DESIGN OF ANION EXCHANGE MEMBRANES FOR ELECTROCHEMICAL
CARBON DIOXIDE REDUCTION TO CARBON MONOXIDE

by

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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 thesis entitled:

Design of Anion Exchange Membranes for Electrochemical Carbon Dioxide Reduction to Carbon Monoxide

submitted by Angelica Reyes in partial fulfillment of the requirements for

the degree of Master of Applied Science

in Chemical and Biological Engineering

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Abstract

Electrochemical CO₂ reduction technologies provide a platform for transforming 
renewable electricity, water, and waste CO₂ into synthetic building blocks (e.g., CO) and 
chemicals. However, CO₂ electrolysers are not yet available in the market due to poor efficiencies 
at high reaction rates. Emerging CO₂ electrolysers containing an anion exchange membrane 
(AEM) offer promise in overcoming this challenge, but limited design principles exist for AEMs 
in CO₂ electrolysis application. This thesis reports on my investigation of the designs of AEMs 
that improve CO₂ electrolyzer performance for CO production.

I first interrogate two analogous AEM designs to determine the effect of AEM functional 
group on product selectivity, cell voltage, and stability. This relationship between the membrane 
and CO₂ electrolysers performance has not yet been established at reaction rates greater than 10 
mA/cm². I demonstrate that an imidazolium-based AEM achieves a higher cell performance than 
a trimethylamine analog at reaction rates up to 100 mA/cm². I find that the low water uptake (i.e., 
water content) and improved chemical stability of an imidazolium group are contributing factors 
that lead to increased performance for CO production.

I explore further how AEM water uptake and thickness, and cathode hydrophobicity impact 
the amount of water transported to the cathode. Water serves as a proton source for the CO₂ 
reduction reaction to CO, but excess water at the cathode (i.e., flooding) can block the pores of 
catalytic sites and impede mass transport of reactants and products. Theoretical simulations predict 
that flooding will occur at reaction rates greater than 750 mA/cm², but this thesis demonstrates that 
cathode flooding is an issue at merely 200 mA/cm². I find that thin, low water uptake AEMs paired 
with hydrophobic cathodes mitigate cathode flooding and improve product selectivity and cell 
voltage for CO production.
Lay summary

Fuels and chemicals consumed globally are primarily produced by burning fossil fuels, and this process releases harmful carbon dioxide (CO₂) into the atmosphere. A cleaner alternative to producing chemical feedstocks is by converting renewable solar electricity, water, and CO₂ in a reactor called a CO₂ electrolyzer. This technology, however, is not yet commercially available because it is difficult to achieve high conversion efficiencies. One of the important components in CO₂ electrolyzers that affect efficiency is the anion exchange membrane, which is a solid polymer material that facilitates the transport of ions and water across the electrolyzer. This thesis demonstrates the design of membranes that enable high conversion efficiencies of CO₂ into useful products.
Preface

Chapter 3 is based on my unpublished work under the supervision of Prof. Curtis P. Berlinguette. Fabrication of electrodes, membrane characterization, and electrochemical testing in CO$_2$ electrolyzers were carried out by myself. Synthesis of ionomers and NMR experiments were performed by Dr. Yang Cao in the Berlinguette group. The fabrication of ionomers into membrane films were carried out by Ryan P. Jansonius in the Berlinguette group.

Chapter 4 is adapted from the paper “Managing Hydration at the Cathode Enables Efficient CO$_2$ Electrolysis at Commercially Relevant Current Densities”, *ACS Energy Lett.* 2020, 5, 1612-1618. The work was supervised by Prof. Curtis P. Berlinguette. Membrane characterizations and electrochemical experiments were carried out by myself. Synthesis of ionomers, electrochemical surface area measurements, and NMR experiments were conducted by Benjamin P. Mowbray and Dr. Yang Cao in the Berlinguette group. The fabrication of ionomers into membrane films were carried out by Ryan P. Jansonius in the Berlinguette group. Cathodes were prepared by Jacky Chau in the Berlinguette group. SEM and EDX experiments were carried out by David J. Dvorak in the Berlinguette group. COMSOL modelling was simulated by Danika G. Wheeler in the Berlinguette group. The manuscript was written by myself, Ryan P. Jansonius, and Benjamin P. Mowbray with contributions from Prof. Curtis P. Berlinguette.
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</tr>
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<td>EtOH</td>
<td>ethanol</td>
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<tr>
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F_m  molar flow rate
FTIR  Fourier-transform infrared spectroscopy
F_v  volume flow rate
GC  gas chromatography
GDE  gas diffusion electrode
h  hour
H^+  protons
H_2  hydrogen
H_2O  water
HCO_3^-  bicarbonate
HCOO^-  formate
HER  hydrogen evolution reaction
HWUM  high water uptake membrane
Hz  hertz
I  total current
IEC  ion exchange capacity
j  current density
J_{BC}  back convection flux
J_{DIFF}  diffusion flux
J_{EOD}  electro-osmotic drag flux
J_{H_2O,cathode}  excess flux of water to cathode
J_{H_2O,inlet}  water flux entering cathode inlet
J_{H_2O,net}  net flux of water
J_{H_2O,outlet}  water flux exiting cathode outlet
J_{H_2O,reduction}  water consumed by reduction reactions
K  kelvin
K^+  potassium ion
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<td>potassium hydroxide</td>
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<td>LWUM</td>
<td>low water uptake membrane</td>
</tr>
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</tr>
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<td>nuclear magnetic resonance</td>
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<td>PSMIM</td>
<td>poly[(4-vinylbenzyl-1-methylimidazolium chloride)-co-styrene]</td>
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<td>Pt</td>
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<tr>
<td>PTFE</td>
<td>polytetrafluoroethylene</td>
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<tr>
<td>QAPPT</td>
<td>quaternary ammonia poly(N-methyl-piperidine-co-p-terphenyl)</td>
</tr>
<tr>
<td>R</td>
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<tr>
<td>RHE</td>
<td>reversible hydrogen electrode</td>
</tr>
<tr>
<td>R&lt;sub&gt;mem&lt;/sub&gt;</td>
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Acknowledgements

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To my parents, thank you for sacrificing your comfortable lives in the Philippines and restarting from nothing to provide a better life for our family in Canada. This one is for you. Ate Elaine and Princess, thanks for celebrating my achievements, no matter how big or small they may be. Glad to have you both as my sisters/best friends/favourite people to annoy for life.
Dedicated to God
and my family

Psalm 34:8
Chapter 1: Introduction

Balancing the intermittent supply of renewable energy and the fluctuating demands for electricity necessitates scalable energy storage technologies. Electrochemical CO\(_2\) reduction is a compelling route for storing renewable electricity while recovering value from energy-intensive carbon capture technologies. CO\(_2\) electrolyzers transform electrons, captured CO\(_2\), and water into synthetic building blocks (e.g., CO) and commodity chemicals (e.g., ethanol). This technology offers the opportunity for the meaningful abatement of greenhouse gas emissions by electrifying the manufacturing of fossil fuel-derived chemicals. Electrochemical CO\(_2\) reduction could also leverage the infrastructure already established from existing supply chains for distribution and handling of products generated from the CO\(_2\) reduction reaction (CO\(_2\)RR), thereby facilitating the widespread adoption of this technology. Despite these advantages, there remain technological barriers that need to be overcome for CO\(_2\) electrolyzers to be economically viable and be deployed at industrial scale. A key part to addressing this challenge is the design of CO\(_2\) electrolyzers that can operate at high current densities (\(j > 200\ mA/cm^2\)), high faradaic efficiencies (\(FE > 90\%\)), and low cell voltages (\(E_{\text{cell}} < 3\ V\)) for extended periods of time (>1 year).

Amongst the different electrolyzers proposed to drive the CO\(_2\)RR, we find the zero-gap design to be particularly promising. A zero-gap CO\(_2\) electrolyzer consists of porous cathodes and anodes that sandwich a solid polymer electrolyte (i.e., membrane; Figure 1.1). Many zero-gap CO\(_2\) electrolyzers that utilize an anion exchange membrane (AEM) have shown superior performance compared to other types of membranes. In an AEM-based zero-gap CO\(_2\) electrolyzer, water provides the necessary protons to convert CO\(_2\) to a CO\(_2\)RR product at the cathode/AEM interface. Water can be delivered to the cathode by humidifying the cathode feedstock and/or from the anolyte that permeates through the AEM. Anions generated at the cathode (e.g., OH\(^-\)) migrate
through the AEM and are oxidized at the anode, where the oxygen evolution reaction occurs. These ion and water transport processes through AEMs have been examined extensively in zero-gap water electrolyzers and fuel cells, but far less so in the context of zero-gap CO$_2$ electrolyzers. This thesis serves to teach how the structure (e.g., functional group) and physical attributes (e.g., thickness) of the AEM impact the flow of ions and water through the membrane and, ultimately, CO$_2$RR performance (i.e., selectivity, energy efficiency, stability).

Figure 1.1 Schematic of a gas-fed zero-gap CO$_2$ electrolyzer.
Chapter 2: Literature review

2.1 Advantages of the zero-gap architecture

Zero-gap CO$_2$ electrolyzers effectively have “zero” gap between the porous cathodes and anodes because the two electrodes are each pressed against the membrane (5-100 μm). This reactor design minimizes the total cell voltage by decreasing the distance for ion transport (i.e., ohmic resistance). Zero-gap CO$_2$ electrolyzers can also achieve high current densities (≥100 mA/cm$^2$) by delivering gaseous CO$_2$ to the cathode as a means of overcoming the mass transport limitations that arise in aqueous feedstocks.$^{3,9}$ The efficiency of zero-gap CO$_2$ electrolyzers depends on the choice of electrocatalyst (e.g., Ag-coated carbon paper), operating conditions (e.g., CO$_2$ flow rate, cell temperature), and membrane. This thesis focuses on the effect of the membrane on the conversion of CO$_2$ to a single product using a Ag cathode, which catalyzes the desirable CO$_2$RR to CO and the competing hydrogen evolution reaction (HER):

\[
\text{CO}_2\text{RR}: \quad 2\text{CO}_2 + 2\text{H}_2\text{O} + 4\text{e}^- \to 2\text{CO} + 4\text{OH}^- \quad E_1 = -0.11 \text{ V (vs. RHE)} \quad (\text{Eq. 2.1})
\]

\[
\text{HER}: \quad 4\text{H}_2\text{O} + 4\text{e}^- \to 2\text{H}_2 + 4\text{OH}^- \quad E_2 = 0.00 \text{ V (vs. RHE)} \quad (\text{Eq. 2.2})
\]

2.2 Review of membranes in zero-gap CO$_2$ electrolyzers

The membrane is an important component in zero-gap CO$_2$ electrolyzers because it impacts the local pH at the cathode, modulating selectivity for CO$_2$RR products and energy efficiency. Membranes facilitate ion and water transport between the cathode and anode while preventing reactant and/or product crossover.$^{9-12}$ Aside from anion exchange membranes (AEMs),$^{8,12-14}$ cation exchange membranes (CEMs)$^{15-18}$ and bipolar membranes (BPMs)$^{9,19}$ are also being actively used in zero-gap CO$_2$ electrolyzers (Figure 2.1a). CEMs transport cations (e.g., H$^+$) from the anode to cathode, AEMs transport anions (e.g., OH$^-$) from the cathode to anode, and BPMs transport H$^+$ to the cathode and OH$^-$ to the anode from the dissociation of H$_2$O at the AEM/CEM
interface under a reverse bias. Zero-gap CO₂ electrolyzers containing AEMs have demonstrated higher conversion efficiencies and energy efficiencies than CEM and BPM systems (Figure 2.1b). AEMs may be more suitable than CEMs and BPMs likely because the concentration of H⁺ at the catalyst surface is minimized, thereby suppressing the competing HER.²⁰

![Diagram of ion transport between cathode (labeled “C”) and anode (labeled “A”) for an anion exchange membrane (AEM), cation exchange membrane (CEM), and bipolar membrane (BPM) under reverse bias.](image)

**Figure 2.1** Ion transport between the cathode (labeled “C”) and anode (labeled “A”) for an anion exchange membrane (AEM), cation exchange membrane (CEM), and bipolar membrane (BPM) under reverse bias.

### 2.3 Ion transport mechanisms in AEMs

#### 2.3.1 Anion transport through AEMs

AEMs contain hydrophilic positively-charged groups (e.g., imidazolium) that can be anchored as side chains or directly onto the hydrophobic polymer backbone (e.g., polystyrene). The presence of both hydrophobic and hydrophilic components in the AEM contributes to a phase segregated microstructure, forming percolated ionic domains that facilitate the flow of anions from the cathode to the anode.²¹–²³ Anion transport through these hydrophilic domains relies on the water content in the AEM and this topic remains to be an active area of research.²⁴–²⁶ Previous reports describe ion transport through AEMs as a combination of the Grotthuss, diffusion, and surface site hopping mechanisms (Figure 2.2).²⁷,²⁸
Figure 2.2 Anion transport in the AEM depends on the structure and water content of the membrane, and may be a combination of Grotthus, diffusion, and surface site hopping mechanisms. Figure adapted from Grew and Chiu.²⁸

Grotthuss mechanism is one of the dominant modes of anion (e.g. OH⁻) transport through the AEM.²²,²⁷,²⁹,³⁰ In this mechanism, OH⁻ are shuttled through the hydrogen bond network of water molecules by the formation and cleavage of covalent O–H bonds with neighbouring molecules. The diffusion mechanism is operative when there is a concentration or electrical potential gradient across the membrane. Surface site hopping (also known as the vehicular mechanism) involves the movement of OH⁻ ions from one side chain of the AEM to another through continuous overlapping first solvation shells of cationic functional groups.³¹ The contribution of each transport mechanism depends on the structure and water content of the AEM.³⁰,³¹ Both surface site hopping and diffusion mechanisms require unbound water within the membrane. In a membrane with low hydration levels, the ionic conductivity of the AEM is limited.
because the hydrophilic domains are small, thus, restricting the diffusion and surface site hopping mechanisms. In a highly hydrated membrane, the ionic conductivity is expected to be higher because water-filled channels expand and anion transport will occur through diffusion mechanisms (i.e. Grotthuss and diffusion mechanisms).

### 2.3.2 Cation transport through AEMs

An ideal AEM should exhibit a high permselectivity by facilitating anion transport between the anode and cathode while excluding the flux of co-ions (e.g., K⁺). Migration of cations in AEM-based CO₂ electrolyzers is undesirable because salt can precipitate at the cathode and limit mass transport to/from catalytic sites (further discussed in Section 2.7.1). There are two mechanisms for co-ion transport through the AEM: i) diffusion due to a difference in concentration gradient across the membrane and/or ii) electromigration due to an externally applied electric field. In electric field-driven migration, cations from the anolyte are electrostatically attracted to the negatively-charged cathode. Undesirable cation transport through the AEM can be minimized by optimizing the cell operating conditions (e.g., applied current or anolyte concentration) and through materials design. In a materials design perspective, AEMs that contain a high concentration of positively-charged functional groups, for example, generally decrease cation transport through electrostatic exclusion. This exclusion effect, however, decreases if increasing the concentration of positively-charged functional groups significantly leads to a high membrane water content.

### 2.4 Water transport mechanisms in anion exchange membranes

Water transport through the AEM is another important factor that influences the performance of the CO₂RR as is the case in alkaline fuel cells. Water is a reactant for the desired CO₂RR, but excess amounts of water present at the cathode could hinder CO₂ diffusion to
the catalyst and promote the undesired HER. There are two methods for delivering water to the CO₂RR catalyst in a zero-gap reactor: i) through the humidified CO₂ feedstock and/or ii) from the anolyte that permeates through the AEM. In the latter case, the net flux of water \( (J_{H₂O, net}) \) to the cathode can be described by diffusion \( (J_{\text{DIFF}}) \), electro-osmotic drag \( (J_{\text{EOD}}) \), and back convection \( (J_{\text{BC}}) \) processes (Figure 2.3). Water diffuses from the anolyte to the cathode CO₂RR catalyst because of the liquid concentration gradient between the aqueous anode environment and the gas-fed cathode. Water is also driven from the cathode to the anode through electro-osmotic drag as solvated anions migrate toward the anode. Back convection of water from the cathode to the anode is driven by the liquid pressure gradient across the membrane.

![Figure 2.3 Net water flux to the cathode \( J_{H₂O, net} \) is the sum of diffusion \( J_{\text{DIFF}} \), electro-osmotic drag \( J_{\text{EOD}} \), and back convection \( J_{\text{BC}} \) processes.](image)

The rate of each water flux depends primarily on the transport properties of the AEM. For example, water diffusivity \( (D_{H₂O}) \) and electro-osmotic drag \( (\eta_{EOD}) \) coefficients both increase for membranes that exhibit a higher water content or uptake \( (\lambda) \); Figure 2.4). Previous reports also highlight that the back convection of water from the cathode to the anode increases with thinner
membranes.\textsuperscript{44,47,52} It is therefore important to design AEMs with suitable properties (e.g., water uptake and thickness) in order to deliver the optimal amount of water to the CO\textsubscript{2}RR catalyst.

\textbf{Figure 2.4} (a) Water diffusivities ($D_{\text{H2O}}$) and (b) electro-osmotic drag ($\eta_{\text{EOD}}$) coefficients of anion exchange membranes as a function of different water content ($\lambda$) at different temperatures. Figures adapted from Li and coworkers.\textsuperscript{49}

\section{2.5 Characterization of anion exchange membranes}

I highlight in this section the three key characterization techniques for measuring the performance and chemical stability of AEMs: ionic conductivity, ion exchange capacity, and water uptake.

\subsection{2.5.1 Ionic conductivity}

Ionic resistances contribute to the total cell voltage of CO\textsubscript{2} electrolyzers. Ionic conductivity can be measured along the plane (i.e., in-plane) or through the thickness of the membrane (i.e., through-plane).\textsuperscript{53,54} Conductivity values from these two measurements are not equal because of anisotropic resistances that arise from the polymer casting method or use of support materials in the membrane (e.g., reinforcements).\textsuperscript{55-57} Through-plane measurements are more difficult to implement than in-plane measurements because this technique requires other resistances (e.g., contact resistance from electrical leads and connections, interfacial resistance between the
electrode and the membrane) to be minimized or accounted for.\textsuperscript{54,58} The through-plane conductivity, however, is more relevant because anions in a CO\textsubscript{2} electrolyzer migrate between the cathode to the anode through the thickness of the AEM.

Through-plane membrane resistances are typically determined using an ex-situ or in-situ two-probe electrochemical impedance spectroscopy (EIS) approach, and I use both methods in this thesis. For ex-situ measurements, a membrane is sandwiched between two electrodes (e.g., Pt sheets) and this conductivity cell is either submerged in a water bath or placed in a controlled humidity chamber to ensure that the water content in the membrane remains constant throughout the experiment. In-situ conductivity measurements are performed using the same conditions as an operating zero-gap cell. For both ex-situ and in-situ diagnosis, an AC signal (\textit{ca} 10-100 mV) is applied to the cell in a wide frequency range (10 MHz to 1 Hz) to obtain a Nyquist plot. The anion conductivity ($\sigma$ in S/cm) can be calculated from the resistance of the membrane ($R_{\text{mem}}$ in $\Omega$) obtained from the high-frequency data in the Nyquist plot, the contact area between the electrodes ($A$ in cm$^2$) and the thickness of the membrane ($L$ in cm):

$$\sigma = \frac{L}{R_{\text{mem}} \cdot A} \quad \text{(Eq. 2.3)}$$

Current protocols for ex-situ conductivity measurements assume that OH$^-$ is the sole charge carrier, however, AEMs contain a mixture of OH$^-$ and less mobile HCO$_3^-$ and CO$_3^{2-}$ ions under CO$_2$ electrolysis experiments. Anion conductivities collected in-situ are more representative of the conditions in a CO$_2$ electrolyzer, but requires considerable time and material (e.g., catalysts, gas diffusion layers) to reproducibly gather the required data.
2.5.2 Ion exchange capacity

The ion exchange capacity (IEC) provides clues about the suitability of newly developed AEMs for electrochemical CO$_2$ reduction before testing for ionic conductivity or performance in an electrolyzer. IEC (in meq/g) is defined as the number of exchangeable functional groups per dry weight of polymer, and is typically reported for AEMs in Cl$^-$ form (i.e. Cl$^-$ is the mobile counter-ion in the membrane). To determine the IEC, the membrane is pre-treated in an aqueous electrolyte (e.g., 1.0 M KOH) as a means of exchanging the Cl$^-$ ions in the membrane with the counter-ions in the solution (e.g., OH$^-$). The concentration of Cl$^-$ ions in the solution can be determined using titration (e.g., Mohr method, acid/base) or an ion selective electrode.$^{59,60}$ Spectroscopy techniques (e.g., FTIR, NMR) can also be used to approximate IEC of the ionomer in powder form.$^{59,61}$

There are variabilities between IECs determined using each procedure due to inaccurate measurement of weakly or strongly basic functional groups in the AEM that may not dissociate depending on the pH of the pre-treatment solutions.$^{59,62}$ Titration-based methods are the most common techniques for determining the IEC. However, a significant source of error for this method arises from using colour change as an indicator for the equivalence point. FTIR and NMR spectroscopy can determine the theoretical total number of functional groups in the membrane, but this value is generally different from the number of functional groups that participate in ion exchange. In this thesis, I utilize a Cl$^-$ selective electrode to determine IEC, but this approach may underestimate the true IEC value because weakly basic functional groups may not be detected. IEC measured using a Cl$^-$ selective electrode is calculated from the concentration of Cl$^-$ in solution ([Cl$^-$] in ppm) obtained from a calibration curve, the mass of the pre-treatment aqueous KNO$_3$
solution \((m_{\text{KNO}_3} \text{ in g})\), molar mass of \(\text{Cl}^-\) \((M_{\text{Cl}} \text{ in g/mol})\) and the dried mass of the membrane \((m_d \text{ in g})\):

\[
IEC = \frac{[\text{Cl}^-] \cdot m_{\text{KNO}_3}}{M_{\text{Cl}} \cdot m_d} \quad \text{(Eq. 2.4)}
\]

2.5.3 Water uptake

It is also important to characterize the amount of water in the AEM because water facilitates anion transport through the AEM, but high water contents can compromise the mechanical integrity of the AEM due to excessive swelling.\(^{63}\) The water content of the AEM is related to the water uptake property, which is described as the \(\%\) increase in the mass of the AEM when it is fully hydrated in liquid or water vapor \((m_h)\) relative to when the membrane is completely dry \((m_d)\).\(^{64}\) Water uptake of AEMs are typically reported in the \(\text{Cl}^-\) form and when the membrane is hydrated with liquid water. In this measurement, AEM in \(\text{Cl}^-\) form is immersed in deionized water for 24 hours while replacing the solution at least three times over this duration to ensure excess ions are removed from the membrane. Water from the surface of the AEM is removed with tissue immediately before weighing the membrane in an analytical balance to yield \(m_h\). Complete drying of the membrane is typically performed in a dry, sealed environment (e.g. a glass container containing desiccants) for a specific duration (e.g. 5 days) before weighing the dried mass of the membrane. Water uptake values are then calculated as follows:

\[
WU = \frac{m_h - m_d}{m_d} \times 100\% \quad \text{(Eq. 2.5)}
\]

2.6 Challenges with AEMs in CO\(_2\) electrolyzers

Early reports of AEM-containing CO\(_2\) electrolyzers used membranes that were originally developed for other electrochemical applications: electrodialysis, water electrolyzers, and fuel
cells.\textsuperscript{15,17,65,66} As such, I highlight in this section the major operational challenges that have been encountered when using AEMs in CO\textsubscript{2} electrolyzers.

2.6.1 Crossover of reactant CO\textsubscript{2} and cations

The amount of free CO\textsubscript{2} available to the catalyst decreases due to the reaction between the CO\textsubscript{2} feed and CO\textsubscript{2}RR-generated OH\textsuperscript{−} (Eq. 2.6 and 2.7).

\[
\text{CO}_2 + \text{OH}^- \rightarrow \text{HCO}_3^- \quad \text{(Eq. 2.6)}
\]

\[
\text{CO}_2 + \text{HCO}_3^- \rightarrow \text{CO}_3^{2-} + \text{H}_2\text{O} \quad \text{(Eq. 2.7)}
\]

The generated HCO\textsubscript{3}\textsuperscript{−} and CO\textsubscript{3}\textsuperscript{2−} from these reactions could also crossover the AEM from the cathode to the anode electrolyte, where they can be oxidized to O\textsubscript{2} and CO\textsubscript{2} (Eq. 2.8 and 2.9).

\[
\text{HCO}_3^- \rightarrow \frac{1}{2}\text{O}_2 + \text{H}_2\text{O} + 2e^- + 2\text{CO}_2 \quad \text{(Eq. 2.8)}
\]

\[
\text{CO}_3^{2-} \rightarrow \frac{1}{2}\text{O}_2 + 2e^- + \text{CO}_2 \quad \text{(Eq. 2.9)}
\]

A recent report shows that crossover of CO\textsubscript{2} through the AEM exceeds the amount of CO\textsubscript{2} converted to the target product.\textsuperscript{67} Negatively charged CO\textsubscript{2}RR products (e.g., HCOO\textsuperscript{−}) are also readily transported across the positively-charged AEM while neutral products (e.g., MeOH, EtOH) are able to crossover through diffusion.\textsuperscript{68} This situation implicates the need for separation units downstream of the CO\textsubscript{2} electrolyzer to recover valuable CO\textsubscript{2}RR products and a high purity O\textsubscript{2} stream.

Co-ion transport of K\textsuperscript{+} from the anolyte (typically aqueous KHCO\textsubscript{3} or KOH solution) to the cathode forms KHCO\textsubscript{3} and K\textsubscript{2}CO\textsubscript{3} crystals when combined with the HCO\textsubscript{3}\textsuperscript{−} and CO\textsubscript{3}\textsuperscript{2−} ions at the cathode. These reactions are undesirable because salt precipitates at the cathode block the pores of the gas diffusion electrode and accelerate the accumulation of excess water at the cathode (i.e., flooding).\textsuperscript{45,69} Both of these phenomena impede the transport of reactant CO\textsubscript{2} to the catalytic sites
and limit the surface area available for CO$_2$RR. The use of pure water or diluted solution (e.g. 10 mM KHCO$_3$) at the anode reduces the formation of CO$_3^{2-}$ and HCO$_3^-$ crystals, but compromises ionic conductivity and increases the cell potential.

### 2.6.2 Mechanical and chemical stability

Another major operational challenge is the mechanical and chemical stability of AEMs in CO$_2$ electrolyzers. Due to the high water uptake (up to 80%) of the membrane, AEMs have limited mechanical strength due to swelling.$^{63,70}$ The chemical stability of AEMs primarily synthesized for other electrochemical applications are also not necessarily suitable for the conditions in a CO$_2$ electrolyzer. Narayan and coworkers, for example, utilized a commercially-available electrodialysis AEM that is chemically stable up to a pH of 10.$^{71}$ However, AEM-based CO$_2$ electrolyzers operate at a higher pH (>11) than electrodialysis systems because OH$^-$ ions are electrolytically generated at the cathode.$^{19,67,72,73}$

### 2.6.3 Ohmic and interfacial losses

High cell voltages arise due to interfacial and ohmic losses in AEM zero-gap CO$_2$ electrolyzers. Zhuang and coworkers demonstrate state-of-art CO$_2$RR performance using a catalyst-coated AEM and gas diffusion layers impregnated with anion exchange ionomers.$^8$ This configuration likely minimizes the interfacial resistances in the cell, however, many CO$_2$ electrolyzers use bare AEMs with catalyst-coated gas diffusion layers. Our research group also recently demonstrated using an analytical reactor that the ohmic losses of the membrane during operation of the reactor are a significant contribution to the overall cell potential.$^{74}$ High ohmic losses occur, in part, HCO$_3^-$ and CO$_3^{2-}$ ions displace OH$^-$ ions as charge carriers in the AEM and these ions are less mobile than OH$^-$.}$^{62}$
### 2.7 Review of state-of-art performance of AEM-based CO₂ electrolyzers

There are only a few reports of AEM-based zero-gap cells that achieve high current densities (≥200 mA/cm²) while maintaining high selectivities (>90%) and low cell voltages (≤3 V).\textsuperscript{7,8} Incompatibility issues between the operational requirements in a CO₂ electrolyzer and the chemical properties of many existing AEMs is a root cause for the limited cell performance. Significant improvements in CO₂RR performance (i.e., energy efficiency, conversion efficiency, and stability) have since been realized with the recent developments of AEMs tailored for gas-phase CO₂ electrolysis experiments, but there remains room to innovate new membrane technology to bring these systems closer to commercial viability.

Sustainion®, an N-methylimidazolium-functionalized styrene polymer, marked the first viable AEM designed for gas-fed CO₂ electrolyzers.\textsuperscript{75} Sustainion® features a high OH⁻ conductivity (100 mS/cm at 80°C), contains a high IEC (2.5 meq/g), exhibits a high WU (80%), and is thin (50 μm).\textsuperscript{76} Masel and coworkers maintained the high conductivity of Sustainion® in the CO₂ electrolyzer by supplying a humidified gaseous CO₂(g) feed and circulating an aqueous anolyte at the anode. This electrolyzer configuration reached commercially-relevant current densities (200 mA/cm²) while sustaining >95% CO selectivity at 3 V for 3800 h. Many studies have since used Sustainion® in gas-fed CO₂ electrolyzers;\textsuperscript{12,77–79} however, salt precipitation at the cathode occurs when a concentrated electrolyte is supplied at the anode (≥0.5 M KOH or KHCO₃).\textsuperscript{72} Moreover, Sustainion® is prone to crossover of CO₂RR products (e.g., ethanol), particularly at the high current densities.\textsuperscript{77} Our group also recently demonstrated high ohmic losses across the membrane in a zero-gap reactor utilizing a Sustainion® for CO₂RR.\textsuperscript{74}

A quaternary ammonia poly(N-methyl-piperidine-co-p-terphenyl) (QAPPT) was introduced by Zhuang and coworkers as another candidate AEM material for gas-fed CO₂
electrolyzers. QAPPT exhibits a high OH\textsuperscript{−} conductivity (137 mS/cm\textsuperscript{1} at 80\textdegree C) and is chemically stable in basic solutions.\textsuperscript{8,80} The high conductivity of QAPPT eliminates the need to humidify the CO\textsubscript{2} feed or the use of an ionically-conductive anolyte. With an operating cell temperature of 60\textdegree C, the QAPPT-containing CO\textsubscript{2} electrolyzer demonstrated the highest current density reported to date (500 mA cm\textsuperscript{−2}) with a F.E. for CO >90\% and an \(E_{\text{cell}}\) of 3 V. This result encourages further research on how QAPPT can mitigate the other challenges for AEMs in CO\textsubscript{2} electrolyzers (e.g. CO\textsubscript{2}RR product crossover from the cathode to the anode).

The two case studies involving Sustainion\textsuperscript{®} and QAPPT draw attention to the importance of synthesizing AEMs with properties (e.g. conductivity, chemical stability, and water uptake) that match the requirements in a CO\textsubscript{2} electrolyzer. These properties of an AEM are related to the type of cation functional group embedded in the polymer matrix. While there have been reports that attempt to correlate the functional group with the transport and chemical properties of AEMs and CO\textsubscript{2}RR performance, these studies were conducted at current densities remote from commercial operating conditions (\(j < 10 \text{ mA/cm}^2\)).\textsuperscript{14,81}

2.8 Thesis objectives

The overall objective of this thesis is to understand the influence of the AEM physical and chemical structure (i.e., ionic group concentration, thickness, and functional group) on electrochemical CO\textsubscript{2} reduction to CO. Specifically, the objectives are:

A. To determine the chemical properties (ion exchange capacity, water uptake, and ionic conductivity) of AEMs fabricated in-house with different types of functional groups, concentration of functional groups, and thicknesses.

B. To evaluate the performance of the AEMs in a zero-gap CO\textsubscript{2} electrolyzer for CO production using Faradaic efficiency (as a measure of product selectivity) and cell voltage
C. To design a diagnostic tool for studying the water flux to the cathode of different AEMs and cathode materials

2.9 Thesis organization

In Chapter 3, I study how CO$_2$RR performance at $j$ up to 100 mA/cm$^2$ is affected when incorporating an imidazolium or trimethylamine cation groups in the AEM. I characterized the properties of these AEMs (IEC, water uptake, thickness, and anion conductivity) and correlated these values to the performance in a gas-fed CO$_2$ electrolyzer. In Chapter 4, I investigate further the imidazolium-functionalized AEM by varying the water uptake and thickness of the membrane. The goal of this chapter is to diagnose how these properties of the AEM impact the water flux to the cathode and, ultimately, CO$_2$RR performance. Water serves as the proton source for CO$_2$RR, but excess water present at the cathode block the pores of the cathode and impede mass transport of reactants and products.$^{72}$ I designed a series of experiments to empirically track the water flux to the cathode while varying AEM thicknesses and water uptakes, and cathode hydrophobicity. Chapter 5 outlines the main conclusions of this thesis and future directions towards improvement in experimental set-up and characterization techniques, and additional materials design consideration to minimize cathode flooding.
Chapter 3: Linking structure and properties of anion exchange membranes to gas-fed CO₂ electrolysis performance in a zero-gap reactor

3.1 Introduction

There is a growing interest in the use of anion exchange membranes (AEMs) for gas-fed CO₂ electrolysis, yet there are merely two reports that demonstrate >90% Faradaic efficiencies for CO (FE_CO) and cell voltages (E_cell) ≤3 V at current densities (j) ≥200 mA/cm². These studies highlight the use of two AEM designs: i) an N-methylimidazolium-functionalized styrene polymer (commercially known as Sustainion®) and; ii) a quaternary ammonia poly(N-methyl-piperidine-co-p-terphenyl) (QAPPT). There has been considerable improvement in cell performance using these membranes, but there remains room to innovate new AEMs for CO₂ electrolysis application. This situation provides the imperative to develop design principles that link AEM structure to CO₂ reduction reaction (CO₂RR) activity.

AEMs facilitate the flow of ions and water to and from the CO₂RR cathode. These transport properties of the AEM are intrinsically linked to the type of cation functional group, amongst other parameters of the membrane including concentration of functional group, polymer backbone, and membrane thickness. While there have been reports that attempt to establish the relationship between AEM functional group and CO₂RR performance, these studies were conducted at low j (<10 mA/cm²). This knowledge gap is striking because the catalytic environment for CO₂RR is known to be particularly sensitive at higher j, where the cathode pH is higher and ion and water transport rates are faster.

In this Chapter 3, I study the effect of cation functional groups (imidazolium and trimethylamine) on CO₂RR performance in a gas-fed CO₂ electrolyzer at j up to 100 mA/cm². Our results show that an AEM functionalized with an imidazolium group facilitates a consistently higher (~10-25%) FE_CO than a trimethylamine analog under the same operating conditions. We
were able to resolve these differences by fabricating two AEMs with either an imidazolium or trimethylamine group while maintaining the same polymer backbone, fabrication conditions, membrane thickness, and concentration of functional groups. We assert that AEMs functionalized with an imidazolium group achieves a higher $F_{E_{\text{CO}}}$ than the trimethylamine analog presumably because it exhibits a lower water uptake, which is important in minimizing salt precipitation at the cathode. We further show that an imidazolium group is more chemically stable than a trimethylamine at higher current densities ($j = 100 \text{ mA/cm}^2$). This work demonstrates the importance of designing AEMs that are chemically stable and exhibit lower water uptakes for improved CO$_2$RR performance.

3.2 Results and discussions

3.2.1 Design of zero-gap CO$_2$ electrolyzer and MEA materials

CO$_2$RR experiments in this study were performed in a gas-fed zero-gap electrolyzer (Figure 3.1) similar to a previous report.$^9$ The reactor consists of end plates, flow field plates, gaskets, and the membrane electrode assembly (MEA). Two stainless steel end plates served as inlets and outlets for the reactants and products. The titanium cathode and stainless steel anode flow field plates were machined with serpentine channels that are 1.5-mm wide and 1.5-mm deep with 1-mm landings. The flow plates sandwiched the MEA (active area = 2 × 2 cm$^2$) and served to facilitate the delivery of reactants and products to and away from the reactive interface. The MEA comprised a silver-coated cathode gas diffusion electrode (GDE; 2 × 2 cm$^2$), an AEM (3 × 3 cm$^2$), and a nickel foam anode (2 × 2 cm$^2$). The AEM component of the MEA was manipulated as described below, and both the cathodes and anodes were unchanged for all experiments. The gaseous CO$_2$ was humidified by flowing the inlet stream through a water bath (heated at 35 °C) at 11 or 20 sccm before entering the cathode; the anode was supplied with 1.0 M KOH at 10 or 15
mL/min (Figure 3.1b). Chronopotentiometry experiments were performed by applying a constant $j$ of 0.75, 1, 5, 10, or 25 mA/cm$^2$ to the entire cell for 1500s using a potentiostat. In-line gas chromatography (GC) analyses of the cathode outlet gas were taken after 800s from the start of electrolysis to determine the $F_{E_{CO}}$.

![Figure 3.1](image.png)

**Figure 3.1** (a) Schematic of the zero-gap reactor used in this study and (b) operating conditions for CO$_2$RR experiments.

Cathodic GDEs were prepared to contain the same silver catalyst and Nafion binder composition in order to correlate differences in CO$_2$RR performance to the change in functional group of the AEM. To prepare the GDEs, I used an airbrush to manually spray coat a Toray carbon paper (TGP-H-120) with a catalyst ink mixture consisting of fixed amounts of commercially available silver nanopowder and Nafion® dispersed in a 1:1 (v/v) solvent mixture of isopropanol and water. The GDEs were coated with a constant silver loading of ~1.5 mg/cm$^2$ and X-ray fluorescence measurements (XRF) confirmed a constant silver signal intensity of ~65 cps for each of the GDEs (Table A3.1).$^{84}$

The Sustainion-inspired AEMs in this study consisted of a polystyrene backbone functionalized with either an imidazolium or a trimethylammonium group. The polystyrene
backbone was prepared by radical polymerization of styrene \((m)\) with 4-vinylbenzyl chloride \((n)\), and then the benzylic chloride was substituted with either a 1-methylimidazolium or a trimethylammonium ionic group in a second reaction. The synthesized polymers are poly[(4-vinylbenzyl-1-methylimidazolium chloride)-co-styrene (PSMIM) and poly[(4-vinylbenzyl-trimethylammonium chloride)-co-styrene (PSTMA) (Figure 3.2a). Solid ionomer powders were subsequently dissolved in 5 wt% ethanol and were cast onto a glass substrate by doctor blade coating to achieve AEMs with a thickness of ~60 μm (Figure 3.2b). The thickness of the dry membranes was confirmed at three separate locations using a digital micrometre (Mitutoyo) with a variance of ± 1 μm.

![Figure 3.2](image)

**Figure 3.2** (a) Structures of AEMs synthesized in this study and (b) fabricated with the same thickness.

### 3.2.2 Characterization of AEMs

The IECs of PSTMA and PSMIM samples in chloride form (i.e., Cl\(^{-}\) is the counter-ion attached to the functional groups) were collected as a measure of the functional group concentration in the AEM. PSTMA and PSMIM resulted in the same IECs of 2.32 ± 0.06 and 2.34 ± 0.12 mmol/g, respectively (Figure 3.3), which was expected for AEMs synthesized with the same \(m:n\).
I characterized the water content of the AEM and ion conductivity to understand how different ionic groups impact these properties of the membrane. The water content of the AEM, defined by water uptake (WU), was gravimetrically measured by quantifying the increase in the mass of each membrane when it is fully hydrated with liquid water relative to when the membrane is dry (Figure 3.4a). PSTMA achieved a higher WU value (114 ± 6%) than PSMIM (66 ± 13%), which is an expected trend that corroborates with observations made in literature comparing the same functional groups.\textsuperscript{85–88} I also performed ex-situ electrochemical impedance spectroscopy (EIS) measurements of PSTMA and PSMIM in OH\textsuperscript{–} form to determine the ionic conductivities of the membranes (Figure 3.4b). PSTMA achieved a slightly higher conductivity (98 ± 14 mS/cm) than PSMIM (82 ± 6 mS/cm), which again aligns with observations in literature that report the higher OH\textsuperscript{–} conductivity of AEMs decorated with a quaternary amine than imidazolium functional groups.\textsuperscript{85,86} This result is also expected given that PSTMA has a higher water content in the membrane (i.e., water uptake), which facilitate the efficient transport of anions from the cathode to the anode.
3.2.3 \textit{CO}_2\textit{RR performance of AEMs in a zero-gap reactor}

I tested the performance of PSMIM and PSTMA in a zero-gap reactor in order to investigate the relationship between structure of the AEMs and \textit{CO}_2\textit{RR} activity. Both AEMs achieved similar $FE_{CO}$ at $j \leq 1$ mA/cm$^2$, but PSTMA resulted in lower cell performance (i.e., higher $E_{cell}$ and lower $FE_{CO}$) at higher $j$ than PSMIM (Figures 3.5a and 3.5b). This result is unexpected because the higher ionic conductivity of PSTMA should result in lower ohmic resistance and, thus, lower $E_{cell}$. However, PSTMA also exhibits a high WU and this property is typically linked to a decrease in the ability of the AEM to exclude the flow of co-ions such as K$^+$ (i.e., permselectivity).\textsuperscript{34} I hypothesize therefore that the limited \textit{CO}_2\textit{RR} performance of PSTMA is due to increased K$^+$ crossover from the anode, which can react with CO$_2$ at the cathode. This reaction yields salt precipitates (e.g., K$_2$CO$_3$) that block the pores of the cathode GDE resulting in decreased catalytic sites available for \textit{CO}_2\textit{RR}, and poor mass transport of reactants and products.\textsuperscript{45,72} An inspection of the electrolyzers after \textit{CO}_2\textit{RR} experiments show that PSTMA resulted in more salt precipitates at the cathode flow field than PSMIM, which supports my hypothesis that the higher rates of K$^+$ crossover through PSTMA limits \textit{CO}_2\textit{RR} activity (Figure A3.1).
Figure 3.5 (a) The Faradaic efficiency for CO production ($FE_{CO}$) and (b) cell voltage ($E_{cell}$) in the applied current density ($j$) of 0.75, 1, 5, 10, 25 mA/cm$^2$ using a gas-fed zero-gap CO$_2$ electrolyzer containing PSTMA (green) or PSMIM (blue).

I investigated further if the difference in CO$_2$RR performance between PSTMA and PSMIM is also related to differences in the stability of the cation functional groups. The stability of PSTMA and PSMIM was tested by applying a constant $j$ of 25 or 100 mA/cm$^2$ for 5000 s (Figures 3.6a and 3.6b). At $j$ of 25 mA/cm$^2$, PSTMA achieved a stable, yet lower (~75%) formation for CO compared to PSMIM (>85%). While PSMIM was able to maintain a $FE_{CO}$ of ~25% at higher $j$ of 100 mA/cm$^2$, PSTMA resulted in effectively zero CO production ($FE_{CO} < 2\%$). The lower CO$_2$RR performance of PSTMA could be due, in part, to the nucleophilic attack from OH$^-$ ions that are electrochemically generated at the cathode.$^{85,86}$ An inspection of the AEMs after CO$_2$ electrolysis shows PSMIM remained transparent while a visibly brown tint on PSTMA indicates chemical degradation of the membrane.
Figure 3.6 The CO Faradaic efficiency ($F_{\text{CO}}$) for (a) PSMIM and (b) PSTMA during an applied current density ($j$) of 25 and 100 mA/cm$^2$ for 5000s.

3.3 Conclusion

AEMs offer promise in reaching commercially relevant CO$_2$ electrolysis performance, but there remains room to innovate new AEMs tailored for CO$_2$RR. Our work establishes the first relationship between the structure of AEMs and CO$_2$RR activity at $j$ up to 100 mA/cm$^2$. Synthesizing membranes that differ only in the type of cation functional group illuminate the importance of using an imidazolium cation group instead of a trimethylamine to boost CO$_2$RR performance (i.e., higher CO selectivities, lower cell voltage, and improved cell stability). We also demonstrate that an imidazolium group is more chemically stable than a trimethylamine analog, especially at the high current densities relevant to commercial operation ($j = 100$ mA/cm$^2$). Our results further show that AEMs exhibiting a high water uptake are susceptible to excessive salt precipitation at the cathode, which is detrimental to CO$_2$RR performance. This study motivates the work described in Chapter 4, where a detailed investigation on how AEMs with different water uptakes and thicknesses modulate the amount of water transported to the cathode and, ultimately, CO$_2$RR performance.
3.4 Experimental methods

Ethanol (100%, ACS grade) was purchased from Greenfield Global Inc. Nafion 117 solution (5 wt% in a mixture of lower aliphatic alcohols and water) and silver nanopowder (trace metal basis, >99%) were purchased from Sigma-Aldrich. Carbon paper (TGP-H-120) and PTFE gaskets (0.01”) were purchased from Fuel Cell Store. Nickel foam gas diffusion layer material was purchased from MTI (EQ-BCNF-16m).

3.4.1 Electrode preparation

I prepared the Ag cathode catalyst inks by sonicating 32 mg of silver nanopowder, 800 μL of deionized water, 800 μL of isopropyl alcohol, and 60 μL Nafion 117 solution similar to a previous report. I coated eight 4-cm² carbon papers by using an airbrush technique and subsequently dried using an infrared lamp. Each electrode was prepared to have a Ag mass loading of ~1.5 mg/cm² after spray coating. I prepared anodes by cutting nickel foam to size (2 × 2 cm²). Nickel foam was cleaned using a standard cleaning procedure of sonication in acetone and then deionized water. A fresh cathode, anode, and AEM were used for each electrolysis test.

3.4.2 Membrane characterization

Ion exchange capacity

I soaked four samples of each membrane (in Cl⁻ form) in individual containers containing 30 g of 1.0 M KNO₃ (m₁ M KNO₃) for 24 h to exchange chloride counter ions to nitrate. The concentration of chloride ([Cl⁻] in ppm) released in the solution was determined by using an ion-selective electrode (Cl⁻ ISE, Cole Parmer on Accumet AE 150 pH meter, Fisher Scientific). The membranes were then soaked in 1.0 M KCl for 24 h to exchange the nitrate counter ions back to chloride. I thoroughly washed each sample with DI water before soaking in DI water for an additional 24 h. The DI water was replenished three times over this period. The membrane samples
were then dried at room temperature for 24 h, and the mass of the dried membranes \((m_d \text{ in g})\) were recorded using an analytical balance. I calculated the ion exchange capacity (IEC) of the membranes using the following expression, where \(M_{Cl}\) is the molar mass of chloride (g/mol).

\[
IEC = \frac{\left[Cl^-\right] \cdot m_{1M\,KNO_3}}{M_{Cl} \cdot m_d} \quad \text{(Eq. 3.1)}
\]

**Water uptake**

Four samples of each membrane were soaked in 1.0 M KCl at room temperature for 24 h. The membranes were thoroughly washed with DI water to remove excess KCl from the membrane and soaked in DI water for an additional 24 h at room temperature. The water was replaced with fresh DI water three times over this period. The membrane samples were then removed from the water, surface water was gently removed with a paper tissue, and the mass of each hydrated membrane \((m_h \text{ in g})\) was immediately measured using an analytical balance. The hydrated membranes were then dried at room temperature for 24 h, and the mass of the dried membranes \((m_d \text{ in g})\) were recorded. The water uptake (WU) values were calculated as follows:

\[
WU (\%) = 100\% \times \frac{m_h - m_d}{m_d} \quad \text{(Eq. 3.2)}
\]

**3.4.3 Product analysis**

CO2RR experiments were performed using a potentiostat (CH instruments 660D with a picoamp booster) through a two-electrode set-up at ambient temperature and pressure. The CO2 electrolyzer cathode outlet stream passed through a condenser before entering the gas chromatograph (GC, Perkin Elmer; Clarus 580) to avoid liquid damage of the equipment. The GC was calibrated at different gas concentrations as previously reported.90 The flow rate of CO2 entering the cell was measured using a CO2 mass flow controller (AALBORG) and was used as the volumetric flow rate in Equation. 3.3. The faradaic efficiency \((FE)\) of a gaseous product \(k\) was determined in accordance with Equation 3.3.
\[ FE = \frac{n_k F x_k F_m}{I} \]  
(Eq. 3.3)

where \( n_k \) is the number of electrons exchanged for CO\(_2\)RR, \( F \) is Faraday’s constant (96,485 C/mol), \( x_k \) is the mole fraction of the gas k in the gaseous mixture determined from the peak areas from the GC peak, \( F_m \) 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:

\[ F_m = P F_v / RT \]  
(Eq. 3.4)

with \( P \) being the atmospheric pressure in Pa, \( R \) the ideal gas constant of 8.314 J/mol K, and \( T \) is the temperature in K.

### 3.4.4 Electrochemical impedance spectroscopy measurements

Ex-situ electrochemical impedance measurements (EIS) were performed using a 2-probe technique by immersing a conductivity cell in a beaker containing 1.0 M KOH. The conductivity cell consists of two perforated stainless steel cathodes (surface area = 2.01 cm\(^2\)) that serve to sandwich the membrane. EIS measurements were performed over a frequency range of 10 MHz to 1Hz and a sinusoidal amplitude of 10 mV. The electrolyte resistance (\( R_s \)) was subtracted from the measured total resistance that included both the membrane resistance (\( R_{\text{mem}} \)) and \( R_s \). The OH\(^-\) conductivity of the membranes was calculated from \( R_{\text{mem}} \) (in \( \Omega \)) obtained from the high-frequency data in the Nyquist plot, the contact area between the electrodes (\( A \) in cm\(^2\)) and the thickness of the membrane (\( L \) in cm):

\[ \sigma = \frac{L}{R_{\text{mem}} A} \]  
(Eq. 3.5)
Chapter 4: Managing hydration at the cathode enables efficient CO₂ electrolysis at commercially relevant current densities

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4.1 Introduction

There are many electrochemical reactor designs proposed to selectively reduce CO₂ at high reaction rates and energy efficiencies, yet there are no low temperature CO₂ electrolyzers available to the market. A range of techno-economic studies have highlighted that a commercially relevant CO₂ electrolyzer needs to drive the CO₂ reduction reaction (CO₂RR) at current densities \( j \geq 200 \text{ mA/cm}^2 \) while maintaining high faradaic efficiencies \( (FEs > 90\%) \) at low cell voltages \( (E_{cell} < 3 \text{ V}) \). Zero-gap CO₂ reactors (i.e., reactors that position the porous electrodes in contact with an anion exchange membrane) offer promise towards reaching these performance metrics; however, selecting suitable materials and operating conditions to achieve this performance remains a challenge. In this Chapter, I highlight the importance of water management in the design of CO₂ electrolyzers.

Water is critical to facilitating ion transport between the anode and cathode and is a proton source for CO₂RR, yet excess water can starve the cathode of CO₂ and promote the competing hydrogen evolution reaction (HER). This accumulation of excess water at the cathode (i.e., “flooding”) is especially important at the high \( j \) relevant to commercial operation. While flooding is known to exist in other CO₂ electrolyzer types, it is generally not explicitly considered in a zero-gap design, which is more aligned with commercial electrochemical cells. Our experiments show that cathode flooding is an issue at \( j \) values < 200 mA/cm², and is responsible for substantial decreases in product selectivity and electrolyzer energy efficiency. This observation illuminates the importance of water management in a CO₂ electrolyzer.
A zero-gap CO₂ electrolyzer contains a membrane electrode assembly (MEA) consisting of porous anode and cathode gas diffusion electrodes (GDEs) in contact with opposite sides of an ion-exchange membrane. In gas-fed CO₂ reactors, the mass transport limitations inherent to aqueous feedstocks are obviated by continuously delivering gaseous CO₂ to the cathode, which then diffuses through the GDE for reaction at the membrane/catalyst interface. Anion exchange membranes (AEMs) facilitate the flow of OH⁻ and water between the anode and the cathode, and have been used to achieve record-setting CO₂RR performance. While the zero-gap configuration is known to enable these high CO₂ conversion rates, there are currently no empirical studies on cathode flooding in zero-gap reactors, and very little has been reported on how water delivery to the cathode influences CO₂RR performance in any reactor architecture. This knowledge gap is striking considering that water is a reactant for all CO₂RR reactions, and how it is delivered to the cathode will almost certainly affect CO₂RR chemistry.

Herein, I experimentally quantify the extent of cathode flooding in zero-gap CO₂ reactors and demonstrate a materials design approach to manage water effectively in these electrolyzers. I first show that cathode flooding is indeed an issue in zero-gap reactors, and that this flooding occurs at j values of merely 200 mA/cm². Importantly, I was able to link this cathode flooding to decreases in faradaic efficiency for CO production (FECO), and increases in Ecell and faradaic efficiency for H₂ (FEH₂). I drew these conclusions by designing a gravimetric method to measure water flux to the cathode during electrolysis. Cathode flooding occurs when the water transported from the anode to the cathode is in excess (i.e., >5 mg/cm²·h) of the required amount of water for CO₂RR. I discovered that flooding can be mitigated by using thin (≤40 μm) membranes with low water uptake, in tandem with a hydrophobic cathode. Effective water management yields more
4.2 Results

4.2.1 Design of zero-gap CO\textsubscript{2} electrolyzer and MEA materials

All CO\textsubscript{2} reduction experiments in this study were performed in a zero-gap reactor configuration with a MEA containing an AEM sandwiched between a silver cathode GDE and a nickel foam anode (Figure 4.1a; see section 4.4.6 for detailed description).\textsuperscript{9} The electrolyzer consists of: (i) stainless steel end plates (containing reactant and product inlet and outlets); (ii) flow field plates to deliver CO\textsubscript{2} to the reactive site; and (iii) an MEA with a 2×2 cm\textsuperscript{2} active area. Gaseous CO\textsubscript{2} delivered to the cathode was humidified by flowing the inlet stream through a water bath (heated at 50 °C) while the anode was supplied with 1.0 M KOH (Figure 4.1b). Chronopotentiometry experiments were performed by applying a constant \(j\) of 25, 50, 100, or 200 mA/cm\textsuperscript{2} for 25 min each while in-line gas chromatography (GC) analyses of the cathode outlet gas were taken after 800 s of electrolysis to determine the \(F_{E_{CO}}\) and \(F_{E_{H2}}\) (See section 4.4.6 for details). I used this electrolyzer configuration to test a series of custom-made AEMs and GDEs and measured the resulting CO\textsubscript{2}RR performance metrics and water flux to the cathode.
Figure 4.1 (a) Expanded and (b) cross-sectional diagrams of the gas-fed zero-gap CO$_2$ reactor used in this study. The membrane electrode assembly consists of a nickel foam anode, anion exchange membrane, and Ag/polytetrafluoroethylene (PTFE) on carbon paper as the cathode.

The Sustainion-inspired AEMs in this study consisted of a hydrophobic polystyrene backbone functionalized with hydrophilic tetramethylimidazolium ionic groups.$^{7,61,75,76,99}$ Using this molecular platform, we were able to vary the water uptake of the membrane by manipulating the ionic group concentration. The polystyrene backbone was prepared by radical polymerization of styrene ($m$) with 4-vinylbenzyl chloride ($n$) and then the benzylic chloride was substituted with the 1,2,4,5-tetramethylimidazolium ionic group in a second reaction. Adjusting the ratio of the styrene ($m$) to imidazolium-containing 4-vinylbenzyl ($n$) monomers used in the polymerization step yielded membranes with an $m:n$ ratio of 1:1 and 3:1. Ionomers were then cast from the reaction solution into membranes of desired thicknesses (20 μm, 40 μm, and 55 μm) by doctor blade coating (Table 4.1).

The ion exchange capacity ($IECs$) of each membrane was recorded as a measure of imidazolium group concentration. Membranes made from ionomers with $m:n$ values of 1:1 and 3:1 exhibited $IECs$ of $2.13 \pm 0.09$ mmol/g and $1.43 \pm 0.05$ mmol/g, respectively. I also measured
the relative mass of water each membrane absorbed, denoted as water uptake (WU). The WUs of the AEMs were found to increase with IEC: the membrane made from 1:1 \((m:n)\) ionomer yielded a WU value of 144 ± 8\%, while the membrane from 3:1 \((m:n)\) ionomer yielded a WU value of 43 ± 4\% (Figure BA4.1). I therefore define membranes made from 1:1 and 3:1 \((m:n)\) ionomers to be high water uptake membranes (HWUM) and low water uptake membranes (LWUM), respectively.

Cathode GDEs of varying hydrophobicity were prepared by modulating the amounts of polytetrafluoroethylene (PTFE) in the catalyst ink. These GDEs were prepared by ultrasonically spray coating catalyst inks containing a constant amount of commercially-available silver nanopowder and varying amounts of PTFE (6, 17, and 29 wt\%) onto carbon paper. A silver loading of ~1 mg/cm\(^2\) was obtained regardless of PTFE content and was confirmed by a constant X-ray fluorescence (XRF) Ag signal intensity of ~55 cps (Figure B4.2).\(^\text{84}\)

### 4.2.2 MEA materials influence water flux and CO\(_2\)RR performance

I next designed experiments to show how the MEA materials (i.e., AEM ionomer composition, AEM thickness and GDE hydrophobicity) influence water flux and performance in a CO\(_2\) electrolyzer. I used a water trap filled with anhydrous desiccant (Drierite) placed at the cathode outlet to capture expelled liquid and gaseous water \((J_{\text{H}_2\text{O, outlet}}\text{ in mg/cm}^2\text{-h})\) while CO\(_2\) electrolysis was performed at a constant \(j\) value (25, 50, 100, or 200 mA/cm\(^2\)) for 25 min. The water trap was weighed immediately before and after electrolysis and I took the change in mass of the trap divided by the electrolysis time (25 min) and active area (4 cm\(^2\)) to correspond to \(J_{\text{H}_2\text{O, outlet}}\) (in mg/cm\(^2\)-h). I also measured the flux of water supplied to the cathode inlet (i.e., before the humidified CO\(_2\) enters the cell; \(J_{\text{H}_2\text{O, inlet}}\)) using the same technique after flowing 100 sccm of humidified CO\(_2\) through the cell for 25 min. The change in mass of the water trap was used to calculate \(J_{\text{H}_2\text{O, inlet}}\). I define the excess flux of water to the cathode \((J_{\text{H}_2\text{O, cathode}})\) according to Eq. 4.1:
Using this water-trap method for measuring water flux across an MEA in a zero-gap CO\textsubscript{2} electrolyzer, I quantified $J_{H2O,\text{cathode}}$ for reactors containing 55-μm thick HWUMs and LWUMs at each $j$ value of 25, 50, 100, or 200 mA/cm\textsuperscript{2}. The HWUM yielded consistently positive $J_{H2O,\text{cathode}}$ values that increased with current density (Figure 4.2a). The experiments with the LWUM, however, yielded negative $J_{H2O,\text{cathode}}$ values from 25 to 100 mA/cm\textsuperscript{2}, but sharply increased to 11.8 mg/cm\textsuperscript{2}\cdot h at 200 mA/cm\textsuperscript{2}. These results show that LWUM can suppress $J_{H2O,\text{cathode}}$ at lower $j$, but promotes flooding at 200 mA/cm\textsuperscript{2}.

I also measured the CO\textsubscript{2}RR performance (i.e., $FE_{CO}$, $FE_{H2}$ and $E_{cell}$) of the MEA materials, and found that the choice of membrane (i.e., HWUM and LWUM) had minimal effects at $j \leq 100$ mA/cm\textsuperscript{2}. At higher current densities (200 mA/cm\textsuperscript{2}), however, the HWUM yielded an $FE_{CO}$ of $>80\%$ while the LWUM yielded a much lower $FE_{CO}$ of $\sim 50\%$ (Figure 4.2c). These differences correlate with higher $FE_{H2}$ values (15.2%) with the LWUM compared to the HWUM (<1%) (Figure 4.2d). Moreover, the $E_{cell}$ values were consistently higher with the LWUM, particularly at the highest measured $j$ of 200 mA/cm\textsuperscript{2} (Figure 4.2b).
Figure 4.2 (a) The water flux to the cathode ($J_{\text{H}_2\text{O, cathode}}$) after applying current densities ($j$) of 25, 50, 100, and 200 mA/cm$^2$ for MEAs with 55-μm thick HWUM (green) and LWUM (orange). (b) Total cell voltage ($E_{\text{cell}}$), (c) CO faradaic efficiency ($FE_{\text{CO}}$), and (d) H$_2$ faradaic efficiency ($FE_{\text{H}_2}$) at applied current densities ($j$) of 25, 50, 100, and 200 mA/cm$^2$. Error bars represent the standard deviation for three independent experiments.

Given that membranes with high water uptake (i.e., >100%), suffer from poor mechanical strength due to swelling,$^{63,70}$ we sought to improve the performance of LWUM by decreasing the thickness of the membrane from 55 μm down to 40 and 20 μm. I quantified $J_{\text{H}_2\text{O, cathode}}$ as a function of LWUM thickness and found that $J_{\text{H}_2\text{O, cathode}}$ values measured at 200 mA/cm$^2$ decreased with decreasing thicknesses (Figure 4.3a). The best CO$_2$RR performance (i.e., highest $FE_{\text{CO}}$ and lowest $E_{\text{cell}}$) was observed for the thinnest membranes at 200 mA/cm$^2$ (Figure 3b-d).
Figure 4.3 Effect of LWUMs with different thicknesses (20, 40 and 55 μm) on the flux of water to the cathode ($J_{\text{H}_2\text{O, cathode}}$) and CO$_2$RR performance. (a) $J_{\text{H}_2\text{O, cathode}}$ after applying a current density ($j$) of 200 mA/cm$^2$. (b) CO faradaic efficiencies ($FE_{\text{CO}}$), (c) H$_2$ faradaic efficiencies ($FE_{\text{H}_2}$) and (d) total cell voltage ($E_{\text{cell}}$) at $j$ of 25, 50, 100, and 200 mA/cm$^2$. Error bars represent the standard deviation for three independent experiments.

For the last set of experiments, I determined how $J_{\text{H}_2\text{O, cathode}}$ and CO$_2$RR performance are affected by the hydrophobicity of the cathode. To illustrate these effects, I tested cathodes with lower PTFE loadings (6 wt% PTFE) and higher PTFE loadings (29 wt% PTFE) relative to the cathodes in the above experiments (17 wt% PTFE). The lowest value of $J_{\text{H}_2\text{O, cathode}}$ at 200 mA/cm$^2$ (1.5 mg/cm$^2$·h) was observed with the highest PTFE cathodes (Figure 4.4a). These high PTFE cathodes also yielded the best CO$_2$RR performance. The differences in cathode hydrophobicities did not affect CO$_2$RR at $j$ <50 mA/cm$^2$, but differences at 100 mA/cm$^2$ were statistically meaningful, and even more substantial at 200 mA/cm$^2$ (Figure 4b-d). A higher PTFE content at
the cathode (44 wt%) in tandem with the thinnest membrane (20 μm) did not lead to further improvements in the $E_{cell}$ and $FE_{CO}$.

Finally, we constructed a 1D model to support our empirical investigation of water flux to the cathode. This model was constructed in COMSOL (see Appendix A4 for details) and calculated the flux of H$_2$O by diffusion ($J_{DIFF}$), back-convection ($J_{BC}$), and electro-osmotic drag ($J_{EOD}$) from the anode/AEM interface to the cathode flow channel (See Figure B4.11 for details). We used this simple model to determine the influence of membrane thickness and cathode hydrophobicity on these individual fluxes (i.e., $J_{DIFF}$, $J_{BC}$ and $J_{EOD}$) that comprise the net flux of water across the cathode. Figure 4.4 Effect of cathode hydrophobicity (manipulated by varying the PTFE content from 6-29 wt%) on the flux of water to the cathode ($J_{H2O,cathode}$) and CO$_2$RR performance. (a) $J_{H2O,cathode}$ after applying a current density ($j$) of 200 mA/cm$^2$. (b) CO faradaic efficiencies ($FE_{CO}$), (c) H$_2$ faradaic efficiencies ($FE_{H2}$) and (d) total cell voltage ($E_{cell}$) at $j$ of 25, 50, 100, and 200 mA/cm$^2$. Error bars represent the standard deviation for three independent experiments.
AEM ($J_{\text{H}_2\text{O,net}}$). Our model found membrane thickness to have the most dramatic influence on the flux of water to the cathode (i.e., $J_{\text{BC}}$ increases for thinner membranes), supporting our empirical observation that thinner membranes can mitigate flooding in a zero-gap electrolyzer.

4.3 Discussions

In this work, I show that cathode flooding occurs in gas-fed CO$_2$ reactors at modest current densities ($j \leq 200$ mA/cm$^2$). Accumulation of water at the cathode is undesirable because it can block pores in the GDE and impede the transport of gaseous CO$_2$RR reagents and products to and away from the catalytic sites. These problems lead to poor electrolyzer performance because CO$_2$-limited active sites favour the parasitic HER that occurs at a lower onset potential than the desired CO$_2$RR. It is therefore important to manage the flux of water to the cathode in order to realize efficient CO$_2$ electrolysis in zero-gap reactors.

Inspired by fuel cell studies, I performed water mass balance experiments under controlled operating conditions (i.e., cell temperature, cell compression, flow rates and relative humidity of CO$_2$ and anolyte feedstock) to resolve how $J_{\text{H}_2\text{O,cathode}}$ is affected by $j$, AEM water uptake and thickness, and GDE hydrophobicity. Under steady-state operation, the water mass balance at the membrane/cathode interface is expressed in Eq. 4.2,

$$J_{\text{H}_2\text{O,outlet}} - J_{\text{H}_2\text{O,inlet}} = J_{\text{H}_2\text{O,net}} - J_{\text{H}_2\text{O,reduction}} \quad \text{(Eq. 4.2)}$$

where $J_{\text{H}_2\text{O,outlet}}$ is the water flux from the cathode outlet, $J_{\text{H}_2\text{O,inlet}}$ is the water flux to the cathode inlet, $J_{\text{H}_2\text{O,net}}$ is the net flux of water permeating from the anode through the membrane, and $J_{\text{H}_2\text{O,reduction}}$ is the water consumed by the reduction reactions at the cathode (Figure 4.5a).

Combining Equations 4.1 and 4.2 yields the relationship between the reported $J_{\text{H}_2\text{O,cathode}}$ values and $J_{\text{H}_2\text{O,net}}$ and $J_{\text{H}_2\text{O,reduction}}$:

$$J_{\text{H}_2\text{O,cathode}} = J_{\text{H}_2\text{O,net}} - J_{\text{H}_2\text{O,reduction}} \quad \text{(Eq. 4.3)}$$
I show that $J_{\text{H}_2\text{O},\text{reduction}}$ was effectively the same for each zero-gap configuration at the same $j$ (Tables A4.1 and A4.2); thus, I infer that $J_{\text{H}_2\text{O,cathode}}$ is directly correlated to $J_{\text{H}_2\text{O,net}}$ under the same operating conditions.

**Figure 4.5** (a) Illustration of the water mass balance at the AEM/cathode interface that accounts for water from the humidified cathode inlet CO$_2$ stream ($J_{\text{H}_2\text{O,inlet}}$); expelled at the cathode outlet ($J_{\text{H}_2\text{O,outlet}}$); consumed from CO$_2$RR ($J_{\text{H}_2\text{O,reduction}}$); and from the anode that permeated through the membrane ($J_{\text{H}_2\text{O,net}}$). (b) $J_{\text{H}_2\text{O,net}}$ is the sum of diffusion ($J_{\text{DIFF}}$), electro-osmotic drag ($J_{\text{EOD}}$), and back convection ($J_{\text{BC}}$) processes.

The $J_{\text{H}_2\text{O,net}}$ in zero-gap reactors can be described by three key processes: i) diffusion ($J_{\text{DIFF}}$); ii) electro-osmotic drag ($J_{\text{EOD}}$); and iii) back convection ($J_{\text{BC}}$) (Figure 4.5b).

$$J_{\text{H}_2\text{O,net}} = J_{\text{DIFF}} - J_{\text{EOD}} - J_{\text{BC}} \quad \text{(Eq. 4.4)}$$

For our experiments, $J_{\text{DIFF}}$ describes water transport from the anode to the cathode driven by the water concentration gradient between the aqueous anode and the gas-fed cathode. $J_{\text{EOD}}$ represents water transported from the cathode to the anode due to the flow of solvated anions, and $J_{\text{BC}}$ describes water repelled by the hydrophobic cathode towards the anode (as well as differences in water permeation through the membranes). The individual contributions of $J_{\text{H}_2\text{O,net}}$ (i.e., $J_{\text{DIFF}}$, $J_{\text{EOD}}$, $J_{\text{BC}}$) are functions of the water transport properties of the MEA components (i.e., gas
diffusion electrodes and the membrane). It is for this reason that we designed AEMs with varying water uptakes and thicknesses, and cathodes with varying hydrophobicities.

Our studies show that AEM water uptake has a profound effect on $J_{\text{H}_2\text{O,cathode}}$ and, in turn, CO$_2$RR performance, particularly at high current densities. At 200 mA/cm$^2$, LWUM yields a ~30% lower $FECO$ while also requiring an additional 350 mV to drive CO$_2$ electrolysis compared to HWUM (Figure 4.2b, 3c). We assert that these differences are due to cathode flooding, which is more significant for LWUM than HWUM at 200 mA/cm$^2$ (Figure 4.2a). The shift in product selectivity from CO to H$_2$ for LWUM at 200 mA/cm$^2$ (Figure 4.2c, 4.2d) is also consistent with cathode flooding, where a high concentration of H$_2$O would favour HER over CO2RR. From these experiments, I define that cathode flooding occurs when the flux of water delivered from the anode exceeds the required amount of water for CO2RR by more than 5 mg/cm$^2$·h (i.e., $J_{\text{H}_2\text{O,net}}$ - $J_{\text{H}_2\text{O,reduction}} = J_{\text{H}_2\text{O,cathode}} > 5$ mg/cm$^2$·h). Cathode flooding occurs with LWUM, presumably because the electroosmotic drag coefficient of the membrane ($\eta$) is reduced (i.e., lower JEOD) for membranes with lower water uptakes.

By reducing the thickness of the LWUM, I found that the CO$_2$RR performance can be significantly improved (i.e., a 30% increase in $FECO$ and a 450 mV decrease in $E_{\text{cell}}$). Thinner membranes seemingly act to mitigate flooding (Figure 4.3a, 4.3c), presumably because of a higher back convection flux ($J_{\text{BC}}$). This assertion is aligned with predictions from our 1D numerical model of the MEA (see Appendix A for more details). Fuel cell studies have also shown that thinner membranes decrease the water flux from the anode to the cathode. While multiphysics modelling of a gas-fed CO$_2$ electrolyzer predicts that membrane thickness is not expected to impact $FECO$, our empirical data show that decreasing the membrane thickness does indeed improve $FECO$ at high current densities (200 mA/cm$^2$). Decreasing the thickness of an LWUM could be a more
desirable design strategy to mitigate cathode flooding than using high water uptake membranes because HWUMs exhibit poor mechanical stability.\(^7\)

Finally, increasing the cathode hydrophobicity also improved CO\(_2\)RR performance by suppressing cathode flooding, evidenced by the lower \(J_{\text{H}_2\text{O,cathode}}\) (Figure 4.4a) and minimal \(FE_{\text{H}_2}\) (Figure 4.4c). I observed that the most hydrophobic cathode (29 wt% PTFE) yielded statistically meaningful improvements in CO\(_2\)RR performance (Figure 4.4b, 4.4d) at \(j \geq 100\) mA/cm\(^2\). I assert that the cathode with 29 wt% PTFE is able to alleviate cathode flooding because the back convection flux (\(J_{\text{BC}}\)) is higher for more hydrophobic GDEs.\(^{100}\) Our results again align with fuel cell literature that shows hydrophobic cathodes decrease the water flux from the anode to the cathode.\(^{44}\) I note that catalyst layer morphology and ECSA were not significantly influenced by PTFE content (see Figures A4.7 through A4.10 for details).

### 4.3 Conclusions

Efficient electrocatalytic reduction of CO\(_2\) in a zero-gap reactor requires a proton source, which is usually water. Providing too little water (which starves the electrode of a reagent) or too much water (which prevents CO\(_2\) from reaching the catalyst) to the cathode compromises the energy efficiency and selectivity for CO\(_2\)RR products. Our investigations provide the first empirical evidence that shows the factors affecting the flux of water to the cathode (\(J_{\text{H}_2\text{O,cathode}}\)). Moreover, water mass balance experiments demonstrate that cathode flooding is an issue at \(j \leq 200\) mA/cm\(^2\), which is much less than values as high as 750 mA/cm\(^2\) that have been previously predicted.\(^9\) We also show that using thin, low water uptake membranes with hydrophobic cathodes suppresses flooding, even at high current densities (200 mA/cm\(^2\)). The water management strategies that we present in this study aim to inform the design of membranes and GDEs to optimize water management in zero-gap CO\(_2\) electrolyzers.
4.4 Experimental methods

4.4.1 Materials

Reagents were used as received unless otherwise specified. Styrene (99%, stabilized with TBC) and 1,2,4,5-tetramethylimidazole (>98%) were purchased from TCI America. 4-Vinylbenzyl chloride (90%, stabilized with TBC), 2,2′-azobis(2-methylpropionitrile) (98%), toluene (ACS grade), methanol (ACS grade), chlorobenzene (ACS grade), and diethyl ether (ACS grade) were obtained from Sigma Aldrich. Ethanol (100%, ACS grade) was purchased from Greenfield Global Inc. PTFE dispersion (PTFE DISP 30, 60% in non-ionic surfactant), carbon paper (Sigracet 39BC), and PTFE gaskets (0.01”) were purchased from Fuel Cell Store. Nickel foam gas diffusion layer material was purchased from MTI (EQ-BCNF-16m). Sustainion X37-50 Grade RT anion exchange membrane was purchased from Dioxide Materials. The reference electrodes used for ECSA measurements were Ag/Ag Cl (3M NaCl) purchased from Bioanalytical Systems Inc. Styrene (99%, stabilized with TBC) and 1,2,4,5-tetramethylimidazole (>98%) were purchased from TCI America. 4-Vinylbenzyl chloride (90%, stabilized with TBC), 2,2′-azobis(2-methylpropionitrile) (98%), toluene (ACS grade), methanol (ACS grade), chlorobenzene (ACS grade), and diethyl ether (ACS grade) were obtained from Sigma Aldrich. $^1$H NMR spectra were collected on a 400 MHz Bruker Avance 400inv spectrometer with TopSpin 2.1 software at ambient temperature.

4.4.2 Electrode preparation

We prepared the Ag cathode catalyst inks by sonicating 0.1575 g of silver nanopowder, 7.5 mL of deionized water, 7.5 mL of isopropyl alcohol, and 0.12, 0.42, or 0.84 mL of PTFE DISP 30 (60 wt% diluted to 5 wt%). We then coated the catalyst inks on eight 4-cm$^2$ carbon papers using an automated ultrasonic spray coater (ExactaCoat, SONO-TEK) equipped with 1-Watt ultrasonic
nozzle operated at a frequency of 120 Hz. The catalyst ink delivery rate during spray coating was fixed at 0.6 mL/min. Each electrode was prepared to have a Ag mass loading of ~1 mg/cm² after spray coating, which was confirmed by X-ray fluorescence spectroscopy (XRF) using a calibration between Ag mass loading and corresponding XRF values. We then prepared anodes by cutting nickel foam (pressed at 100 psi before cutting) to size (2 × 2 cm²). Nickel foam was cleaned using a standard cleaning procedure of sonication in acetone and then deionized water.

4.4.3 Ionomer synthesis

Materials and reagents: Reactions carried out under nitrogen utilized standard Schlenk line and inert atmosphere techniques. ¹H NMR spectra were collected on a 400 MHz Bruker Avance 400inv spectrometer with TopSpin 2.1 software at ambient temperature. Samples for NMR analysis were prepared by dissolving ~10 mg of dried solid with the selected solvent and transferring the sample into a 5 mm borosilicate NMR tube. Compounds A₁ and B₁ were dissolved in acetone-d₆ while A₂ and B₂ were dissolved in methanol-d₄. Chemical shifts reported in ppm were calibrated against the residual solvent signals δ 2.09 for acetone-d₆ and δ 3.34 for methanol-d₄.

Preparation of A₁: Inhibitor free styrene (20.60 g, 19.78 mmol) and 4-vinylbenzyl chloride (4-VBC) (29.62 g, 19.41 mmol) were prepared by washing the reagents in a 250 ml separatory funnel three times with 100 ml of 0.5 M KOH until the aqueous phase became colourless, indicating the complete removal of the catechol inhibitor. The mixture was further washed three times with 50 ml of distilled water and once with 100 ml NaCl (24%, w/w) before drying over anhydrous MgSO₄ for 2 hours. Styrene and 4-VBC were filtered and transferred to a 250 ml round-bottom flask along with 40 ml of chlorobenzene. The flask was purged for 30 minutes with N₂ before the initiator AIBN (0.540 g, 0.00329 mol) dissolved in 10 ml of
chlorobenzene was added using a syringe. The reaction mixture was stirred and heated to 65 °C with an oil bath and the polymerization proceeded for 96 h under a constant N₂ flow. The resulting product was precipitated in large access of MeOH (2 L) and 45.89 g (90%) of a white solid was collected and dried under vacuum. Yields of >90% were routinely achieved for batch sizes up to 60 g. ¹H NMR (400 MHz, acetone-­d₆, ppm) δ: 7.39-6.66 (m, 9H), 4.64 (m, 2H), 1.89-1.58 (m, 6H).

**Preparation of B1:** The procedures described for A1 were repeated to make B1, adjusting only the relative amounts of reagents used. Styrene (45.40 g, 43.59 mmol) and 4-VBC (23.45 g, 15.37 mmol) were washed free of inhibitor and combined with AIBN (0.550 g, 3.36 mmol) in chlorobenzene (~50 ml) and the reaction was left to proceed for 96 h under constant N₂ flow. The product was isolated by adding the viscous reaction solution dropwise to 2 L of MeOH under constant stirring and the resulting precipitate was collected by vacuum filtration. The brittle white solid [65.12 g (94%)] was collected and dried under vacuum.¹H NMR (400 MHz, acetone-­d₆, ppm) δ: 7.40-6.67 (m, 19H), 4.63 (m, 2H), 1.92-1.51 (m, 12H).

**Preparation of A2:** 11.520 g of A1 was added to 2.583 g (0.020.64 mmol) of 1,2,4,5-tetramethylimidazole (TMIM) in a 100 ml round-bottom flask with 16.242 g and 10.962 g of anhydrous solvents EtOH and toluene respectively. The flask was purged for 30 minutes with N₂ and heated to 78 °C over 2 hours under constant stirring until the contents dissolved completely and the solution turned clear. The temperature was reduced to 55 °C and the reaction was left to proceed for 72 hours before it was removed from the heat source. Once cooled to room temperature, the viscous, pale-yellow solution was transferred to a polypropylene bottle for storage. Rinsings from the reaction flask were precipitated with diethyl ether and dried before ¹H NMR analysis, which indicated approximately 50% substitution of the benzylic chloride groups,
based on the integration of distinct substituted and unsubstituted benzylic proton signals. Unreacted TMIM was observed as sharp singlets at similar chemical shifts as the broad peaks of TMIM groups incorporated into the polymer. $^1$H NMR (400 MHz, methanol-$d_4$, ppm) $\delta$: 7.05-6.53 (m, 9H), 5.22 (m, 1H), 4.52 (m, 1H), 3.68 (m, 3H), 2.55 (m, 3H), 2.23 (m, 3H), 2.06-1.48 (m, 15H).

**Preparation of B2:** The procedures described for A2 were repeated to synthesize B2. 13.395 g of B1 was reacted with 5.114 g (41.18 mmol) of TMIM in a mixture of anhydrous EtOH (22.170 g) and toluene (13.592 g) for 72 hours. The resulting viscous solution was transferred to a separate container and the residual material in the reaction flask was precipitated, dried, and a $^1$H NMR spectrum was collected. $^1$H NMR (400 MHz, methanol-$d_4$, ppm) $\delta$: 7.06-6.50 (m, 9H), 5.25 (m, 1H), 4.56 (m, 1H), 3.70 (m, 3H), 2.55 (m, 3H), 2.28 (m, 3H), 2.08 (m, 3H), 1.45 (m, 6H).

4.4.4 Membrane fabrication

The membranes were prepared by directly casting each reaction solution onto borosilicate substrates by doctor blade coating. Borosilicate substrates (8” x 4” x $\frac{1}{8}$”, McMaster-Carr) were rinsed with ultrapure water, dried in air, then cleaned with ethanol immediately prior to casting the ionomer dispersion. We placed the substrate onto the coating table (MSK-AFA-II, MTI), and set the doctor blade spacing depending on the desired thickness of the membrane (Table S1). The ionomer dispersion was poured (~8 mL) onto the substrate within ~5 mm of the doctor blade, and the blade was actuated at a speed of 18 mm/s. The membrane was immediately placed in an oven preheated at a targeted temperature and duration depending on the membrane (Table 4.1) to remove the solvent and improve the mechanical properties of the membrane. Membrane thickness was measured upon removal from the oven using an inside micrometre accurate to $\pm 1$ μm (293-344-30, Mitutuyo). The membrane was subsequently delaminated from the borosilicate substrate.
by immersing in 1.0 M KOH solution (for >20 min), which caused the membrane to swell, soften, and separate from the rigid substrate. The membrane films were stored in 1.0 M KOH for at least 24 hours prior to testing in a reactor to exchange the chloride counter ions with hydroxide. We stored completed membranes in 1.0 M KCl after casting for long-term storage and ex-situ characterization.

### 4.4.5 Membrane characterization

**Ion exchange capacity**

I soaked four samples of each membrane (in Cl$^-$ form) in individual containers containing 30 g of 1 M KNO$_3$ ($m_{\text{KNO}_3}$) for 24 h to exchange chloride counter ions to nitrate. The concentration of chloride ([Cl$^-$] in ppm) released in the solution was determined by using an ion-selective electrode (Cl$^-$ ISE, Cole Parmer on Accumet AE 150 pH meter, Fisher Scientific). The membranes were then soaked in 1.0 M KCl for 24 h to exchange the nitrate counter ions back to chloride. I thoroughly washed each sample with DI water before soaking in DI water for an additional 24 h. The DI water was replenished three times over this period. The membrane samples were then dried at room temperature for 24 h, and the mass of the dried membranes ($m_d$ in g) were recorded using an analytical balance. I calculated the ion exchange capacity (IEC) of the membranes using the following expression, where $M_{\text{Cl}}$ is the molar mass of chloride (g/mol).

$$ IEC = \frac{[\text{Cl}^-] \cdot m_{\text{KNO}_3}}{M_{\text{Cl}} \cdot m_d} \quad \text{(Eq. 4.5)} $$

**Water uptake**

Four samples of each membrane were soaked in 1.0 M KCl at room temperature for 24 h. The membranes were thoroughly washed with DI water to remove excess KCl from the membrane and soaked in DI water for an additional 24 h at room temperature. The water was replaced with fresh DI water three times over this period. The membrane samples were then removed from the
water, surface water was gently removed with a paper tissue, and the mass of each hydrated membrane \( (m_h \text{ in g}) \) was immediately measured using an analytical balance. The hydrated membranes were then dried at room temperature for 24 h, and the mass of the dried membranes \( (m_d \text{ in g}) \) were recorded. The water uptake \((WU)\) values were calculated as follows:

\[
WU \% = \frac{100\% \times (m_h - m_d)}{m_d} \quad (\text{Eq. 4.6})
\]

4.4.6 Electrochemical measurements and product analysis

The electrolyzer consists of end plates, flow field plates, gaskets, and the MEA. We used a fresh Ag spray-coated cathode, Nickel foam anode, and AEM for each electrolysis test. Two stainless steel (SS 316) end plates served as inlets and outlets for the reactants and products. A titanium (grade 2) cathode and stainless steel (SS 316) anode flow field plates were machined with serpentine channels that are 1.5 mm wide and 1.5 mm deep with 1 mm wide landings. The flow plates sandwiched the MEA (geometric active area = 2 \( \times \) 2 cm\(^2\)) and served to facilitate the delivery of reactants and products to and away from the reactive interface. The MEAs comprised a silver-coated cathode GDE (2 \( \times \) 2 cm\(^2\)), an AEM (3 \( \times \) 3 cm\(^2\)), and a nickel foam anode (2 \( \times \) 2 cm\(^2\)). The cathode and AEM components of the MEAs were manipulated as described below, and the anodes were unchanged for all experiments. The entire assembly was compressed by stainless steel end plates using eight, evenly spaced fasteners. A constant torque of 3 N\(\cdot\)m was applied to each fastener to provide a fixed compression to the MEA and to minimize interfacial contact resistances. The gaseous CO\(_2\) was humidified by flowing the inlet stream through a water bath (heated at 50 °C) at 100 sccm by a CO\(_2\) mass flow controller (GFC17, AALBORG) before entering the cathode; the anode was supplied with 1.0 M KOH at 15 mL/min using a peristaltic pump (43205K11, McMaster-Carr). Chronopotentiometry experiments were performed by applying a constant \( j \) of 25, 50, 100, or 200 mA/cm\(^2\) to the entire cell for 25 min using a power supply (2280S-32-6,
Keithley). A Mandel gas chromatograph (SRI-8610C) was used to analyze the cathode outlet gas. Complete CO\textsubscript{2} electrolysis performance characterization took place over 2 hours of sustained electrolysis (i.e., 25 minutes each at 25, 50, 100, and 200 mA/cm\textsuperscript{2}).

Current density is expressed as the total current divided by the geometric surface area of the electrodes (4 cm\textsuperscript{2}). The faradaic efficiency \((FE)\) of a gaseous product \(k\) was determined in accordance with this equation:

\[
FE = \frac{n_k F x_k F_m}{I} \quad \text{(Eq. 4.7)}
\]

where \(n_k\) is the number of electrons exchanged, \(F\) is Faraday’s constant \((F = 96,485 \text{ C/mol})\), \(x_k\) 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 \(F_m = p F_v / R T\), 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.

\subsection*{4.4.7 Electrochemical impedance spectroscopy measurements}

Electrochemical impedance measurements (EIS) were conducted in the flow cell setup using conditions selected to closely-mirror CO\textsubscript{2} electrolysis experiments. These measurements were performed using a CH instruments potentiostat (660D) over a frequency range of 0.03 Hz to 1kHz, sinusoidal amplitude of 5 mV, and an operating voltage of -1.75 V. We used the following conditions: i) humidified CO\textsubscript{2} gas (85\% relative humidity, see above) was fed to the cathode at a rate of 100 sccm; ii) 1 M KOH was flowed through the anode flow plate at a rate of 15 mL/min. A Ni foam anode and a 17 wt \% PTFE GDE cathode were used.
4.4.8 Electrochemical surface area measurements

The double-layer capacitance ($C_{dl}$) of the prepared cathodes was determined ex-situ by measuring the capacitive charging current at different scan rates in a non-Faradaic potential window using a conventional 3-electrode electrochemical setup, with the sample immersed in 1 M H$_2$SO$_4$. A $1 \times 1$ cm$^2$ square of the prepared cathode was used as a working electrode with a Pt wire counter and a Ag/AgCl reference. Cyclic voltammograms were collected at scan rates of 25, 50, 75, 100, 150, and 200 mV/s between 0.2 V and 0.3 V vs Ag/AgCl and the capacitive current was measured at 0.25 V on the third scan. The slope of the straight line resulting from a plot of current versus scan rate yielded the double-layer capacitance. Each $1 \times 1$ cm$^2$ sample was tested three times, and three $1 \times 1$ cm$^2$ squares were prepared for each cathode; $C_{dl}$ values were reported as the mean of triplicate measurements.

Table 4.1 Doctor blade spacing and annealing conditions to fabricate ionomer solutions into membranes.

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Doctor blade spacing$^a$</th>
<th>Annealing conditions</th>
<th>Thickness</th>
</tr>
</thead>
<tbody>
<tr>
<td>(m:n)</td>
<td>in</td>
<td>°C/mmHg</td>
<td>μm</td>
</tr>
<tr>
<td>LWUM (3:1)</td>
<td>0.010</td>
<td>70/500</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td>0.028</td>
<td>70/500</td>
<td>40</td>
</tr>
<tr>
<td></td>
<td>0.035</td>
<td>70/500</td>
<td>55</td>
</tr>
<tr>
<td>HWUM (1:1)</td>
<td>0.030</td>
<td>165/ambient</td>
<td>55</td>
</tr>
</tbody>
</table>

$^a$measured from the surface of the glass substrate
Scheme 4.1 Synthesis of intermediate copolymer poly(4-vinylbenzyl chloride-co-styrene), and anion exchange polymer poly[(4-vinylbenzyl-1,2,4,5-tetramethylimidazolium chloride)-co-styrene]

Figure 4.6 $^1$H NMR of A1 in acetone-d$_6$ at 400 MHz and ambient temperature.
Figure 4.7 $^1$H NMR of B1 in acetone-$d_6$ at 400 MHz and ambient temperature.
Figure 4.8 $^1$H NMR of A2 in acetone-$d_6$ at 400 MHz and ambient temperature.
Figure 4.9 $^1$H NMR of B2 in acetone-d$_6$ at 400 MHz and ambient temperature.
Chapter 5: Conclusions and future directions

5.1 Conclusions

This thesis highlights the judicious designs of anion exchange membranes for achieving efficient CO$_2$ reduction reaction (CO$_2$RR) to CO in gas-fed electrolyzers. Chapter 3 demonstrates the link between membrane functional groups and CO$_2$RR selectivity, voltage, and stability. To establish this relationship, two membranes functionalized with imidazolium or a trimethylamine groups were successfully synthesized and fabricated with the same thickness, polymer backbone, and ionic group concentration. The CO$_2$RR performance to CO is improved with the use of an imidazolium group because this membrane exhibits a low water uptake, which is an important property for minimizing undesired salt formation at the cathode. An imidazolium group was also shown to be more stable than a trimethylamine at high current densities.

Chapter 4 shows different membrane and cathode design strategies to optimize water management in CO$_2$ electrolyzers. This chapter presents a method for quantifying water flux to the cathode and provides empirical evidence that AEM-based CO$_2$ electrolyzers are susceptible to flooding at current densities lower than theoretically predicted. Chapter 4 shows that the water uptake and thickness of the membrane, and hydrophobicities of the cathode can be used to tune CO$_2$RR selectivity and voltage. In this study, the optimal water management strategy is a thin, low water uptake membrane paired with a hydrophobic cathode.

5.2 Future directions

Chapter 3 examines the CO$_2$-to-CO performance of AEMs containing imidazolium or trimethylamine functional groups, but both membranes resulted in limited CO selectivities at high current densities (100 mA/cm$^2$). We can establish new structure-activity relationships at even
higher current densities by extending the experiments designed in Chapter 3 to include cation chemistries with improved alkali stability, such as completely substituted imidazolium groups or quaternary ammonium cations with long $n$-alkyl groups.\textsuperscript{85,102–104} Future work should use NMR characterization of the membranes or expelled cathode liquid after CO$_2$ electrolysis experiments to confirm stability of cation groups at higher current densities.

Our experimental set-up used in Chapter 4 for quantifying the amount of water flux to the cathode can be improved in many ways. In our current setup, the liquid expelled from the cathode outlet is collected using a desiccating agent but can be replaced with a differential pressure gauge. This previous setup is also problematic because liquids exiting the cathode cannot be further analyzed for CO$_2$RR liquid products or presence of ions (e.g. K$^+$). Using a cold trap to capture the cathode drain for further analyses with ICP-MS can provide clues on how water and salt crossover impact product distribution at the cathode. Dry CO$_2$ gas should also be used instead of a humidified feed to provide a more accurate representation of water flux from the anode to the cathode.

CO$_2$ electrolysis experiments in this thesis were performed at short periods of time (2 hours), but future work should focus on extending cell testing to better understand how water management at the cathode impacts the stability of the system. Electrochemical experiments in this thesis did not account for gas (e.g., CO, CO$_2$, and H$_2$) permeation through the AEM, but future work should characterize this property as well.

This thesis shows that the membrane and cathodic gas diffusion electrode parameters can optimize salt and water crossover from the anode to the cathode. A nickel foam anode was kept unchanged throughout the experiments in this thesis, but other anode designs with tunable parameters (e.g. hydrophilicity, porosity, and electrode composition) can be beneficial in modulating ion and water transport mechanisms. It has been reported in fuel cells that high PTFE
coating (up to 40 wt%) on the anodic gas diffusion layer and microporous layers minimize water crossover from the anode to the cathode. Modulating the carbon and ionomer compositions at the anode has also shown to improve the balance of water in fuel cells. Future work should focus on systematically engineering the anode and providing design principles that increase CO$_2$RR activity at the cathode.
References


(58) Cooper, K. Characterizing Through-Plane and In-Plane Ionic Conductivity of Polymer Electrolyte Membranes. ECS Trans. 2011, 41 (1), 1371–1380.


Appendices

Appendix A: Chapter 3 supplementary material

Table A3.1. X-ray fluorescence (XRF) measurements and corresponding Ag cathode catalyst loadings measured by gravimetric analysis.

<table>
<thead>
<tr>
<th>Cathode sample #</th>
<th>XRF count (cps/μA)</th>
<th>Ag catalyst loading (mg/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>62.84</td>
<td>1.1</td>
</tr>
<tr>
<td>2</td>
<td>64.31</td>
<td>1.0</td>
</tr>
<tr>
<td>3</td>
<td>63.70</td>
<td>1.0</td>
</tr>
<tr>
<td>4</td>
<td>64.91</td>
<td>1.0</td>
</tr>
</tbody>
</table>

Figure A3.1. Salt precipitates formed on cathode flow field plates of CO₂ electrolyzers containing (a) PSMIM and (b) PSTMA after applied current density of 100 mA/cm².
Appendix B: Chapter 4 supplementary materials

Figure B4.1 Water uptake (WU) and ion exchange capacity (IEC) values for membranes made from 1:1 and 3:1 (m:n) ionomers, defined as high water uptake membranes (HWUM) and low water uptake membranes (LWUM), respectively. The m:n corresponds to the ratio of styrene (m) and the imidazolium-containing 4-vinylbenzyl (n).
Figure B4.2 X-ray fluorescence (XRF) measurements of Ag cathodes with PTFE contents of 6, 17, and 29 wt% PTFE taken before electrolysis.

Figure B4.3 Sample chronopotentiometry data at applied currents of 0.1, 0.2, 0.4, and 0.8 A, (i.e. 25, 50, 100, and 200 mA/cm²) held for 25 min each. Cell potentials ($E_{\text{cell}}$) in this study were taken as the average over a 200 s window within initiation of gas chromatography (GC) analysis, indicated by the light grey region. The data shown correspond to a reactor containing Ag cathodes with 17 wt% and 20 μm LWUM.
Figure B4.4 Vertical cell configuration used to measure $J_{\text{H}_2\text{O, outlet}}$ and $J_{\text{H}_2\text{O, inlet}}$ for the comparison of HWUM and LWUM at applied current densities ($j$) of 25, 50, 100 and 200 mA/cm$^2$. Each electrolysis experiment held $j$ for 25 min and used the same cathode (1 mg/cm$^2$ of Ag with 17 wt% of PTFE on carbon paper).

Figure B4.5 Horizontal cell configuration used to measure $J_{\text{H}_2\text{O, outlet}}$ and $J_{\text{H}_2\text{O, inlet}}$ for the comparison of different LWUM thicknesses (20, 40, and 55 μm) and cathode hydrophobicities (6, 17, 29 wt% PTFE). Each electrolysis experiment applied a current density of 200 mA/cm$^2$ for 25 min. The horizontal configuration enabled detectable amounts of liquid to be collected at the cathode in a shorter period of time.
Determination of the $J_{\text{H}_2\text{O}, \text{reduction}}$

The Faradaic efficiencies reported in this study were used to determine $J_{\text{H}_2\text{O, reduction}}$ (in mg/cm$^2 \cdot$ h), which is a function of the molar ratio between the consumed water and the number of electrons transferred ($n$ in mol$_{\text{H}_2\text{O}}$/mol e$^-$), the total current density ($I$ in A/cm$^2$), Faradaic efficiency for product $k$ ($FE_k$ in %), molar mass of water ($M_{\text{H}_2\text{O}}$ in g/mol) and Faraday’s constant (96485 C/mol).

$$J_{\text{H}_2\text{O, reduction}} = \sum_k \frac{3600 \cdot 1000 \cdot n \cdot FE_k \cdot M_{\text{H}_2\text{O}}}{F}$$

(Eq. A4.1)

**Table B4.1** Reaction variables and water fluxes for HWUM and LWUM collected after electrolysis experiments at applied current densities ($j$) of 25, 50, 100, and 200 mA/cm in a CO$_2$ electrolyzer in the vertical configuration. Each electrolysis experiment held $j$ for 25 min.

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Reaction variables</th>
<th>Flux of water</th>
<th></th>
<th></th>
<th>J$_{\text{H}_2\text{O, reduction}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Current density</td>
<td>Membrane thickness</td>
<td>PTFE cathode content</td>
<td>$J_{\text{H}_2\text{O outlet}}$</td>
<td>$J_{\text{H}_2\text{O inlet}}$</td>
</tr>
<tr>
<td></td>
<td>mA/cm$^2$</td>
<td>µm</td>
<td>%</td>
<td>mg/cm$^2 \cdot$ h</td>
<td>mg/cm$^2 \cdot$ h</td>
</tr>
<tr>
<td>HWUM</td>
<td>25</td>
<td>55</td>
<td>17%</td>
<td>29.2</td>
<td>28.3</td>
</tr>
<tr>
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<td>50</td>
<td>55</td>
<td>17%</td>
<td>30.7</td>
<td>28.3</td>
</tr>
<tr>
<td>HWUM</td>
<td>100</td>
<td>55</td>
<td>17%</td>
<td>31.9</td>
<td>28.3</td>
</tr>
<tr>
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<td>200</td>
<td>55</td>
<td>17%</td>
<td>33.4</td>
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<tr>
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<td>17%</td>
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<td>28.3</td>
</tr>
<tr>
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<td>55</td>
<td>17%</td>
<td>20.9</td>
<td>28.3</td>
</tr>
<tr>
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<td>17%</td>
<td>23.8</td>
<td>28.3</td>
</tr>
<tr>
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<td>55</td>
<td>17%</td>
<td>40.0</td>
<td>28.3</td>
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Table B4.2 Reaction variables and water fluxes for LWUM at various thicknesses and PTFE cathode contents collected at an applied current density (j) of 200 mA/cm² in a CO₂ electrolyzer in the horizontal configuration. Each electrolysis experiment held j for 25 min.

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Current density</th>
<th>Membrane thickness</th>
<th>PTFE cathode content (%)</th>
<th>Flux of water</th>
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</thead>
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<tr>
<td></td>
<td>mA/cm²</td>
<td>μm</td>
<td></td>
<td>J_{H₂O, outlet}</td>
</tr>
<tr>
<td>LWUM</td>
<td>200</td>
<td>20</td>
<td>17%</td>
<td>41.0</td>
</tr>
<tr>
<td>LWUM</td>
<td>200</td>
<td>40</td>
<td>17%</td>
<td>50.8</td>
</tr>
<tr>
<td>LWUM</td>
<td>200</td>
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<td>17%</td>
<td>77.3</td>
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<tr>
<td>LWUM</td>
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<td>66.7</td>
</tr>
<tr>
<td>LWUM</td>
<td>200</td>
<td>40</td>
<td>29%</td>
<td>41.6</td>
</tr>
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</table>

Impedance spectroscopy

We performed in situ electrochemical impedance spectroscopy (EIS) measurements to rule out differences in ionic conductivity between HWUM and LWUM as the reason for CO₂RR performance differences between these membranes (Figure B4.6). At 200 mA/cm², the measured 0.5 Ω⋅cm² ohmic resistance difference should account for only a ~100 mV gain in the $E_{cell}$ (of the 350 mV observed) for LWUM. We thereby point to cathode flooding as the primary reason for differences in CO₂RR performance rather than this modest change in membrane conductivity.
**Figure B4.6** In situ electrochemical impedance spectroscopy measurements at an applied cell voltage of -1.75 V over a frequency range of 0.03 Hz to 10 kHz, showing the reduced semicircle diameter for HWUM compared to LWUM. Inset shows a magnified AC impedance spectra at the high frequency range (HFR), showing the lower ionic transport resistance at the HFR for HWUM compared to LWUM.

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**Gas diffusion electrode characterization**

We confirmed that the differences in CO$_2$RR performance between cathodes were not related to differences in surface area or morphology by collecting double-layer capacitance ($C_{dl}$) measurements (Figures B4.7 and B4.8), scanning electron microscopy (SEM) micrographs (Figures B4.9 and B4.10), and energy-dispersive X-ray (EDX) maps of each cathode. The $C_{dl}$ values (directly proportional to electrochemically active surface area) for all three GDE designs were effectively identical at ~2 μF/cm$^2$ (Figure B4.8). SEM images of the cathodes revealed no meaningful differences in morphology, but samples with higher PTFE content showed a higher distribution of PTFE than Ag at the surface (Figure B4.10). This trend is consistent with energy-dispersive X-ray (EDX) elemental maps of the GDEs that confirm an increase in fluorine and a
decrease in Ag present at the surface for more hydrophobic cathodes (Figure B4.10). Focused ion beam-SEM (FIB-SEM) micrographs of the GDEs also showed that a higher PTFE content at the cathode led to thicker catalyst layers (Figure B4.9). Higher PTFE content at the cathode surface is known to decrease porosity and increase hydrophobicity of the GDE microporous layer, thereby increasing the resistance for water transport from the anode to the cathode.\textsuperscript{106,107} An increased catalyst layer thickness is purported to elongate hydrophobic channels for improved transport of reactant gases to the catalytic sites.\textsuperscript{108} These results therefore support our hypothesis that increasing the PTFE content in the cathode catalyst layer leads to an increase in CO$_2$RR performance because flooding is mitigated and reactant CO$_2$ transport is improved.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure_B4_7.png}
\caption{Electrochemical surface area measurements for a 29 wt\% PTFE cathode yielded (a) cyclic voltammograms at different scan rates in a non-Faradaic potential window collected in 1M H$_2$SO$_4$ [dashed line indicates the potential (0.25116 V vs Ag/AgCl) at which the capacitive current was measured for all scan rates] and (a) a linear plot of capacitive current versus scan rate.}
\end{figure}
Figure B4.8 Double layer capacitance ($C_{dl}$) of cathodes with PTFE loadings of 6 wt%, 17 wt% and 29 wt%, showing no significant change in the $C_{dl}$ of cathodes used in this study.
Figure B4.9 Scanning electron microscopy (SEM) images of the surface (left) and cross-section (right) for cathodic GDEs comprising a microporous layer (MPL) coated with Ag nanoparticles (AgNPs) and a) 6 wt% b) 17 wt% or c) 29 wt% PTFE.
Figure B4.10 SEM images (left) and energy-dispersive X-ray (EDX) elemental maps (right) of the cathode surface for GDEs coated with AgNPs and a) 6 wt% b) 17 wt% or c) 29 wt% PTFE.
Analysis of fluxes using 1D model

We constructed a 1D model in COMSOL Multiphysics 5.3a to determine the effect of changing AEM thickness and PTFE loading on the diffusive \((J_{DIFF})\), electro-osmotic \((J_{EO})\), and back convective \((J_{BC})\) fluxes.

The physical scope of the 1D model extends from the anode/AEM interface to the cathode gas channel (Figure B4.11). A boundary condition of 100% water \((n_{H2O,AN} = 1)\) was assumed for the anode channel AEM interface. The boundary conditions at the cathode gas diffusion layer (GDL)/gas channel interface were set such that the mass fraction of water in the humidified CO\(_2\) stream equals 85% relative humidity for the flow conditions measured experimentally by a digital flow meter on the cell outlet \((n_{H2O,CAT} = 0.22, T = 25 \, ^\circ\text{C}, \text{ and } P_{ch} = 107.9)\).

![Summary of model domains and dimensions.](image)

**Figure B4.11** Summary of model domains and dimensions.

The system was assumed to be isothermal. Diffusion was estimated using Fick’s law with effective diffusivity through porous media calculated using Bruggeman’s correction. Ion migration within an electric field aside from the water flux arising from electro-osmotic drag were not considered. Water in the AEM is in the liquid phase, while water, CO\(_2\) and CO in the catalyst layer
and GDL are assumed to be gas phase. Darcy’s law was used to describe transport through porous media. Transport parameters of the membrane, catalyst layer, and gas diffusion layer were sourced from literature (Table S4). The CO₂ reduction reaction was assumed to occur solely in the porous catalyst layer with 100% \( FE_{CO} \) used to calculate the stoichiometric rates of electrochemical CO₂ and H₂O consumption for a set current density.

\[
\text{CO}_2 + \text{H}_2\text{O} + 2e^- \rightarrow \text{CO} + \text{OH}^- \quad \text{(Eq. A4.2)}
\]

A case study was completed that changed the membrane thickness from 20 µm, 40 µm, and 55 µm with the corresponding changes in \( J_{\text{DIFF}} \), \( J_{\text{BC}} \), and \( J_{\text{EO}} \) compared in Figure B4.12.

**Figure B4.12** The effect of membrane thickness on (a) each of the water flux (\( J_{\text{H}_2\text{O}} \)) to the cathode (diffusion, back convection, and electro-osmotic drag) and (b) the mol fraction of water (\( n_{\text{H}_2\text{O}} \)) from the anode/AEM interface to the cathode GDE at \( j = 200 \text{ mA/cm}^2 \).

Increasing PTFE loading from 6 wt% to 17 wt% and 29 wt% was found to increase the thickness of the catalyst layer from 2.7 µm, to 3.4 µm, and 4.5 µm, and contact angle of 140°,
145°, and 145°, respectively (Figure B4.13). Changing these parameters in the model was found to have little effect on water flux. As the model contradicts the experimental results in this case, it highlights the shortcomings that most existing models cannot yet accurately describe the processes that occur inside a CO₂ electrolyzer and therefore the need for empirical studies into complex phenomena such as flooding.

**Figure B4.13** The effect of cathodic PTFE content on (a) each of the water flux ($J_{H₂O}$) to the cathode (diffusion, back convection, and electro-osmotic drag) and (b) the mol fraction of water ($n_{H₂O}$) from the anode/AEM interface to the cathode GDE at $j = 200$ mA/cm$^2$.

Fluxes for $J_{EOD}$ and $J_{BC}$ at the AEM/cathode catalyst layer interface were calculated using the equations below. To calculate the back convection flux (Eq. B4.3) a liquid water saturation value ($s = 0.01$) was assumed in order to calculate the Leverett function (Eq. B4.4).

$$J_{BC} = \frac{K_{mem} \rho \sigma \cos \theta}{\mu M_{H₂O} J_{mem}} \left( \frac{\varepsilon}{K_{GDE}} \right)^{1/2} J(s)$$  \hspace{1cm} (Eq. B4.3)

$$J(s) = 1.417s - 2.120s^2 + 1.263s^3$$  \hspace{1cm} (Eq. B4.4)
\[ J_{EO} = \kappa \frac{j}{F} \] 

(Eq. B4.5)

The diffusive flux for species \( i \) in the catalyst layer or GDL is calculated using Eq. B4.6. Density of gaseous mixtures is calculated using the ideal gas law for the calculated mass fractions.

\[ J_{\text{DIFF},i} = -\left( \rho D_{e,i} \nabla n_i + \rho n_i D_{e,i} \frac{\nabla M_n}{M_n} - \rho n_i \sum_k \frac{M_k}{M_n} D_{k}^{f} \nabla X_k \right) \] 

(Eq. B4.6)

\[ M_n = \left( \sum_i \frac{n_i}{M_i} \right)^{-1} \] 

(Eq. B4.7)

\[ D_{e,i}^{f} = f_e (\epsilon_p, \tau_F) D_{l}^{f} \] 

(Eq. B4.8)

\[ \tau_F = \epsilon_p^{-1/2} \] 

(Eq. B4.9)

\[ f_e = \frac{\epsilon_p}{\tau_F} \] 

(Eq. B4.10)

Diffusive mass flux of species \( i \) in the membrane is calculated by Eq. A4.11 with a density equivalent to liquid water:

\[ J_{\text{DIFF},i} = -\left( \rho D_{l}^{f} \nabla n_i + \rho n_i D_{l}^{f} \frac{\nabla M_n}{M_n} - \rho n_i \sum_k \frac{M_k}{M_n} D_{k}^{f} \nabla X_k \right) \] 

(Eq. B4.11)
### Table B4.3 Model parameters and variable definitions

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<th>Parameter/ Variable</th>
<th>Symbol</th>
<th>Value [units]</th>
<th>Reference</th>
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