yet to be considered in CO$_2$RR literature. In contrast to fuel cells, GDE design for CO$_2$ reduction has not yet been optimized.

### 2.4 Water Management

The management of water within CO$_2$ membrane reactors has emerged as an important factor in influencing the performance because the balance of water is critical in the CO$_2$RR. Water acts as a reactant for the conversion of CO$_2$, but if too much water is available, the reaction can proceed through the HER instead. Water can be transported to the CO$_2$ catalyst through two different mechanisms (Figure 2.9): i) from the humidified gas stream and/or ii) from the membrane. In the humidified gas stream the gas flow rate and the level of humidification modulates the amount of water in the CO$_2$ feed. Three processes describe the movement of water across the membrane: diffusion, electro-osmotic drag, and back convection (Figure 2.9).$^{96-99}$ Water
diffuses from the anode to the cathode because of the concentration gradient between the aqueous anode environment and the gas-fed cathode. Water is also drawn from the cathode to the anode through electro-osmotic drag as solvated anions migrate toward the anode. Back convection of H₂O from the cathode to the anode is driven by the increased liquid pressure associated with using hydrophobic cathode GDEs and by the higher water permeation through thinner membranes. The net amount of water transported to the cathode electrocatalyst can be optimized through the judicious selection of the membrane, cathode GDE, and cathode feed.

**Figure 2.9** Schematic illustration of water transport across the anode, cathode and membrane of a CO₂ reactor.

In Chapter 3, I demonstrate stark differences in cell stability for a CO₂ to CO reactor, where only the humidity of the gaseous CO₂ stream is modified. A CO₂ stream, containing a relative humidity of 15%, afforded stable electrolysis for 1 hr at 100 mA/cm², while an analogous setup supplied with a relative humidity of 90% preserved stable electrochemical performance at the same current density for over 24 h. The decline in cell performance for the low humidity setup was attributed to the dehydration of the solid electrolyte support layer and the membrane.
Several strategies have been employed to prevent membrane dehydration. For example, the membrane can be hydrated by humidifying the CO$_2$ feed,\textsuperscript{37} by incorporating a solid-supported electrolyte layer,\textsuperscript{65} or by a catholyte compartment adjacent to the membrane.\textsuperscript{85} However, in the latter cases, the cell potential is driven up due to high ohmic losses. Bell, Weber, and Weng highlighted the effects of operating conditions on H$_2$O transport processes of diffusion and electro-osmotic drag.\textsuperscript{88} Their work shows that thinner membranes can mitigate membrane dehydration in zero-gap reactors with humidified gaseous feeds at both the cathode and anode. However, this strategy may increase the risk of flooding in reactors with a liquid electrolyte at the anode. They also highlight major flooding issues encountered in the GDE with hybrid architectures where the liquid catholyte is present.

Water and CO$_2$ management can also be impacted by the electrolyzer components that govern the fluid dynamics of gas and liquid flows within a reactor. For example, the hydrophobicity of the GDE can be modulated by changing the PTFE content of the GDE to achieve an optimal H$_2$O balance.\textsuperscript{38} Furthermore, the flowplate can constitute various patterns and designs with different path lengths, channels numbers and channel thicknesses, which impact the distribution of CO$_2$ and H$_2$O across the MEA.\textsuperscript{102–104} If this distribution is non-uniform, it can lead to efficiency gradients and non-uniform current densities serving to convolute the analysis of overall cell performance.\textsuperscript{105} These issues are extensively documented in PEM fuel cell literature, where techniques such as computational fluid dynamic simulations, water gradient mapping, and pressure/temperature sensing are tested with different flow field patterns in order to better understand how these geometric parameters impact electrolytic performance.\textsuperscript{105,106} In studies within electrolytic reactors, 3D-printing techniques allow for rapid prototyping and optimization.
of different flow field geometries for liquid water electrolyzers. Similar tools to aid in the design and optimization of flow fields for CO₂ reactors have yet to be reported.

2.5 Landscape of The Field

Research in the CO₂RR field has largely focused on batch type H-cell experiments, which do not account for the significant influence of non-catalytic components and feedstock characteristics on overall cell performance. Electrochemical flow reactors provide a more commercially relevant testing platform than H-cells because flow reactors enable the systematic manipulation of non-catalytic components that affect the industrial viability of CO₂ electrolyzers. This literature review emphasized the importance of testing the CO₂RR in flow reactors and highlighted promising strategies to optimize the CO₂ feedstock, membrane, gas diffusion electrodes, and water management to drive CO₂ electroreduction towards these higher current densities required for commercialization. A summary of the CO₂ reactor field is provided in Figure 2.10 and Table 2.1. In order to have a commercially relevant technology, a CO₂ reactor must have performance metrics in the top right corner of Figure 2.10 (i.e., high J and high FE). The work in this thesis, in Chapter 3 and Chapter 5, represent advances in gas-fed membrane reactors. While many of the optimization strategies provided in this literature review have enabled the field to reach relevant operational performance (high FE at J > 200 mA/cm²), many reports do not include $V_{cell}$ measurements (Table 2.1). The work in Chapter 4 provides an analytical device to compare the voltage losses across both hybrid and membrane architectures.
Figure 2.10 Landscape of $J$ (mA/cm$^2$) vs. FE for CO (%) for gas fed hybrid and membrane CO$_2$ reactor architectures for the reaction of CO$_2$ to CO. Only works at room temperature and where the total current density is 100 mA/cm$^2$ and above are included.
Table 2.1 A summary of literature showing reactor type, catalysts, GDE substrate, FE, J, \( V_{\text{cell}} \) and lifetime of GDEs for the synthesis of CO from \( \text{CO}_2 \) reduction. Only works at room temperature and where the total current density is 100 mA/cm\(^2\) and above are included.

<table>
<thead>
<tr>
<th>Reactor Type</th>
<th>Catalyst</th>
<th>Catholyte</th>
<th>membrane</th>
<th>GDE type</th>
<th>FE</th>
<th>( J ) (mA/cm(^2))</th>
<th>( V_{\text{cell}} )</th>
<th>Lifetime</th>
<th>ref.</th>
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<td>Carbon GDL</td>
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<td>4.5 V</td>
<td>24 h</td>
<td>Chapter 3</td>
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<tr>
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<td>-</td>
<td>AEM</td>
<td>Carbon GDL</td>
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<td>2.5 V</td>
<td>24 h</td>
<td>Chapter 5</td>
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<td>2M KOH</td>
<td>-</td>
<td>Carbon GDL</td>
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<td>158</td>
<td>-</td>
<td>8 h</td>
<td>49</td>
</tr>
<tr>
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<td>-</td>
<td>AEM</td>
<td>Carbon GDL</td>
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<td>200</td>
<td>3 V</td>
<td>4380 h</td>
<td>32</td>
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<td>-</td>
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<td>-</td>
<td>4 h</td>
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<td>-</td>
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<td>480</td>
<td>-</td>
<td>-</td>
<td>35</td>
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<td>AEM</td>
<td>PTFE GDL</td>
<td>90%</td>
<td>&gt;150</td>
<td>-</td>
<td>100 h</td>
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Chapter 3: Electrolysis of Gaseous CO$_2$ to CO in a Flow Reactor with a Bipolar Membrane


3.1 Introduction

CO$_2$ has the potential to be a feedstock for the scalable production of carbon monoxide, formate, methanol, ethylene, and longer chain alkanes.$^{109,110}$ This possibility has drawn a significant effort towards the discovery of electrocatalysts capable of mediating these transformations with high efficiency and selectivity.$^{28,111–114}$ The economic viability of using renewable electricity to electrolytically convert CO$_2$ into certain carbon products remains an open question, but there is a potential case for generating CO from CO$_2$.$^{115}$ The annual global CO production of 210,000 Mt is already significant, and CO serves as an important chemical precursor for a number of industrial processes, including Fischer-Tropsch chemistry that could effectively enable the conversion of sunlight into liquid fuels.$^{116,117}$

Electrocatalysts capable of converting CO$_2$ to CO with high selectivity are now known.$^{112,117–121}$ For example, oxide-derived Au electrodes reported by Kanan reach a $FE$ of 99% for CO formation at a $J$ of 10 mA/cm$^2$.$^{122}$ Highly porous silver and copper electrodes reported by Jiao$^{67}$ and Mul$^{123}$ are also capable of producing CO at these current densities with comparable selectivities. Studies of mixed metal catalysts, such as copper-indium alloys that can produce a CO$_2$-to-CO $FE$ of ~90% at $J = 3$ mA/cm$^2$, $^{28,124}$ highlight the possibility of tuning the activity of catalysts by incorporating a secondary metal to yield higher activities. Mediating these reactions in ionic liquids also enables the selective formation of CO at high current densities.$^{14,114}$
The majority of CO$_2$ electrolysis studies test catalytic performance at low overpotentials and $J$ values ($<20$ mA/cm$^2$) or use expensive materials (e.g., ionic liquids), yet commercial electrolyzers employ conventional aqueous electrolytes and operate at much higher current densities ($>200$ mA/cm$^2$). The translation of these catalysts therefore needs to be proven out in flow reactors (and multiple-cell stacks) in order to realize the commercial electrolyzer architectures capable of reducing CO$_2$ effectively. This line of inquiry has been followed by Masel and co-workers, who reported a flow system based on the ionic-liquid-mediated conversion of CO$_2$ to CO with a 96% FE for CO at a $J$ of $\sim5$ mA/cm$^2$. In a prior report, we utilized a BPM to accommodate the OER in basic media, in order to utilize efficient and earth-abundant transition metal catalysts at the anode, while feeding CO$_2$-saturated NaHCO$_3$ solution to the cathode. The FE for CO production was stable at $\sim50\%$ at 30 mA/cm$^2$ using this architecture, but the cells showed a diminution in CO evolution efficiencies at progressively higher current densities. This observation is consistent with other liquid-fed electrolyzers, where the maximum electrocatalytic partial current of CO evolution that has been reached is approximately 30 mA/cm$^2$.

In order to overcome the inherent diffusion limitations that exist in a liquid-fed CO$_2$ electrolyzer, several groups have modified cells in order to enhance CO$_2$ availability to reaction sites. Kenis and co-workers introduced a hybrid electrochemical flow reactor, where the liquid electrolyte flows between the cathode gas diffusion electrode and a membrane while a gaseous CO$_2$ feed flows on the opposing side of the cathode electrode, to reach current densities of 300 mA/cm$^2$ for CO production (and 120 mA/cm$^2$ for HCOO$^-$ production). This chemistry was extended to a three-compartment electrochemical cell configuration capable of producing HCOO$^-$ at 140 mA/cm$^2$ by Masel and co-workers. McIlwain and co-workers used a pressurized...
electrochemical system to increase the quantity of CO generated by 5-fold (92% FE at 350 mA/cm²) over what was measured at ambient pressures.¹²⁷

The diffusion limitation in liquid phase CO₂ electrolyzers originates from the solubility of CO₂ in aqueous electrolyte solutions (~30 mM in H₂O at atmospheric pressure) as well as a low diffusion coefficient of CO₂ in water (0.0016 mm²/s).³¹ Gas-phase electrolysis, therefore, has the potential to increase mass transport and achieve current densities several orders of magnitude greater than liquid phase electrolysis at atmospheric pressures, yet this strategy has been very rarely used.⁷² There are currently merely two gas-phase CO₂ electrolysis reports to date, one using a CEM and a second with an AEM. Newman et al. introduced a dual solid electrolyte configuration consisting of an 800-µm thick glass fiber impregnated with 0.5 M KHCO₃ in between the cathode GDL and CEM layers.⁶⁵ The cathode was fed with a humidified stream of CO₂ and the anode was exposed to the aqueous solution for the OER chemistry. There was a significant decrease in FE for CO from 80% at 20 mA/cm² to 20% at 100 mA/cm² with this dual solid electrolyte design. Masel & co-workers, reported a gas-phase system utilizing their specifically designed AEM membranes, achieving high current densities (130 mA/cm²) and 98% FE for CO.³² These membranes incorporate an imidazolium group, similar to the ionic liquid they reported for high conversion of CO₂ to CO.¹⁴,³²

In this chapter, I demonstrate a BPM-based gas fed membrane reactor that converts CO₂ to CO at high current densities of 200 mA/cm². This CO₂ membrane reactor was designed around the use of a BPM that dissociates water into H⁺ and OH⁻ under reverse bias (Figure 3.1). BPMs are more commonly used in electrodialysis¹²⁸ and solar water splitting,¹²⁹,¹³⁰ but have shown recent use in CO₂ conversion devices.⁷²,⁷³,¹³¹ We have previously shown that a Nafion-based cell suffers from stability issues because the anolyte and catholyte become progressively more acidic.
and basic, respectively, during electrolysis. In contrast, the dissociation of water in a BPM drives H\(^+\) and OH\(^-\) ions toward the cathode and anode, respectively, enabling the pH of the anode and cathode to remain constant. Using a BPM enables the use of earth-abundant metal anodes that are only stable in basic conditions (e.g., Ni, Fe\(_2\)NiO\(_4\))\(^{90,132-138}\) and highly active acid-stable cathodes for CO\(_2\) reduction (e.g., silver).\(^{7,113,139}\) Gas-diffusion electrodes also overcome the diffusion limitation of CO\(_2\) in water at ambient conditions and alleviate mass-transport limitations across the gas-liquid interface and to the catalyst surface, thereby allowing the cell to operate at higher current densities. A silver catalyst was selected to mediate the cathodic reaction on the basis that it is known to exhibit high selectivity for converting CO\(_2\) to CO.\(^{7,113,118,139}\) A nickel anode was used because of the high stability and activity towards the OER in basic media.\(^{132,140}\) I was able to enhance the FE\(_s\) and reach current densities for gas fed CO\(_2\) electrolysis on the order of 200 mA/cm\(^2\) with a FE for CO production of 50% by incorporating a solid-supported aqueous layer (1.0 M NaHCO\(_3\)). I demonstrate an apparent correlation between long-term stability and hydration of the CO\(_2\) inlet stream. I am able to maintain stability for over 24 h at 100 mA/cm\(^2\) when the solid-state support was adequately hydrated. This result is important for understanding the role of water management in CO\(_2\) electrocatalysis and provides an important guideline for the development of new electrolyzer technologies.
3.2 Results and discussion

Cyclic voltammograms over the -1.0 to -3.0 V range were collected for both liquid- and gas-phase reactors for the reduction of CO₂ (Figure 3.2). The cell architectures were the same for both cells (BPM-separated nickel GDL and silver-coated carbon GDL), and the anode feed was 1.0 M NaOH. For liquid-phase electrolysis, the cathode feed was CO₂-saturated 0.5 M NaHCO₃; for gas-phase electrolysis, the cathode feed was a humidified gaseous stream of CO₂. Both configurations yielded an increase in $J$ with increasing potential ($V$); however, the gas-fed stream achieves a $J$ approximately double that of the liquid-fed system at -3.0 V (100 mA/cm² vs. 48 mA/cm²). These differences in current densities, while holding all other experimental parameters
at parity, provide a clear demonstration of the potential to overcome mass-transport limitations in liquid-fed CO₂ electrolyzer systems by using a gas-phase feed.

![Cyclic voltammograms for gas and liquid phase CO₂ electrolyzer cells](image)

**Figure 3.2** Cyclic voltammograms for gas and liquid phase CO₂ electrolyzer cells show higher rates of product formation for gas-fed cathodes. (Scan rate = 100 mV s⁻¹, anode: nickel foam, cathode: silver on carbon-GDL, anolyte: 10 mL/min 1 M NaOH, liquid catholyte: 10 mL/min 1 M NaHCO₃, gas catholyte: 100 SCCM humidified CO₂.)

The physical characteristics of silver-based cathodes before and after gas-phase electrolysis were determined by scanning electron microscopy (SEM), X-ray fluorescence (XRF) and powder X-ray diffraction (XRD) techniques. The cathodes were subjected to 3000-s chronopotentiometric experiments from 20 up to 200 mA/cm² in 20-mA/cm² increments amounting to ca. 10 h of cumulative electrolysis. The SEM images presented in Figure A3.1a indicate that the ca. 100 nm nanoparticles remain unchanged during electrolysis on the basis that there is no apparent loss in surface coverage or change in morphology. XRF analysis of the cathode shows nominal differences in metal loading before and after electrolysis experiments (Figure A3.1b), and the powder XRD diffractograms show superimposable reflections corresponding to the silver signals indicating no change in the crystalline structure of the catalysts (Figure A3.1c). These collective
results show that the catalytic components of the cell are robust during gas phase CO$_2$ electrolysis on the timescale of our experiments.

Gas chromatography (GC) measurements of the expelled gases were used to evaluate the $FE$ values for CO and H$_2$ production in the gas-phase membrane reactor system described above. $FE$s were calculated (as described in section 3.4.2 Electrolysis and Product Analysis) for $J$ values between 20 and 100 mA/cm$^2$ after 700 s of electrolysis (Figure 3.3a). The results show a $FE$ of 25% for CO at low current densities ($J = 20$ mA/cm$^2$), and diminish to below 10% with increasing $J$ up to 100 mA/cm$^2$. In the only other previous example of gas-phase CO$_2$ reduction to CO in a membrane reactor (Newman et al.),$^{65}$ the authors were able to increase the selectivity for CO by introducing a solid-supported aqueous NaHCO$_3$ (1.0 M) layer between the CEM and the electrocatalyst. I was able to reproduce this result by incorporating this layer into my configuration (Figure 3.3b): A dramatic improvement in CO selectivity was observed for all $J$ values (Figure 3.3b), with moderate $FE$ for CO (67%) retained at $J = 100$ mA/cm$^2$. Indeed, I was able to reach even higher $J$ values (200 mA/cm$^2$) and only witness a minor decrease in $FE$ for CO (50% at 200 mA/cm$^2$) with this configuration. These results demonstrate the ability to perform CO$_2$ to CO reduction in a flow reactor at the high current densities relevant to industrial electrolysis.$^{30}$
Figure 3.3 (a) Cross-sectional configuration of the gas-fed CO$_2$ membrane reactor showing the location of the solid-supported aqueous NaHCO$_3$ layer between the BPM and cathode silver catalyst. (b) FE (%) for CO production at current densities between 20 and 100 mA cm$^{-2}$, both with (blue) and without (black) the aforementioned NaHCO$_3$ layer. (c) Faradaic efficiencies for CO$_2$ to CO and H$_2$ products measured by GC after 700 s of gas-phase CO$_2$ electrolysis in a flow-cell configuration containing a solid-supported aqueous NaHCO$_3$ solution. (Anode: nickel foam; cathode: silver on C-GDL; anolyte: 10 mL/min 1 M NaOH; gas catholyte: 100 SCCM humidified CO$_2$.)

While the inclusion of the solid-supported aqueous electrolyte layer is necessary to achieve high CO selectivity in our membrane reactor configuration, the exact role of this layer is unclear. I, therefore, sought to clarify this role by replacing the solid-supported aqueous NaHCO$_3$ layer with a solid-supported water layer (i.e., NaHCO$_3$ was omitted). The FE for CO production in the bicarbonate-free system was comparable (within 15% discrepancy) at all $J$ values up to 200 mA/cm$^2$ to the system containing NaHCO$_3$ (Figure 3.4). This result suggests that the water component of the solid-support layer is responsible for mediating electrolytic performance and not NaHCO$_3$. The addition of the solid-supported aqueous layer (with or without NaHCO$_3$) made no significant differences in the voltages required to drive chemistry at higher current densities. This point is supported by the data shown in Figure A3.2 that reveals nominal changes in the measured cell potential for three cases where the support layer is modified (i.e., no support layer, H$_2$O layer, and NaHCO$_3$ layer) and held at a constant current of 100 mA/cm$^2$. I conclude from this result that no apparent voltage or resistance losses are arising from the solid support layer.
**Figure 3.4** FE for CO and H\(_2\) production measured by GC after 700 s of gas-phase CO\(_2\) electrolysis in a flow-cell configuration containing a solid-supported aqueous NaHCO\(_3\) layer (blue) and a solid-supported water layer (black). (Anode: nickel foam, cathode: silver on C-GDL, anolyte: 10 mL/min 1 M NaOH, gas catholyte: 100 SCCM humidified CO\(_2\).)

I then set out to validate the importance of maintaining a hydrated solid-support layer by running my reactor continuously at 100 mA/cm\(^2\) with a low-humidity CO\(_2\) inlet stream. A 15% relative humidity (RH) for the CO\(_2\) inlet stream can be achieved by bypassing the CO\(_2\) inlet water bath (passing CO\(_2\) through the water bath reaches a RH of 90%). The result of using a low-humidity CO\(_2\) inlet was a rapid decay in reactor performance within 2 h, as indicated by the sharp rise in required bias above 4 V (Figure 3.5a). This decline in performance occurred concomitantly with dehydration of the aqueous support layer. This result suggests that the physical change of the cathode support layer induced by dehydration precludes facile delivery of the protons to the catalytic sites. Replenishing the support layer with water resulted in a full recovery of \(J\) and \(FE\) for CO production (relative to the initial values) (Figure A3.3), supporting my hypothesis that adequate hydration of the support layer needs to be preserved in order to maintain prolonged electrolytic stability. Adequate hydration during sustained electrolysis can be achieved by
supplying the flow reactor with humidified CO\textsubscript{2} on the basis that I measured stable CO\textsubscript{2} to CO electrolysis at 65\% FE and 100 mA/cm\textsuperscript{2} (Figure 3.5b).

**Figure 3.5** Faradaic efficiencies and chronopotentiometry data showing required bias (\(V\)) for CO\textsubscript{2} to CO measured by GC of gas-phase CO\textsubscript{2} electrolysis in a flow-cell configuration containing a solid-supported aqueous H\textsubscript{2}O solution. a) Inlet CO\textsubscript{2} without hydration; RH = 15\%. b) Inlet CO\textsubscript{2} hydrated at RT; RH = 90\%. (Anode: nickel foam, cathode: silver on C-GDL, anolyte: 10 mL/min 1 M NaOH, gas catholyte: 100 SCCM CO\textsubscript{2}.)

3.3 Conclusions

I demonstrate here a membrane reactor for the gas-phase reduction of CO\textsubscript{2} to CO at high current densities (\(J = 200 \text{ mA/cm}^2\)) that provides stable performance for 24 h. Robust performance is contingent on delivering a hydrated gas-phase CO\textsubscript{2} stream to the cathode. This inlet stream produces nearly double the current density than a CO\textsubscript{2}-saturated aqueous solution can produce when all other experimental parameters are held at parity. These differences, which are primarily because of mass transport limitations associated with aqueous CO\textsubscript{2} chemistry that are overcome by working in the gas phase, sets the agenda for all our future flow-reactor designs for CO\textsubscript{2} electrolysis.

I also lay out the critical role that hydration has on the performance of the cathode. It is necessary to include a water support layer (or aqueous NaHCO\textsubscript{3} layer)\textsuperscript{65} in order to achieve
reasonable $FE$s for CO formation at higher current densities (e.g., 200 mA/cm$^2$). By maintaining a hydrated CO$_2$ stream (>90% RH), I am can maintain hydration of the support layer and my cell stability was over 24 h at 100 mA/cm$^2$. These values represent the highest reported current densities for gas phase CO$_2$-to-CO flow-reactor electrolysis in a bipolar membrane-based reactor.

3.4 Experimental

3.4.1 Cell Design

The custom-made electrolyzer cell depicted in Figure 3.1 was built in-house and consists of housing, gaskets, anode and cathode flow-field plates and a MEA. The anode and cathode housings (6 × 6 × 1.2 cm) are made from stainless steel and serve to deliver liquid and gas feeds to the anode and cathode, respectively, through ⅛” NPT ports with barbed tubing adapters. Stainless steel was chosen for its chemical inertness to both anode and cathode feeds. The acid-stable cathode flow plate and base-stable stainless steel anode flow plate sandwich the 4 cm$^2$ MEA. The anode (316 stainless steel) and cathode (Grade 2 titanium) flow-field plates (6 × 6 × 0.6 cm; active area = 4 cm$^2$) contain serpentine channels 1.5 mm wide and 1.5 mm deep with 1-mm ribs. This flow-field plate design is similar to a previously reported design for a water electrolyzer. Stainless steel and titanium were chosen for anode and cathode flow plates, respectively, for their inherent chemical stabilities in basic and acidic conditions, and inactivity towards the OER and CO$_2$RR. All gaskets are cut from 1.5-mm thick chemical resistant compressible PTFE. The PTFE gaskets have good chemical inertness to cathode and anode feeds and high compressibility, ensuring both liquid and gas-tight seals. The gaskets between the housing and the flow-field plate, on both the anode and cathode sides (PTFE gasket A), have 0.2 mm diameter holes for liquid or gas delivery. The gaskets between the flow-field plate and the MEA have a 2 × 2 cm square cut out (PTFE gasket B). The MEA consists of a nickel
foam anode (2.5 × 2.5 cm), a BPM (3 × 3 cm), an intermediate layer (glass fibers impregnated with NaHCO$_3$ or H$_2$O) and a silver nanopowder/Nafion catalyst mixture deposited on a carbon paper GDL cathode (2.5 × 2.5 cm). Nickel foam was used as both the diffusion layer and OER catalyst in basic conditions, while a silver nanopowder/Nafion catalyst mixture was deposited on a carbon paper GDL to afford high surface area and enable rapid mass transport of gas phase CO$_2$ under locally acidic conditions. An intermediate layer consisting of 1.0 M NaHCO$_3$ solution or H$_2$O supported on glass fibers (Whatman® glass microfiber filters, Grade GF/D) was included where specified. The role of this support layer is investigated in my results. The entire assembly is sandwiched between the two stainless housings fastened with 8 bolts of 6.35 mm diameter.

3.4.2 Electrolysis and product analysis

The CO$_2$ flow rate to the cathode was set to 100 sccm by a flow controller (Matheson; 7531-602) and humidified to a relative humidity of >90% (confirmed by a hygrometer; Neoteck) by passing the gas through a water bath at prior to entering the cathode; 1 M NaOH was recirculated through the anode compartment at a flow rate of 10 ml/min using a peristaltic pump (McMaster-Carr; 43205K11). The electrolyzer outlet was introduced into a condenser before being vented directly into the gas-sampling loop of the gas chromatograph (GC, Perkin Elmer; Clarus 580). The flow rate of CO$_2$ was measured prior to each GC run. The GC was equipped with a packed MolSieve 5Å column and a packed HayeSepD column. Argon (Praxair, 99.999%) was used as the carrier gas. A flame ionization detector with methanizer was used to quantify CO concentration, and a thermal conductivity detector was used to quantify hydrogen concentration. The GC was calibrated as previously reported.$^5$

Electrochemical measurements were conducted at room temperature and pressure by means of a potentiostat (CH instruments 660D with a picoamp booster) through two-electrode cell
measurements. Current density is expressed as the total current divided by the geometric surface area of the electrodes (4 cm$^2$). The FE of a gaseous product $k$ was determined in accordance with Equation 3.1.

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

(Eq. 3.1)

Where $n_k$ is the number of electrons exchanged, $F$ is Faraday’s constant ($F = 96,485$ C/mol), $x_k$ is the mole fraction of the gas $k$ in the gaseous mixture analyzed, $F_m$ is the molar flow rate in mol/s, and $I$ is the total current in A. The molar flow rate is derived from the volume flow rate $F_v$ by the relation $F_m = pF_v/RT$, with $p$ being the atmospheric pressure (Pa), $R$ the ideal gas constant (8.314 J/mol K), and $i$ the temperature (K).

3.4.3 Electrode Preparation

The cathodes were prepared using an airbrush method similar to a previous report.$^{47}$ The cathode catalyst ink was prepared by mixing 32 mg of silver nanopowder (Sigma, trace metal basis, >99%), 800 μL of DI water, 800 μL of isopropyl alcohol and 60 μl Nafion 117 solution (Sigma, 5 wt% in a mixture of lower aliphatic alcohols and water). The catalyst ink was then spray-coated on a 4 cm$^2$ area of carbon cloth (Fuel Cell Store, GDL-CT) and dried under a gentle air stream. Kapton tape (McMaster-Carr) was used as a mask during the deposition process to avoid catalyst being deposited outside the active area of the GDL. The catalyst loading was determined to be 1.5 ± 0.2 mg/cm$^2$ by weighing the GDL before and after deposition. The anodes were prepared by cutting as-purchased nickel foam (MTI;EQ-BCNF-16m) to size. A standard cleaning procedure was used to clean both the carbon GDL and nickel foam.$^{46}$ The intermediate layer (Whatman GF/D, 2.7 m pore size) was prepared by soaking in H$_2$O for 1 min, and the BPMs (FuMA-tech; Fumasep FBM) were
stored in 1 M NaCl solution prior to assembly in the cell. A fresh cathode, anode, an intermediate layer and BPM were used for each electrolysis test.

3.4.4 Physical characterizations

SEM was performed using a dual-beam scanning electron microscope. An accelerating voltage of 1.0 keV and a current range of 25 pA to 0.2 nA was used to obtain the images in magnetic immersion mode. XRF measurements were taken with a Thermo Fisher Scientific Niton XL3t analyzer utilizing a shielded test stand. The X-ray source was run with an accelerating voltage of 50 kV and a current of 40 μA. The scan time was 60 s for each sample. XRD data was recorded with a Bruker D8 Advance diffractometer using Cu K radiation. Data were collected between 2θ angles of 5° and 90° with a step size of 0.04° and step time of 0.6 s.
Chapter 4: Voltage Matters in an Electrochemical Flow Reactor for Reducing CO₂

Adapted from: Salvatore, D.A; Berlinguette, C.P. ACS Energy Lett.. 2020, 5, 215-220

4.1 Introduction

CO₂ electrolyzers offer the opportunity to utilize renewable electricity by electrocatalytically reducing CO₂ into useful fuels and chemicals. The economic viability of a CO₂ electrolyzer is contingent on several factors, including the selectivity of the CO₂RR and the rates of product formation. Operational voltage is also an important performance metric because it defines the energy efficiency of the electrolyzer. Commercial units will likely need to operate below 3 V while maintaining current densities in excess of 200 mA/cm² (Figure 4.1). Despite the importance of this metric, the full-cell voltages of pilot-scale CO₂ electrolyzer reactors, or flow reactors, are rarely reported. Moreover, very little is known about where the voltage losses occur in CO₂RR flow reactors. This gap in the literature prompted us to design and build an analytical flow reactor capable of resolving voltage drops across individual electrode and membrane components during CO₂RR electrolysis (with the OER occurring at the anode). Measurements recorded with this apparatus point to the largest voltage losses occurring at the membrane, and not at the catalyst layers. These results, which apply to both membrane and hybrid flow reactor configurations (Figure 4.2) common to the field, illuminate that a better understanding of membranes and the membrane-catalyst interface is needed.
Figure 4.1 Levelized cost of CO generated by a CO$_2$RR electrolyzer as a function of current density. The plot highlights that operational voltages of $<3$ V are needed to be cost-competitive with conventional methods of producing CO, and that the cost of electrolytically generating CO is governed by voltage at high current densities. The data shown corresponds to assumptions ($FE$ for CO production = 90%; electricity price = $0.05$/kWh) that are aligned with techno-economic assessments. The $0.60$/kg used to represent the market price for CO should be considered a high value and does not represent the entire market.

Figure 4.2 Expanded views of membrane and hybrid flow reactors. The blue text indicates where the cell voltages are typically measured.
Most CO\textsubscript{2} electrolyzer architectures reported to date can be described as either hybrid or membrane flow cell reactors (Figure 4.2). In a hybrid reactor, the electrochemistry at the cathode is influenced by the catholyte that separates the cathode GDE and the membrane. This catholyte helps mediate efficient CO\textsubscript{2}RR at low half-cell overpotentials, but this liquid layer will ostensibly be responsible for a significant voltage drop across the cell. This voltage is typically not measured, however, and is simply estimated by the ionic resistance of the electrolyte.

The membrane reactor architecture more closely matches that of a conventional zero-gap water electrolyzer, wherein a polymer electrolyte membrane separates the cathode from the anode. The CO\textsubscript{2} feedstock can be delivered to the cathode directly in the gas phase, as a saturated solution in an aqueous electrolyte, or as a bicarbonate/carbonate solution that converts CO\textsubscript{2} at a catalyst layer in an acidic environment. Regardless of the feedstock, CO\textsubscript{2} is electrochemically converted to a CO\textsubscript{2}RR product at the interface between the membrane and the cathode gas diffusion electrode. Membrane reactors should, in principle, not suffer from the same voltage losses incurred by the catholyte layer in the hybrid reactor. Moreover, the catholyte governs the cathode chemistry in a hybrid reactor, while the membrane figures more prominently in the cathodic electrochemistry of the membrane reactor.

The polymer electrolyte membrane for both reactor types serves to separate the anode and cathode, mediate the flow of ions from electrode to the other, and prevent product crossover. CEMs, AEMs and BPMs are all being actively tested in CO\textsubscript{2} flow reactor systems. The choice of membrane dictates the reaction environments at the electrodes: CEMs and AEMs transport cations (e.g., H\textsuperscript{+}) and anions (e.g., OH\textsuperscript{-}), respectively, between electrodes. BPMs, which consist of an AEM laminated to a CEM, dissociate water at the
AEM|CEM interface under reverse bias conditions to enable H⁺ transport to the cathode and OH⁻ to the anode. Many of the highest performance flow reactors are those that use an AEM, but product crossover between compartments remains a significant issue.⁸⁴,⁸⁶,¹⁴² BPMs better manage this product crossover issue, and also enable higher electrode stability by avoiding the formation of pH gradients that arise during ionic transport across the membrane.⁷²,⁸⁴ A key shortcoming to using BPMs, however, is the large potential required to split H₂O under reverse bias.⁹¹ Robust CO₂RR electrolysis at high current densities has not yet been demonstrated with CEMs,⁶⁵,⁷⁹ but we expect these to be effective as the field explores alternative CO₂ feedstocks that demand an acidic environment at the cathode.¹⁴⁶

The design of an efficient CO₂ electrolyzer, regardless of the reactor or membrane type, requires a clearer understanding of where the energy efficiency losses occur.¹⁰,¹⁴¹ Tracking these losses with voltage measurements can be done more readily for hybrid reactors because the reference electrode can be inserted in the liquid catholyte (which passes through the channel between the cathode and membrane of the hybrid reactor) to measure the cathodic half-cell voltage.⁴³,¹⁴⁸ Indeed, the cathode half-cell voltages measured in hybrid reactors are the only values available in the literature that report on the energy efficiency of CO₂RR catalysts in a flow reactor.⁴³,⁵⁶ Reference electrode measurements are far more difficult to perform for membrane reactors that use a gaseous CO₂ feedstock,¹⁴⁹,¹⁵⁰ where there is no liquid flow path in which to insert a reference electrode, consequently only the voltages of the full cell are reported, Figure 4.2.³⁷,¹⁵¹ Despite the fact that reference electrode measurements have been used extensively in fuel cell studies that also use gaseous feeds.¹⁴⁹,¹⁵² These types of in-situ voltage readings for each of the components would help advance our understanding of the processes that govern CO₂ flow reactor performance and durability, yet there is currently no such information available. We set
out to overcome this shortcoming by building an analytical flow reactor that incorporates reference electrodes on each side of the membrane while maintaining ionic contact with both the membrane and the respective electrodes. This analytical flow reactor was designed to use a gaseous or liquid feedstock, with the flexibility to be configured as either a membrane and hybrid reactor, with any type of membrane. It also enables the voltages across each of the electrode and membrane components to be independently measured during electrolysis. This apparatus revealed that the voltage measured across the membrane ($V_{\text{membrane}}$) represents a significant fraction of the full-cell voltage ($V_{\text{cell}}$), with voltage drops higher than those at the anode ($V_{\text{anode}}$) and cathode ($V_{\text{cathode}}$). I map out how the voltages across each of these components are affected by the choice of membrane (AEM or BPM) and reactor (membrane or hybrid) types in this Chapter.

4.2 Results and Discussion

A flow reactor with a 4-cm$^2$ active area was used for all experiments (Figure 4.3). The flow reactor consists of housing, gaskets, anode, cathode-flow field plates (with serpentine channels), and a MEA. The anode and cathode housings were made from stainless steel and served to deliver liquid electrolyte to the anode flow plate and gaseous CO$_2$ to the cathode flow plate. The MEA consisted of a nickel foam anode, an AEM or BPM, and a silver nanoparticle-coated porous carbon support as the cathode. For each experiment, the flow reactor was subjected to 30 min of electrolysis at the indicated applied voltage ($V$) or current ($i$) provided by an external power supply. The 1.0 M KOH anolyte was delivered to the flow reactor at 50 mL/min, and humidified CO$_2$ gas was supplied to the cathode at a rate of 100 sccm.
Figure 4.3 Exploded views of the membrane and hybrid analytical reactors used in this study. The measurement positions for “anode”, “cathode”, “R1”, “R2”, and “R3” are indicated in red. Schematics of the electrode configurations for each reactor are also shown.

An enabling feature of this study is the use of a bolt hole in the housing and flow plates that serves as a compartment for a reference electrode (“R1”; see Figure 4.3) immersed in electrolyte. This design was inspired by the “edge-type” configuration used for fuel cell testing, where the external reference electrode is placed in a liquid electrolyte connected through an
electrolyte bridge to the membrane. This configuration eliminates junction potentials that arise with the reference electrode sandwiched between two membranes. These measurements nonetheless still demand careful attention to maintaining alignment of the anode and cathode for uniform current distribution, positioning the reference electrode in a uniform potential region and ensuring the distance between the reference electrode and the active electrodes of the cell be at least three times the thickness of the polymer electrolyte layer. While edge-type reference cell configurations are prone to membrane dehydration for fuel cells, the electrolyte in the bolt hole provided the added advantage of keeping the membrane hydrated during our experiments.

The membrane reactors containing an AEM or BPM are denoted herein as membrane/AEM and membrane/BPM, respectively (Figure 4.3a). These reactors contain two reference electrodes placed in direct ionic contact with the measured layer (Figure 4.3a). Reference electrode “R1” was in ionic contact with the membrane on the cathode side of the cell, with “R2” in ionic contact with the anode outlet electrolyte. The membrane/AEM flow reactor was converted into a hybrid reactor (hybrid/AEM) by inserting a teflon catholyte flow field in between the cathode GDE and the membrane (Figure 4.3b), and the 1.0 M KOH catholyte was recirculated using a peristaltic pump at 20 mL/min. The hybrid/AEM reactor included an additional reference electrode, “R3”, placed in the catholyte inlet (Figure 4.3b).

The voltage drop for any single component was measured with the appropriate electrodes (i.e., any two of “anode”, “cathode”, “R1”, “R2”, or “R3”) while passing a current through the full cell in a 4-electrode configuration. All potentials are reported versus a Ag(s)/AgCl(aq, 3 M) reference electrode. The two electrodes used for any voltage reading are indicated herein as (“anode”|“cathode”). The $V_{cell}$ measured for the flow reactor accounts for the half-cell potentials
at the electrodes (\(V_{\text{cathode}}\) and \(V_{\text{anode}}\)) as well as ionic ohmic losses through the cell (primarily \(V_{\text{membrane}}\) and \(V_{\text{catholyte}}\)) in accordance with Equation 1 (Figure 4.4):\(^{153}\)

\[
V_{\text{cell}} = V_{\text{cathode}} - V_{\text{anode}} - V_{\text{membrane}} + V_{\text{catholyte}}
\]  

(Eq. 1)

Electrode voltages on either side of the membrane are governed by the respective equilibrium potentials at the electrodes (\(E_{\text{eq}}\)), activation overpotential (\(\eta_{\text{activation}}\)), diffusion limited overpotential (\(\eta_{\text{diffusion}}\)) and ohmic potential drop due to ionic conductivity (\(\Delta\Phi_{\text{ohmic}}\)) according to Equations 2 and 3:

\[
V_{\text{cathode}} = -E_{\text{eq, cathode}} - \eta_{\text{activation, cathode}} - \eta_{\text{diffusion, cathode}} - \Delta\Phi_{\text{ohmic, cathode}}
\]  

(Eq. 2)

\[
V_{\text{anode}} = E_{\text{eq, anode}} + \eta_{\text{activation, anode}} + \eta_{\text{diffusion, anode}} + \Delta\Phi_{\text{ohmic, anode}}
\]  

(Eq. 3)

To validate the apparatus, we benchmarked the \(V_{\text{membrane}}\) (R1|R2) within the membrane/BPM flow reactor against water electrolysis experiments with a BPM to confirm an expected onset of water dissociation at 0.8 V (Figure A4.1).\(^9\) The \(V_{\text{anode}}\) and \(V_{\text{cathode}}\) for the flow reactor are also closely aligned with half-cell measurements recorded in an H-cell, corroborating that our flow reactor design works effectively for measuring these key components.

**Figure 4.4** Diagram of voltage contributions and components measured for membrane and hybrid reactors used in this study.
The \( V_{\text{cell}} \) (anode|cathode) for the membrane/BPM reactor were recorded after 30 min of successive electrolysis experiments at 25, 50, 100 and 200 mA/cm\(^2\) (Figures 4.5a and A4.2, Table A4.1). The 2.56 \( \pm \) 0.28 V measured for \( V_{\text{membrane}} \) (R1|R2) was much higher than \( V_{\text{cathode}} \) (-1.26 \( \pm \) 0.26 V; R1|Cathode) and \( V_{\text{anode}} \) (0.64 \( \pm \) 0.06 V; Anode|R2). Similar experiments with the membrane/AEM reactor indicate a much lower \( V_{\text{membrane}} \) of 0.71 \( \pm \) 0.10 V (R1|R2). I attribute the higher \( V_{\text{membrane}} \) of the membrane in the membrane/BPM reactor to the free energy required to dissociate water with the BPM.\(^{89,129}\) Nonetheless, the AEM still accounts for 26% of \( V_{\text{cell}} \) at 200 mA/cm\(^2\). The anode (\( V_{\text{anode}} = 0.58 \pm 0.13 \) V; Anode|R2) voltages are, within experimental error, the same as those measured for membrane/BPM, but the \( V_{\text{cathode}} \) (-1.43 \( \pm \) 0.02 V; R1|Cathode) is slightly higher.
Figure 4.5 Voltage measurements for the membrane/BPM, membrane/AEM and hybrid/AEM reactors at 25, 50, 100 and 200 mA/cm$^2$. The voltage for each component is labelled as follows: anode (red); membrane (orange); catholyte (blue); and cathode (navy). The full cell potential (grey horizontal lines) is the sum of all component voltages measured across the cell. The average voltages were taken over 60 s, and are reported with error bars representing standard deviations for five replicates.

Importantly, the $V_{\text{cell}}$ (Anode|Cathode) measured for hybrid/AEM (4.61 ± 0.11 V) were markedly higher than the measurements with membrane/AEM (2.73 ± 0.07 V) particularly at higher current densities (Figures 4.5 and A4.4, Table A4.3). These differences can be sourced to the much higher $V_{\text{membrane}}$ (R2|R1) of 2.17 ± 0.71 V for hybrid/AEM relative to 0.71 ± 0.10 V measured for membrane/AEM. The higher $V_{\text{membrane}}$ for the hybrid flow reactor is presumably
because of the large interfacial resistance at the polymer/liquid interface that does not exist in the zero-gap membrane reactor. An additional voltage penalty of -0.69 ± 0.16 V (R3|Cathode) arises from the catholyte layer in the hybrid flow reactor. The $V_{\text{cathode}}$ (-1.21 ± 0.14 V; R1|Cathode) is lower for the hybrid reactor, presumably due to the higher local pH provided by the catholyte. The $V_{\text{anode}}$ (0.59 ± 0.04 V; Anode|R2) was similar to that of the membrane reactor, as expected given the similar chemical environments of the electrodes.

The key energy losses in the reactor are highlighted in Figure 4.6, which features the excess voltages required at each component. This plot shows that the hybrid reactor used in our study suffers from significant voltage losses and that the majority of these losses occur primarily at the membrane and catholyte. The collective losses contribute to a total $V_{\text{cell}}$ of $>$4.5 V, which is far too high to be cost competitive (Figure 4.1). The membrane flow reactor, even with the BPM, is more efficient than the hybrid flow reactor configuration. The membrane reactor with an AEM operates the most efficiently among the configurations tested. The data in Figure 4.6 also highlights that OER at a standard nickel mesh electrode occurs relatively efficiently,$^{132,138}$ and that the cathodic CO$_2$RR reaction with the AEM shows some loss in efficiency without a catholyte present for pH management.
4.3 Conclusions

This testing platform can be utilized to compare the voltages for both membrane and hybrid flow reactors to identify which cell components should be optimized to most effectively lower the overall $V_{\text{cell}}$. Our analysis of the voltages across the components of three different flow reactor configurations (i.e., membrane/BPM, membrane/AEM, and hybrid/AEM) highlights that the reactions at the anodes and cathodes are relatively efficient, and that much of the voltage loss occurs at the membranes. This outcome draws attention to the need to better understand of membranes and the membrane-catalyst interface. These conclusions were made possible by simply strategically placing reference electrodes in membrane and hybrid flow reactors. I urge those developing CO$_2$RR flow reactors to perform these accessible experiments in order to help resolve the voltage contributions for each of the key functional components.
4.4 Experimental

4.4.1 Materials

Silver nanopowder (trace metal basis, 99%) and Nafion 117 solution (5 wt%, in a mixture of lower aliphatic alcohols and water) were purchased from Sigma Aldrich. Carbon cloth (CeTech GDL) was purchased from the Fuel Cell Store and cut into desired dimensions with a blade. Nickel foam gas diffusion electrode material was purchased from MTI. BPM (Fumasep FBM) were purchased from FuMA-tech and stored in 1M NaCl Solution. AEM Sustainion® X37-50 Grade RT membrane was purchased from Dioxide Materials. The reference electrodes used in this study were Ag/AgCl (3M NaCl) Reference Electrodes purchased from BASi.

4.4.2 Cell Design

The custom-made electrolyzer cell depicted in Figure 3 was built in-house and consists of housing, gaskets, anode and cathode flow-field plates and a MEA. The anode and cathode housings (6 × 6 × 1.2 cm) are made from stainless steel and serve to deliver liquid and gas feeds to the anode and cathode, respectively, through ⅛” NPT ports with barbed tubing adapters. Stainless steel was chosen for its chemical inertness to both anode and cathode feeds. The acid-stable cathode flow plate and base-stable stainless steel anode flow plate sandwich the 4-cm² MEA. The anode (316 stainless steel) and cathode (grade 2 titanium) flow-field plates (6 × 6 × 0.6 cm; active area = 4 cm²) contain serpentine channels 1.5 mm wide and 1.5 mm deep with 1-mm ribs. This flow-field plate design is similar to a previously reported design for a CO₂ electrolyzer. Stainless steel and titanium were chosen for anode and cathode flow plates, respectively, for their inherent chemical stabilities in basic and acidic conditions, and inactivity towards the OER and CO₂RR. All gaskets are cut from 1.5-mm thick
chemical resistant compressible PTFE. The PTFE gaskets have good chemical inertness to cathode and anode feeds and high compressibility, ensuring both liquid and gas-tight seals. The gaskets between the housing and the flow-field plate, on both the anode and cathode sides, have 0.2-mm diameter holes for liquid or gas delivery. The gaskets between the flow-field plate and the MEA have a 2 × 2 cm square cut out. The MEA consists of a nickel foam anode, a membrane, and a silver nanopowder/Nafion catalyst mixture deposited on a carbon paper GDL cathode. The entire assembly is sandwiched between the two stainless housings fastened with 6 bolts of 6.35 mm diameter.

4.4.3 Electrolysis

The CO₂ flow rate to the cathode was set to 100 sccm by a flow controller (Matheson; 7531-602) and humidified by passing the gas through a water bath at prior to entering the cathode; 1 M KOH was recirculated through the anode compartment at a flow rate of 20 ml/min using a peristaltic pump (McMaster-Carr; 43205K11). Electrochemical measurements were conducted at room temperature and pressure by means of a potentiostat (CH instruments 660E) and a Keithley power supply (Keithley 2280). Current density is expressed as the total current divided by the geometric surface area of the electrodes (4 cm²). All electrodes were connected to a Keithley U2751A Modular Switch Matrix. The switch matrix was programmatically controlled to adjust the measurement between the two points (denoted as either the “working electrode” or “the reference electrode”) through relays connected to the CH Instruments Potentiostat. The relays were programmed to switch between each measurement point every 60 s during the constant current measurements to measure the voltage drops through each component of the cell during electrolysis. We were able to assess the voltage during regular operation of the cell by utilizing a power supply to apply a current and measuring the voltage through a separate potentiostat. Throughout all experiments, there was no
compensated resistance for the reference potentials and all potentials are reported vs Ag/AgCl (3M). The summation of the individual electrode contributions were equal to the total cell potential measured through the power supply.
Chapter 5: Molecular Electrocatalysts can Mediate, Fast, Selective CO$_2$ Reduction in a Flow Reactor


5.1 Introduction

The electrolytic reduction of CO$_2$ is an appealing method for making a range of carbon-based products, including CO, methane, formate, methanol, ethylene, and longer alkyl chains.$^{3,154-156}$ Among these CO$_2$RR products, the formation of CO is arguably one of the easier reactions to negotiate during catalysis on the basis that fewer electrons and protons are needed than for all other carbon products aside from formate. Notwithstanding, the best technology known today can produce CO with a $FE$ of >90% at current densities of 200 mA/cm$^2$ for merely 1000 h,$^{32,157}$ which remains inadequate for commercially relevant electrolysis.

CO$_2$RR electrolyzers designed to produce CO typically rely on heterogeneous catalysts, such as gold, silver, or copper.$^{12,154,155,158-160}$ Modifications to these solid-state electrocatalysts have not generally led to significant changes in efficiencies and selectivities at high current densities.$^{109,161}$ This situation prompted us to consider whether molecular catalysts could convert CO$_2$ to CO in a flow reactor, a pilot reactor capable of operating at conditions more relevant to an industrial electrolyzer.$^{3,32,37,65,93}$

The chemical and electronic environment about the active site of a molecular catalyst is often more substantially and acutely tunable than solid-state catalysts.$^{162-164}$ The ligand environment about a transition metal can be modified to yield competent homogeneous catalysts capable of mediating CO$_2$RR with selectivities as high as 99% (Figure 5.1).$^{165-168}$ However, with
one exception,\textsuperscript{169} electrocatalytic testing on these molecular systems were performed in organic media or at low current densities (<40 mA/cm$^2$) in order to accommodate the mass-transport limitations of batch-type (e.g., “H cell”) electrolysis experiments. Immobilizing high concentrations of molecular catalysts on high surface area conductive electrodes has allowed for a current density of 33 mA/cm$^2$ to be reached while being 90% selective for CO production.\textsuperscript{169}

![Graph](image)

**Figure 5.1** Selectivity and activity for CO production as a function of current density and cell voltage for molecular and heterogeneous CO$_2$RR electrocatalysts. (a) Faradaic efficiency for CO production, FE$_{CO}$, as a function of current density, $J$; and (b) CO partial current density, $J_{CO}$, as a function of overall cell voltage, $V_{cell}$, for high performing molecular catalysts\textsuperscript{158,160,164–174} (blue; see Table A5.1 for details) and the state-of-the-art heterogeneous Au\textsuperscript{49} and Ag\textsuperscript{32} catalysts (grey). The data for CoPc featured in this study is indicated in orange.

We report here that a molecular CO$_2$RR electrocatalyst can form CO with >95% selectivity at current densities of 150 mA/cm$^2$ in a flow reactor, and a $J_{CO}$ of 175 mA/cm$^2$ with an overall two-electrode cell voltage ($V_{cell}$) of 2.5 V. This value is 0.4 V lower (or a 4% gain in energy efficiency) than reported for silver solid-state CO$_2$ catalyst at a similar CO partial current density.\textsuperscript{32}

These performance metrics were realized in a zero-gap membrane reactor using a commercially available cobalt phthalocyanine (CoPc) CO$_2$RR catalyst immobilized on a gas diffusion layer in tandem with a nickel foam OER catalyst. This flow reactor provides access to higher current
densities by (i) overcoming the mass transport issues inherent to batch-type electrolysis, and (ii) supplying CO\(_2\) to the cathode in the gas phase in order to overcome the inherently low diffusion and solubility of CO\(_2\) in aqueous media.\(^3,31,65,82,180\) The catalyst was selected because it is inexpensive and is selective for CO\(_2\) to CO conversion in batch-type testing.\(^175,181\)

### 5.2 Results and Discussion

In our custom-designed flow reactor (Figure 5.2b), a catalyst ink, consisting of carbon powder supported CoPc and Nafion, was spray-coated on a hydrophobic carbon paper (that measured 2 cm × 2 cm) with a densely packed layer of microporous carbon to form the GDE.\(^37\) The serpentine cathode and anode flow plates that enable reactant delivery to the carbon supports were made of titanium and stainless steel, respectively. The MEA consists of a nickel foam anode (which acts as both a diffusion layer and the OER catalyst), an anion exchange membrane with high ion conductivity,\(^142\) and the GDE. The active areas of the cathode and anode are each 4 cm\(^2\), respectively. The cathode was fed with a humidified CO\(_2\) gas stream at a flow rate of 100 sccm, while the anode was fed with recirculated 1 M KOH at a flow rate of 20 mL/min.
**Figure 5.2** Membrane flow reactor for efficient CO$_2$RR with a cobalt-based molecular electrocatalyst. (a) Structure of the molecular catalyst, CoPc. (b) Exploded diagram of the zero-gap membrane reactor used for CO$_2$ electroreduction testing. The MEA comprises the cathode and anode GDEs on either side of the AEM. (c) Image of the flow reactor.

CO$_2$RR electrolysis in the flow reactor was measured under constant current conditions. We used in-line GC to detect and quantify the evolution of the CO and H$_2$ electrolytic products over the current density range of 25 to 200 mA/cm$^2$ in 25-mA/cm$^2$ increments (Figure 5.3). The measurements show that FE values of >95% were maintained at current densities up to 150 mA/cm$^2$ (Figure 5.3). The selectivity measured at these high current densities compares favorably to a previously tested molecular catalyst immobilized on carbon nanotubes in a CO$_2$RR flow reactor that showed a FE$_{CO}$ of 56%.$^{49}$ The higher selectivity is likely a result of the delivery of gaseous CO$_2$ to the electrode.$^{37}$ This conjecture is corroborated by experiments where FE$_{CO}$ was tracked at various CO$_2$ flow rates (Figure A5.4): as the flow rate of CO$_2$ entering the flow reactor increased from 2 sccm to 100 sccm, the selectivity towards CO increased from 90% to 99%. However, the single pass conversion efficiencies decreased at progressively higher CO$_2$ flow rates (Table A5.1). The $V_{cell}$ for our flow reactor containing CoPc and a nickel anode remained under 2.7 V at current densities up to 200 mA/cm$^2$. The $V_{cell}$ of 2.61 V measured at 200 mA/cm$^2$ compares favorably to the 2.72 V measured with a solid-state silver catalyst in the same flow.
reactor, and the >2.9 V required for a similar membrane reactor architecture containing solid-state silver and IrO$_2$ catalysts at the cathode and anode, respectively.$^{32,39}$

Figure 5.3 CO$_2$RR selectivity for CO formation and applied voltage as a function of current density. $V_{\text{cell}}$ and the corresponding FE$_{\text{CO}}$ were measured for the CoPc-mediated conversion, with (red) and without (blue) phenol additive, of CO$_2$ to CO at the indicated current densities. See Table A5.2 for CC and TOF at corresponding current densities. (Anode: nickel foam; cathode: carbon supported CoPc with or without PhOH on carbon GDL; anolyte: 20 mL/min 1 M KOH; gas catholyte: 100 SCCM CO$_2$; membrane: Sustainion$^\text{©}$ AEM).

The FE$_{\text{CO}}$ dropped from >90% to ~60% when the current density was increased from 150 to 200 mA/cm$^2$. We hypothesized this drop in selectivity resulted from a suppression of proton concentration at higher current densities. Our search for solutions to this problem converged on reports that phenol can help CoPc-mediated CO$_2$RR.$^{182,183}$ We, therefore, modified our catalyst ink also to include phenol (denoted in Figure 5.3 as “CoPc + phenol”). Experiments performed with this modified ink maintained a high FE$_{\text{CO}}$ of 88% at 200 mA/cm$^2$ (Figure 5.3) while also providing a 90-mV voltage saving ($V_{\text{cell}} = 2.52$ V at 200 mA/cm$^2$; Figure 5.3). This lower cell potential tracks molecular studies showing that phenol can lower the CO$_2$RR overpotential.$^{183}$ We conjecture that
phenol acts as a local pH buffer that slows the formation of catalytically inactive bicarbonate at the electrode interface.

Molecular CO$_2$RR catalysts typically degrade over a period of minutes, but they can be stabilized through molecular design$^{163,168}$ or changing the reaction medium.$^{184}$ Lu et al. reported that the immobilization of molecular CO$_2$RR catalysts on carbon nanotubes can improve the stability of molecular electrocatalysts, but this composite system still lasts for merely a few hours when measured at $<$40 mA/cm$^2$.$^{169}$ We tested the stability of CoPc-mediated CO$_2$RR electrolysis in our flow reactor by quantifying product formation every $\sim$1200 s at a constant current. The FE$_{\text{CO}}$ could be held at $>$90% over 8 hours of electrolysis at 50 mA/cm$^2$ (Figure 5.5a), which corresponds to $>$4000 catalytic cycles (CC) and a turnover frequency (TOF) of 3.6 min$^{-1}$ for each active site. At 100 mA/cm$^2$, the FE$_{\text{CO}}$ could be held at $>$90% over 3 hours of electrolysis prior to dropping to 60% after 5 hours of operation (Figure A5.4).

![Figure 5.4](image_url) Temporal stability of CoPc under flow at 50 mA/cm$^2$. FE$_{\text{CO}}$ as a function of time for CO$_2$RR electrolysis at a constant current density of 50 mA/cm$^2$ in (a) a membrane flow reactor configuration containing carbon supported CoPc and (b) GDE with CoPc in a hybrid cell. Anode: nickel foam; cathode: carbon powder supported CoPc with phenol on carbon GDE; anolyte: 20 mL/min 1 M KOH; gas catholyte: 100 SCCM CO$_2$ humidified at 25 °C. Membrane: Sustainion® AEM. $V_{\text{cell}}$ was measured at the same time when GC measurement was taken.
It was unexpected that CoPc in the hydrodynamic environment of a flow reactor at 50 mA/cm² could match the longevity of a batch-type electrolysis experiment recorded at merely 10 mA/cm². The primary reason for the drop in performance in the flow reactor is not CoPc degradation. Independent experiments performed in a hybrid flow reactor, which allows for the voltage reading at the cathode to be measured in isolation, maintained an >80% FE_CO for >100 hours at 50 mA/cm² (Figure 5.4b), corresponding to a CC of approximately 16,000. We hypothesize the rapid drop in output from the membrane reactor is largely due to a progressively lower proton inventory at the catalyst-membrane interface. This contention is supported by the fact that phenol helps stabilize the activity and selectivity of the reactor. The formation of KHCO₃ crystals on the cathode flow plate during electrolysis also obstruct CO₂ flow and reactor output. This crystal formation is a known phenomenon that arises from the crossover of potassium and hydroxyl ions. The original performance of the reactor can be regenerated by washing the crystals after disassembly of the reactor. We continue to explore different strategies to realize robust CO₂RR electrolysis in a flow reactor by circumventing crystal formation and developing methods to anchor the molecular catalysts to the supports. Regardless of the failure mode(s), there are very few cases of heterogeneous molecular catalysts capable of sustaining electrolysis for longer time periods than the data reported here.

5.3 Conclusions

These results show that a widely available and abundant molecular catalyst is capable of operating in a flow reactor with a high selectivity for CO production at commercially relevant current densities (≥150 mA/cm²). This finding challenges the accepted dogma that molecular catalysts are not capable of performing electrolysis at commercially relevant rates of product
formation. The fact that CoPc lasts merely 10 hours at 10 mA/cm$^2$ in a batch-type electrolysis cell, yet is capable of sustaining electrolysis at 50 mA/cm$^2$ for >100 hours illuminates the potential for studying a myriad of molecular catalysts under flow conditions. The identification that molecular catalysts can be used in a flow reactor also offers the opportunity to lower the high cell potentials required to currently drive CO$_2$RR chemistry at meaningful rates of production.

5.4 Experimental

5.4.1 Materials

Cobalt phthalocyanine (CoPc) and phenol were both purchased from Alfa-Aesar. Potassium hydroxide was purchased from BDH chemicals. The GDL H23C6 and carbon powder (Vulcan XC-72R) were both purchased from Fuel Cell Store. 29H, 31H-phthalocyanine (Pc) was purchased from Sigma-Aldrich. All chemicals were used as received without further purification. AEM Sustainion® X37-50 Grade RT membrane was purchased from Dioxide Materials.

5.4.2 Cell Design

The custom-made electrolyzer cell depicted in Figure A5.1 was built in-house and consists of housings, gaskets, anode and cathode flow-field plates and a membrane electrode assembly (MEA). The anode and cathode housings (6 × 6 × 1.2 cm) are made from stainless steel and serve to deliver liquid and gas feeds to the anode and cathode, respectively, through $\frac{1}{8}$” NPT ports with barbed tubing adapters. Stainless steel was chosen for its chemical inertness to both anode and cathode feeds. The titanium cathode flow plate and stainless steel anode flow plate sandwich the 4 -cm$^2$ MEA. The anode (316 stainless steel) and cathode (grade 2 titanium) flow-field plates (6 × 6 × 0.6 cm; active area = 4 cm$^2$ ) contain serpentine channels 1.5 mm wide and 1.5 mm deep with
1-mm ribs. This flow-field plate design is similar to a previously reported design for a water electrolyzer. Stainless steel and titanium were chosen for anode and cathode flow plates, respectively, for their inherent chemical stabilities in basic and acidic conditions, and inactivity towards the OER and CO$_2$RR. All gaskets are cut from 1.5-mm thick chemical resistant compressible PTFE. The PTFE gaskets have good chemical inertness to cathode and anode feeds and high compressibility, ensuring both liquid and gas-tight seals. The gaskets between the housing and the flow-field plate, on both the anode and cathode sides, have 0.2-mm diameter holes for liquid or gas delivery. The gaskets between the flow-field plate and the MEA have a 2 × 2 cm square cut out. The MEA consists of a nickel foam anode (2.5 × 2.5 cm), a Sustainion$^\text{TM}$ (3 × 3 cm) and a CoPc or Ag catalyst ink deposited on a carbon paper GDL cathode (2 × 2 cm). Nickel foam was used as both the diffusion layer and OER catalyst in basic conditions, while a CoPc or Ag catalyst ink was deposited on a carbon paper GDL to afford high surface area and enable rapid mass transport of gas phase CO$_2$ under locally acidic conditions. The entire assembly is sandwiched between the two stainless housings fastened with 8 bolts of 6.35 mm diameter.

The hybrid cell electrolyzer (Micro Flow Cell$^\text{®}$ purchased by Electrocell) is composed by a sandwich of flow frames, electrodes, gaskets and a membrane, which, when assembled as illustrated in Figure A5.2, constitute a three-compartment flow cell. One compartment delivers the CO$_2$ (at 20 sccm) from the back side and through the gas diffusion electrode (GDE, 1x1 cm$^2$, fixated in a Titanium frame), while another directs the catholyte solution (0.5 M KHCO$_3$, flow rate of 16 sccm) in between the GDE and the anion exchange membrane (AEM, Sustainion$^\text{TM}$ X37-50). On the other side of the latter, the anolyte (0.5 M KHCO$_3$, flow rate of 16 sccm) is directed between the AEM and the Pt/Ti alloy anode. The flow frames are made of PTFE, and the gaskets
of peroxide cured EPDM. Catholyte and anolyte were recycled using peristaltic pumps. All tubings were made of PTFE and connected to the cell with PEEK ferrules and fittings.

5.4.3 Electrolysis and Product Analysis

Ramp experiments were performed at increasing current densities. Each step was at constant current density for 1200 s and the products were analyzed after 500 s of electrolysis. Stability experiments were performed in chronopotentiometry mode at 50 or 100 mA/cm². Electrolysis products were analyzed every 1200 s starting at 500 s until the CO faradaic efficiency decreases to a value of less than 50%.

The CO₂ flow rate to the cathode was set to 100 sccm by a flow controller (AALBORG) and humidified by passing the gas through a water bath at prior to entering the cathode; 1 M KOH was recirculated through the anode compartment at a flow rate of 20 mL/min using a peristaltic pump (McMaster-Carr; 43205K11). The electrolyzer outlet was introduced into a condenser before being vented directly into the gas-sampling loop of the gas chromatograph (GC; SRI-8610C; Mandel). A GC run was initiated every 1200 s. The GC was equipped with a packed MolSieve 5 A column and a packed HaySep D column. Argon (Praxair, 99.999%) was used as the carrier gas. A flame ionization detector (FID) with a methanizer was used to quantify CO, CH₄ and C₂H₄ while a thermal conductivity detector (TCD) was used to quantify hydrogen. The GC was calibrated by injecting different calibration gas mixes from NorLAB from 100 to 50000 ppm containing CO, CH₄, H₂, C₂H₄, C₂H₆, CO₂ and C₃H₈.

Electrochemical measurements were conducted at room temperature and pressure by means of a potentiostat (CH instruments 660D with a picoamp booster) through two-electrode cell measurements. Current density is expressed as the total current divided by the geometric surface
area of the electrodes (4 cm\(^2\)). The FE of a gaseous product \(k\) was determined in accordance with equation 5.1:

\[
FE = \frac{n_k F x_k F_m}{I}
\]  
(Eq. 5.1)

Where \(n_k\) is the number of electrons exchanged, \(F\) is Faraday’s constant (\(F = 96,485\) C/mol), \(x_k\) is the mole fraction of the gas \(k\) in the gaseous mixture analyzed, \(F_m\) is the molar flow rate in mol/s, and \(I\) is the total current in A. The molar flow rate is derived from the volume flow rate \(F_v\) by the relation \(F_m = p F_v / RT\), with \(p\) being the atmospheric pressure in Pa, \(R\) the ideal gas constant of 8.314 J/mol K and \(T\) the temperature in K.

Numbers of catalytic cycles (CCs; Equation 5.2) and turnover frequencies (TOFs; Equation 5.3) have been calculated using the following formulas for each experiment:

\[
CC = \frac{\text{CO produced (mol)}}{n_{\text{CoPc}} (\text{mol})}
\]  
(Eq. 5.2)

\[
TOF (min^{-1}) = \frac{\text{CO produced (mol)}}{n_{\text{CoPc}} (\text{mol}) \cdot \text{time (min)}}
\]  
(Eq. 5.3)

where \(n_{\text{CoPc}}\) is the number of moles of CoPc deposited on the gas diffusion electrode, time is the experiment duration and “CO produced” is the number of moles of CO formed during electrolysis, as quantified by GC. The CC and TOF have been calculated for each point of Figure 5.3 and are listed in Table A5.2. CO production was assumed to be constant over the 600 s of each
measurement. Concerning the stability experiments in Figure. 5.4, CO production was integrated over time to estimate the more accurately the CC and TOF.

Single-pass conversion rate was determined in accordance with the following Equations 5.4 and 5.5:

$$\left(\frac{mc}{s\ cm^2}\right)\left(\frac{1 C}{1000 \ mc}\right)\left(\frac{mol \ e^{-}}{96485 C}\right)\left(\frac{1 mol \ CO}{2 mol \ e^{-}}\right)\left(\frac{1 mol \ CO_2}{1 mol \ CO}\right)\left(\frac{22.4 L}{1 mol \ CO_2}\right)\left(\frac{60 s}{1 min}\right)(4 \ cm^2 \ geometric)$$

= mL min\(^{-1}\) CO\(_2\) consumed by flow reactor for CO synthesis \hspace{1cm} (Eq. 5.4)

$$100 \times \frac{ml \ min^{-1} \ CO_2 \ consumed}{ml \ min^{-1} \ CO_2 \ flow \ rate} = \% \ CO_2 \ conversion \ to \ CO \hspace{1cm} (Eq \ 5.5)$$

The energy efficiency has been calculated with equation 5.6:

$$energy \ efficiency = \frac{FECO\% \times J}{V_{cell}} \hspace{1cm} (Eq \ 5.6)$$

where \(V_{cell}\) is the overall cell voltage, \(J\) is the current density, \(FECO\%\) is the Faraday efficiency towards \(CO_2\) to \(CO\) conversion.

In this work, \(V_{cell}\) was measured as 2.52 V at 200 mA/cm\(^2\) with \(FECO\%\) of 88\%. In reference (6) where Ag solid state catalyst was used, the \(V_{cell}\) was measured at 2.9 V at 200 mA/cm\(^2\) with \(FECO\%\) of 90\%. A relative energy efficiency improvement of 7\% was obtained in this work.
5.4.4 Electrode Preparation

The CoPc ink was prepared by stirring and sonicating 82.9 mg of Vulcan carbon powder (XC-72-r), 89.6 mg of CoPc (Sigma, CAS# 3317-67-7) and 374 µL of Nafion 117 solution (Sigma, 5 wt% in a mixture of lower aliphatic alcohols and water) in an 35 mL absolute ethanol solution. During this step, CoPc molecules were immobilized on the carbon powder with pi-pi interactions. Then, 25 mL of the ink was spray coated on a hydrophobic carbon paper with a microporous layer (Freudenberg paper H23C6) using a SONO-TEK ExactaCoat automated ultrasonic spraycoater equipped with 1 Watt power ultrasonic nozzle with a frequency of 120 Hz. The flow rate was controlled at 0.6 mL/min. The resulting electrode was 4 cm² wide. The CoPc concentration was expected to furnish a 4 mg/cm² CoPc loading after spray coating. For the carbon electrode with CoPc and phenol, additional 3.3 g phenol was dissolved in the ink to form 1 M phenol solution then the same deposition method was applied. The Ag catalyst ink was prepared by mixing 1.26 g of silver nanopowder (Sigma, trace metal basis, >99%), 15 mL of DI water, 15 mL of isopropyl alcohol and 1.68 mL Nafion117 solution (Sigma, 5 wt% in a mixture of lower aliphatic alcohols and water). The catalyst ink was then spray-coated on sixteen 4 cm² carbon cloth (Fuel Cell Store, GDL-CT). The anodes were prepared by cutting as-purchased nickel foam (MTI;EQ-BCNF-16m) to size. A standard cleaning procedure was used to clean both the carbon GDL and nickel foam by sonication in acetone then deionized water. A fresh cathode, anode and AEM were used for each electrolysis test. In the hybrid cell, the CoPc ink was drop-casted onto the hydrophobic carbon paper.
Chapter 6: Conclusions and Future Directions

6.1 Conclusions

The research outlined in this thesis achieves three key goals: the design of a CO₂ gas-fed membrane reactor, the design of an analytical flow reactor to quantify the energy losses, and incorporating an efficient molecular catalyst in a membrane reactor to increase energy efficiency.

Chapter 3 demonstrates a membrane reactor for the gas-phase reduction of CO₂ to CO at high current densities (\(J = 200 \text{ mA/cm}^2\)) that provides stable performance for 24 h. This inlet stream produced double the current density (100 mA/cm²) than a CO₂-saturated aqueous solution (50 mA/cm²) when all other experimental parameters were held constant. In this work, the role that hydration has on the performance of the cathode is also demonstrated. I showed that it was necessary to include a water support layer in order to achieve reasonable FEs for CO formation at higher current densities (e.g., 200 mA/cm²). By maintaining a hydrated CO₂ stream (>90% RH), I was able to maintain hydration of the support layer and my cell stability was over 24 h at 100 mA/cm².

In Chapter 4, I detailed the design and use of an analytical platform to compare the voltages for both membrane and hybrid reactors to identify which cell components should be optimized to most effectively lower the overall \(V_{\text{cell}}\). My analysis of the voltages across the components of three different flow reactor configurations (i.e., membrane/BPM, membrane/AEM, and hybrid/AEM) highlighted that the reactions at the anodes and cathodes are relatively efficient and that much of the voltage loss occurs at the membrane. The analytical tool presents a simple method to incorporate reference electrode measurements in both membrane and hybrid architectures to report membrane, cathode, anode and full cell voltages. I hope that this analytical CO₂RR flow reactor, with strategically positioned reference electrodes, will be used more broadly to resolve the voltage drops of operational flow reactors.
Chapter 6 illustrated the incorporation of a molecular catalyst in a membrane reactor. The results showed that a widely available and abundant molecular catalyst, CoPc, is capable of operating in a flow reactor with high selectivity for CO production at commercially relevant current densities (≥150 mA/cm²). This finding challenges the accepted dogma that molecular catalysts are not capable of performing electrolysis at commercially relevant rates of product formation. We also demonstrated that this catalyst was capable of sustaining electrolysis at 50 mA/cm² for >100 hours. This finding illuminates the potential for studying a myriad of molecular catalysts under flow conditions. The identification that molecular catalysts can be used in a flow reactor also offers the opportunity to lower the high cell potentials required to currently drive CO₂RR chemistry at meaningful rates of production.

6.2 Future Directions

In this thesis, I have demonstrated CO₂-to-CO conversion in a flow reactor at current densities of 200 mA/cm². Through these studies, I have learned how inlet conditions have strong effects on the performance of the CO₂ flow reactor. Flow rate, pressure, the relative humidity of the CO₂ and temperature all have varying effects towards the selectivity and stability of the flow reactor. It is therefore of utmost importance to be able to control each and every parameter. Unfortunately, the current capabilities of our bench set-up prevent accurate repeatability in measured results when the environment in the lab changes (e.g., temperature & humidity). In order to optimize the CO₂ membrane reactor further, a CO₂ electrolyzer test station needs to be developed. An electrolyzer test station would contain humidity, temperature, pressure, and flow controllers to accurately control and measure all variables for CO₂ electrolyzer conditions (temperature, pressure, humidity, voltage/current). The process controls and feedback loops in the
An electrolyzer testing station will allow for the optimization of process conditions for CO₂ flow reactor technologies.

As outlined in Chapter 2, there are no reports of the optimization of GDE materials for CO₂ membrane reactors. In my own work and through literature reviews, it is clear that there are structure-property relationships that can be made. GDEs are typically fabricated by depositing electrocatalysts (e.g., Ag) and ionically conductive polymers such as Nafion® onto an electrode scaffolding. The effect of the relative quantity and distribution of these GDE constituents has been studied for hybrid reactors, but there are no reports of GDE optimization for membrane reactors. I believe that modulating the properties of the electrode scaffolding, ionomer content, and electrocatalyst structure will increase the energy efficiency of CO₂ electrolysis into CO.

In Chapter 5, we incorporated a molecular catalyst (CoPc) in a flow reactor. Solution based cyclic voltammetry and electrolysis have proven a powerful tool to investigate structure-activity relationship in homogeneous conditions for multi-electron multi-proton processes. By installing molecular catalysts in flow reactors, we now have the opportunity to determine mechanistic steps that are otherwise difficult to elucidate. The chemical and electronic environment about the active site of a molecular catalyst is often more substantially and acutely tunable than solid-state catalysts. We can tune molecular catalysts to have unique spectroscopic and electrochemical responses. I believe that utilizing molecular catalysts in a flow reactor platform we can gain insight into the mechanism of CO₂RR at high J/s which has yet to be investigated.

Finally, this thesis outlines the development of a benchtop flow reactor capable of converting gaseous CO₂ into CO using cheap, renewable electricity with high efficiency (FE > 50%) at industrially relevant current densities (200 mA/cm²). In order to make any meaningful impact on the global energy market, the logical next steps to address is scalability. A future
direction of this project would be to increase the scale of this 4 cm$^2$ single cell to a 5-cell electrolyzer stack where each flow reactor has an active area of 50 cm$^2$. The Berlinguette group has already engaged the contracting services of OverDrive Fuel Cell Engineering Inc. in order to obtain complete technical drawings and 3-dimensional SolidWorks models of the electrolyzer stack prototype. These models comprise all the information necessary to purchase or fabricate all components of the stack (Figure 6.1).

**Figure 2.1** 3-dimensional SolidWorks models of the electrolyzer 5x50 cm$^2$ stack prototype.

The next steps of this project include fabricating and/or obtaining the hardware required for a 5-cell stack wherein each cell provides a MEA active area of 50 cm$^2$. Off-the-shelf parts include membrane electrode materials (bipolar membranes, Nafion membranes, gaskets, etc.) and fluid control tools (CO$_2$ humidifier, peristaltic pumps, mass flow controllers. Custom-made components such as housing plates, insulators, sealing, and flow field plates will need to be machined. *Chapter 3* demonstrates that the influence of feedstock characteristics can drastically
alter the overall performance of an electrolytic flow reactor. Finely tuned control of the electrolyzer inlet and outlet flow is vital to achieving reliable performance, particularly given that the small-scale challenges of cell leakage, membrane stability, increased fluid pressures, and temperature control, may be amplified at a larger scale. CO\textsubscript{2} humidification will also need to be controlled, as it affects the hydration of the MEA and electrolytic performance.
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Appendices

Appendix A

Chapter 3

Figure A3.1 (A) Scanning electron microscopy, (B) X-ray fluorescence and (C) x-ray diffraction of the Ag cathode before and after gas-phase CO$_2$ electrolysis in a membrane reactor configuration containing a solid-supported aqueous NaHCO$_3$ solution. Full electrolysis experiments include cyclic voltammograms, and chronopotentiometric experiments up to 3000s from 20 to 200 mA/cm$^2$ in 20-mA increments (~10 hours of total electrolysis on the same MEA)
Figure A3.2. Chronopotentiometric at $J = 100$ mA/cm$^2$ in a flow-cell configuration containing a solid-supported aqueous NaHCO$_3$ solution (blue), a solid-supported H$_2$O solution (black) and no solid support (red). (Anode: nickel foam; cathode: silver on C-GDL; anolyte: 10 mL/min 1 M NaOH; gas catholyte: 100 SCCM humidified CO$_2$.)

Figure A3.3. Chronopotentiometric at $J = 100$ mA/cm$^2$ and corresponding FE (%) for CO evolution measured by GC for gas-phase CO$_2$ electrolysis in a flow-cell configuration containing a solid-supported aqueous NaHCO$_3$ solution. The red asterisk indicates the rewetting of the solid-support layer.
Figure A4.1. Potential measured across the bipolar membrane, $V_{\text{BPM}}$, as a function of current density, $J$, for our gas phase CO$_2$ flow cell, membrane/BPM (orange), and H$_2$O electrolysis (blue). The $V_{\text{BPM}}$ corresponds to the voltage measured across $R_1$ and $R_3$. The gas phase CO$_2$ electrolyzer utilized 1 M NaOH at the anode and humidified CO$_2$ at the cathode. The water electrolysis data is adapted from literature,$^{86}$ where 1M NaOH was used as the anolyte and 1 M HClO$_4$ as the catholyte.
Figure A4.2. Voltage traces for the membrane/BPM flow cell reactor at 25 (navy), 50 (cyan), 100 (orange), and 200 mA/cm$^2$ (magenta). The two electrodes being measured are indicated as Anode|Cathode (e.g., Cathode|R1). The component of the flow cell that is being measured is also indicated; e.g., $V_{cell}$. 
Table A4.1 Voltage measurements for the membrane/BPM flow cell reactor at 25, 50, 100 and 200 mA/cm².

<table>
<thead>
<tr>
<th>Component being measured</th>
<th>Anode</th>
<th>Average (V)</th>
<th>St. Dev (V)</th>
<th>Cathode</th>
<th>Average (V)</th>
<th>St. Dev (V)</th>
<th>25 mA/cm²</th>
<th>50 mA/cm²</th>
<th>100 mA/cm²</th>
<th>200 mA/cm²</th>
</tr>
</thead>
<tbody>
<tr>
<td>-V_cell</td>
<td>Cathode</td>
<td>-2.88</td>
<td>0.05</td>
<td>Anode</td>
<td>-3.25</td>
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<td>-3.69</td>
<td>0.08</td>
<td>-4.42</td>
<td>0.14</td>
</tr>
<tr>
<td>V_cathode</td>
<td>R1</td>
<td>-1.07</td>
<td>0.10</td>
<td>Cathode</td>
<td>-1.16</td>
<td>0.13</td>
<td>-1.26</td>
<td>0.16</td>
<td>-1.26</td>
<td>0.26</td>
</tr>
<tr>
<td>V_membrane</td>
<td>R2</td>
<td>R1</td>
<td>1.29</td>
<td>0.08</td>
<td>Anode</td>
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<td>0.09</td>
<td>1.83</td>
<td>0.24</td>
<td>2.56</td>
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<td>V_anode</td>
<td>Anode</td>
<td>R2</td>
<td>0.52</td>
<td>0.01</td>
<td>Cathode</td>
<td>0.55</td>
<td>0.02</td>
<td>0.59</td>
<td>0.04</td>
<td>0.64</td>
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<td>V_cell</td>
<td>Cathode</td>
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<td>0.04</td>
<td>Anode</td>
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<td>Anode</td>
<td>-3.24</td>
<td>0.07</td>
<td>-3.67</td>
<td>0.09</td>
<td>-4.51</td>
<td>0.23</td>
</tr>
</tbody>
</table>

| Cell summary¹ | -2.88 | 0.19 | -3.27 | 0.24 | -3.68 | 0.44 | -4.46 | 0.60 |
| Cell average² | -2.88 | 0.02 | -3.24 | 0.03 | -3.68 | 0.03 | -4.47 | 0.18 |

| Power supply average³ | -2.87 | 0.02 | -3.33 | 0.1  | -3.66 | 0.21 | -4.57 | 0.31 |

¹ The cell summary is the summation of \( V_{\text{cathode}} \), \( V_{\text{membrane}} \), \( V_{\text{anode}} \)

² The cell average is the average of \( V_{\text{cell}} \)

³ The power supply average is the average of the power supply data
Figure A4.3. Voltage traces for the membrane/AEM flow cell reactor at 25 (navy), 50 (cyan), 100 (orange), and 200 mA/cm² (magenta). The two electrodes being measured are indicated as Anode|Cathode (e.g., Cathode|R1). The component of the flow cell that is being measured is also indicated; e.g., $V_{\text{cell}}$. 
Table A4.2. Voltage measurements for the membrane/AEM flow cell reactor at 25, 50, 100 and 200 mA/cm².

<table>
<thead>
<tr>
<th>Component being measured</th>
<th>Anode</th>
<th>Cathode</th>
<th>Average (V)</th>
<th>St. Dev (V)</th>
<th>25 mA/cm²</th>
<th>Average (V)</th>
<th>St. Dev (V)</th>
<th>50 mA/cm²</th>
<th>Average (V)</th>
<th>St. Dev (V)</th>
<th>100 mA/cm²</th>
<th>Average (V)</th>
<th>St. Dev (V)</th>
<th>200 mA/cm²</th>
<th>Average (V)</th>
<th>St. Dev (V)</th>
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<td>V cathode</td>
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<td>-1.23</td>
<td>0.05</td>
<td>-1.31</td>
<td>0.03</td>
<td>-1.43</td>
<td>0.02</td>
<td>-1.43</td>
<td>0.02</td>
<td>-1.43</td>
<td>0.02</td>
<td>-1.43</td>
<td>0.02</td>
<td>-1.43</td>
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<tr>
<td>V membrane</td>
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<td>R1</td>
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<td>0.07</td>
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<td>0.1</td>
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<td>0.71</td>
<td>0.10</td>
<td>0.71</td>
<td>0.10</td>
<td>0.71</td>
<td>0.10</td>
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<tr>
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<td>Anode</td>
<td>R2</td>
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<td>0.08</td>
<td>0.51</td>
<td>0.05</td>
<td>0.53</td>
<td>0.08</td>
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<td>0.58</td>
<td>0.13</td>
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<tr>
<td>-V cell</td>
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<td>-2.72</td>
<td>0.26</td>
<td>-2.72</td>
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<tr>
<td>Cell average²</td>
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<td>0.03</td>
<td>-2.2</td>
<td>0.02</td>
<td>-2.4</td>
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<td>0.07</td>
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<td>-2.73</td>
<td>0.07</td>
<td>-2.73</td>
<td>0.07</td>
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<tr>
<td>average³</td>
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<td>-2.64</td>
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<td>-2.64</td>
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<td>-2.64</td>
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<td>-2.64</td>
</tr>
</tbody>
</table>

¹ The cell summary is the summation of $V_{\text{cathode}}$, $V_{\text{membrane}}$, $V_{\text{anode}}$

² The cell average is the average of $V_{\text{cell}}$

³ The power supply average is the average of the power supply data
Figure A4.4. Voltage traces for the hybrid/AEM flow cell reactor at 25 (navy), 50 (cyan), 100 (orange), and 200 mA/cm² (magenta). The two electrodes being measured are indicated as Anode|Cathode (e.g., Cathode|R1). The component of the flow cell that is being measured is also indicated; e.g., $V_{\text{cell}}$. 
Table A4.3. Voltage measurements for the hybrid/AEM flow cell reactor at 25, 50, 100 and 200 mA/cm$^2$.

<table>
<thead>
<tr>
<th>Component being measured</th>
<th>Anode</th>
<th>Cathode</th>
<th>25 mA/cm$^2$</th>
<th>50 mA/cm$^2$</th>
<th>100 mA/cm$^2$</th>
<th>200 mA/cm$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Average</td>
<td>St. Dev</td>
<td>Average</td>
<td>St. Dev</td>
<td>Average</td>
<td>St. Dev</td>
</tr>
<tr>
<td>$V_{cell}$</td>
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<td></td>
<td>-2.13</td>
<td>0.03</td>
<td>-2.53</td>
<td>0.1</td>
</tr>
<tr>
<td>$V_{cathode}$</td>
<td>Cathode</td>
<td>R1</td>
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<tr>
<td>$V_{catholyte}$</td>
<td>R1</td>
<td>R3</td>
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<td>0.09</td>
<td>0.34</td>
<td>0.26</td>
</tr>
<tr>
<td>$V_{membrane}$</td>
<td>R2</td>
<td>R1</td>
<td>-0.42</td>
<td>0.19</td>
<td>-0.53</td>
<td>0.21</td>
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<tr>
<td>$V_{anode}$</td>
<td>Anode</td>
<td>R2</td>
<td>0.48</td>
<td>0.02</td>
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<td>0.02</td>
</tr>
<tr>
<td>$V_{cell}$</td>
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<td>Cathode</td>
<td>2.18</td>
<td>0.03</td>
<td>2.5</td>
<td>0.18</td>
</tr>
<tr>
<td>$V_{cell}$</td>
<td>Cathode</td>
<td>Anode</td>
<td>-2.18</td>
<td>0.04</td>
<td>-2.51</td>
<td>0.18</td>
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<tr>
<td>Cell summary$^1$</td>
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<td>-2.15</td>
<td>0.29</td>
<td>-2.47</td>
<td>0.23</td>
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<tr>
<td>Cell average$^2$</td>
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<td></td>
<td>-2.16</td>
<td>0.01</td>
<td>-2.51</td>
<td>0.03</td>
</tr>
<tr>
<td>Power supply average$^3$</td>
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<td>2.22</td>
<td>0.05</td>
<td>2.7</td>
<td>0.1</td>
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</table>

$^1$ The cell summary is the summation of $V_{cathode}$, $V_{catholyte}$, $V_{membrane}$, $V_{anode}$

$^2$ The cell average is the average of $V_{cell}$

$^3$ The power supply average is the average of the power supply data
Techno-economic Analysis (Figure 4.1)

The techno-economic analysis for Figure 1 was performed by modifying the “Economic analysis of CO2 electrolyzer system” spreadsheet from Jiao and coworkers. We utilized “base case” values for our calculations:

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Base Case</th>
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<tbody>
<tr>
<td>Production Rate (ton/day)</td>
<td>100</td>
</tr>
<tr>
<td>Lifetime (years)</td>
<td>20</td>
</tr>
<tr>
<td>Operating time (days/year)</td>
<td>350</td>
</tr>
<tr>
<td>Electricity Price ($/kWh)</td>
<td>0.05</td>
</tr>
<tr>
<td>Product Selectivity (%)</td>
<td>90</td>
</tr>
<tr>
<td>Conversion (%)</td>
<td>50</td>
</tr>
<tr>
<td>CO2 Price ($/ton)</td>
<td>70</td>
</tr>
<tr>
<td>Interest Rate (%)</td>
<td>10</td>
</tr>
<tr>
<td>Electrolyzer Cost ($/m2)</td>
<td>1840</td>
</tr>
</tbody>
</table>

The spreadsheet was modified to include the cost of membrane electrode assembly (“MEA cost”) as follows:

\[
MEA\text{ cost} \ (\$/m^2) = (\text{anode metal cost} \times \text{anode loading}) + (\text{cathode metal cost} \times \text{cathode loading}) + GDL\text{ cost} + \text{membrane cost}
\]

The MEA cost per day was determined as follows:
\[
\text{MEA cost/day} \ (\$/\text{day}) = \frac{\text{MEA cost} \times \text{Electrolyzer Area}}{\text{MEA lifetime} \times 365}
\]

In order to calculate the levelized selling price of CO, the annual total operating costs were calculated as follows:

\[
\text{annual total operating costs} \ (\$/\text{year}) = \text{Operating cost} \times \text{Operating time}
\]

The cost to produce CO was then calculated:

\[
\text{cost to produce CO} \ (\$/\text{kg}) = \frac{\text{annual total operating costs}}{(\text{product production} \times 365)}
\]

Utilizing a gross margin of 30%, the levelized selling price of CO was calculated:

\[
\text{levelized selling price of CO} \ (\$/\text{kg}) = \frac{\text{cost to produce CO}}{(1 - 0.30)}
\]
Chapter 5

Figure A5.1. Graphic illustration of (A) a gas phase flow reactor setup scheme and (B) a membrane electrode assembly.

Figure A5.2. Graphic illustration of a hybrid flow reactor
Figure A5.3. CO$_2$RR selectivity for CO (dot) and H$_2$ (square) as a function of current density for control experiments using GDEs coated with different inks: carbon black on GDE only (black, denoted as “CB”); carbon black, phenol and Pc (blue, denoted as “CB + phenol + Pc”); carbon black and Pc (orange, denoted as “CB + Pc”). Pc is the non-metalated phthalocyanine ligand. (Anode: nickel foam; cathode: carbon powder, carbon powder supported Pc with or without phenol on carbon GDE; anolyte: 20 mL/min 1 M KOH; gas catholyte: 100 SCCM CO$_2$ humidified at 25 °C. Membrane: Sustainion® AEM.)
Figure A5.4 CO\textsubscript{2}RR selectivity (blue dot) for CO formation and single pass conversion (orange square) as a function of CO\textsubscript{2} flow rate. The flow rate was controlled at 2, 3, 5, 10, 25, 50 and 100 sccm by a mass flow controller. The corresponding FE\textsubscript{CO} was measured for the CoPc-mediated conversion of CO\textsubscript{2} to CO under 50 mA/cm\textsuperscript{2} at the indicated CO\textsubscript{2} flow rate after 20 min of electrolysis. (Anode: nickel foam; cathode: carbon supported CoPc on carbon GDL; anolyte: 20 mL/min 1 M KOH; gas catholyte: room temperature humidified CO\textsubscript{2}; membrane: Sustainion\textsuperscript{®} AEM).
Figure A5.5. Temporal stability of CoPc (blue) and CoPc with phenol (red, denoted as “CoPc + phenol”) in a membrane reactor held at a constant current of 100 mA/cm$^2$. (Anode: nickel foam; cathode: carbon powder supported CoPc with or without phenol on carbon GDE; anolyte: 20 mL/min 1 M KOH; gas catholyte: 100 SCCM CO$_2$ humidified at 25 °C. Membrane: Sustainion® AEM.) $E_{\text{cell}}$ was measured at the same time as each GC measurement was taken.
Figure A5.6. GC traces during CO$_2$ electrolysis experiments using a GDE coated with CoPc and phenol. The corresponding FEs are plotted in Fig. 3. (A) Data recorded with a thermal conductivity detector (TCD) to quantify the concentration of H$_2$ (retention time of H$_2$ is ~1 min) produced over the course of the experiment. (B) Data recorded with a flame ionization detector (FID) to quantify the concentration of CO (retention time of CO at ~4.2 min) produced over the course of the experiment. (Other signals correspond to valve switching at ~7 min, air/CO at ~8 min, and CO$_2$ at ~9 min. The CO at 8 min is not quantified.)
Figure A5.7. GC traces during CO₂ electrolysis experiments using a GDE coated with CoPc only. The corresponding FEs are plotted in Fig. 3. (A) Data recorded with a thermal conductivity detector (TCD) to quantify the concentration of H₂ (retention time of H₂ is ~1 min) produced over the course of the experiment. (B) Data recorded with a flame ionization detector (FID) to quantify the concentration of CO (retention time of CO at ~4.2 min) produced over the course of the experiment. (Other signals correspond to valve switching at ~7 min, air/CO at ~8 min, and CO₂ at ~9 min. The CO at 8 min is not quantified.) The shift of CO peaks at 25, 50 and 75 mA/cm² is due to the use of different GC instruments.
Table A5.1. **Single-pass conversion** from CO₂ to CO using GDE with and without phenol as an additive in a membrane reactor **at indicated current densities**. (Anode: nickel foam; cathode: carbon powder supported CoPc with or without phenol on carbon GDE; anolyte: 20 mL/min 1 M KOH; gas catholyte: 100 SCCM CO₂ humidified at 25 °C. Membrane: Sustainion® AEM.).

<table>
<thead>
<tr>
<th>Current density (mA.cm⁻²)</th>
<th>Single-pass conversion</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CoPc (%)</td>
<td>CoPc + phenol (%)</td>
</tr>
<tr>
<td>25</td>
<td>0.73</td>
<td>0.74</td>
</tr>
<tr>
<td>50</td>
<td>1.51</td>
<td>1.51</td>
</tr>
<tr>
<td>75</td>
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<tr>
<td>100</td>
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<td>3.04</td>
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<td>200</td>
<td>3.18</td>
<td>5.19</td>
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Table A5.2. Comparison of the electrochemical performances over this work with other molecular catalysts in the CO$_2$RR reaction reported in the literature.

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<th>Entry</th>
<th>Current Density (mA.cm$^2$)</th>
<th>CO Faradaic Efficiency (%)</th>
<th>Technology</th>
<th>Reference</th>
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<td>30</td>
<td>100</td>
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</tr>
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<td>Electrolytic cell</td>
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<td>91</td>
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Table A53. Numbers of catalytic cycles (CCs) and turnover frequencies (TOFs) for the CoPc-mediated conversion from CO$_2$ to CO, with and without phenol additive, at indicated current densities, in a membrane reactor. (Anode: nickel foam; cathode: carbon powder supported CoPc with or without phenol on carbon GDE; anolyte: 20 mL/min 1 M KOH; gas catholyte: 100 SCCM CO$_2$ humidified at 25 °C. Membrane: Sustainion® AEM.)

<table>
<thead>
<tr>
<th>Current density (mA.cm$^{-2}$)</th>
<th>CoPc</th>
<th></th>
<th>CoPc + phenol</th>
<th></th>
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<tbody>
<tr>
<td></td>
<td>CC</td>
<td>TOF (min$^{-1}$)</td>
<td>CC</td>
<td>TOF (min$^{-1}$)</td>
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<td>12.5</td>
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<td>106</td>
<td>10.6</td>
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**Table A54.** Single-pass conversion from CO\textsubscript{2} to CO using GDE with and without phenol as an additive in a membrane reactor at indicated current densities. (Anode: nickel foam; cathode: carbon powder supported CoPc with or without phenol on carbon GDE; anolyte: 20 mL/min 1 M KOH; gas catholyte: 100 SCCM CO\textsubscript{2} humidified at 25 °C. Membrane: Sustainion\textsuperscript{®} AEM.)

<table>
<thead>
<tr>
<th>Current density (mA.cm\textsuperscript{-2})</th>
<th>CoPc (%)</th>
<th>CoPc + phenol (%)</th>
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