4-26-2019

Anion Exchange Membrane Fuel Cell Performance in the Presence of Carbon Dioxide

Jacob Wrubel
University of Connecticut - Storrs, jacob.wrubel@uconn.edu

Follow this and additional works at: https://opencommons.uconn.edu/dissertations

Recommended Citation
https://opencommons.uconn.edu/dissertations/2141
Anion Exchange Membrane Fuel Cells (AEMFCs) offer some possible advantages over their Proton Exchange Membrane (PEM) counterparts due to more facile oxygen reduction reaction kinetics (enabling cheaper catalysts), easier water management & balance of plant, cheaper membrane materials, and improved stability of fuel cell stack materials. However, AEMFCs perform significantly worse when exposed to carbon dioxide (CO$_2$), which is present in most applications. Furthermore, because CO$_2$ is so pervasive inside the AEMFC system, its effects are difficult to isolate experimentally. Therefore, a modeling approach was developed which can offer independent control of membrane properties and operating conditions, as well as the contextual freedom to isolate specific aspects of operation.

For instance, AEMFCs exhibit a phenomenon known as “self-purging”, whereby CO$_2$ is removed from the system during normal operation. Due to self-purging, AEMFCs approach their CO$_2$-free performance as the current density is increased. Without this effect, it would be impractical to use AEMFCs. Despite its importance, the mechanism behind the self-purging phenomenon is still relatively obscure, which makes it difficult to design these devices with this effect in mind.

In this modeling approach, existing *ex situ* AEM models are built up to include operating effects such as current density and gas stream conditions. A morphology model is also developed to investigate the effects of CO$_2$ on electrospun AEMs, which are a class of AEMs with unique morphologies. Finally, we present a study that implements and evaluates the two leading explanations for self-purging, and discuss their relative merits.
Anion Exchange Membrane Fuel Cell Performance in the Presence of Carbon Dioxide

Jacob A. Wrubel

B.S., University of Connecticut, 2014

A Dissertation
Submitted in Partial Fulfillment of the
Requirements for the Degree of
Doctor of Philosophy
at the
University of Connecticut

2019
Anion Exchange Membrane Fuel Cell Performance in the Presence of Carbon Dioxide

Presented by
Jacob A. Wrubel, B.S.

Major Advisor
Wilson K. S. Chiu

Associate Advisor
Brice Cassenti

Associate Advisor
Kyle N. Grew

Associate Advisor
George Matheou

Associate Advisor
Ugur Pasaogullari

University of Connecticut
2019
Acknowledgements:

I would like to express my gratitude to my major advisor, Professor Wilson K. S. Chiu, for his mentorship throughout my time in his lab. I would also like to thank my advisory committee for their support and guidance: Brice Cassenti, who is a skilled mathematician; Kyle Grew, who has elevated my work in countless ways; George Matheou, who was always available for discussions about numerics and general philosophy; and Ugur Pasaogullari, who has helped me maintain the focus of this work. Thank you as well to my former and current lab mates: Alex Cocco, Peter Damian, Matt DeGostin, Tim Lynch, Ryan Murphy, and Tim Myles.

I would like to thank my family for their constant encouragement and support. Thank you to my friends who lent me their confidence and politely feigned interest when I started talking about research. Lastly, I would like to extend special thanks to Dr. Aldo Peracchio, without whom this would not have been possible. In addition, I would like to thank Dr. Jane Cercena and Dr. Claire Jalbert for being such great personal and professional role models.
# Table of Contents:

Chapter 1: Introduction .................................................................................................................. 1

Chapter 2: Modeling the Conductivity of *in situ* Anion Exchange Membranes Exposed to Carbon Dioxide using a Spatially Averaged Model ........................................................................ 9

2.1 - Overview ................................................................................................................................. 9
2.2 - Theory ...................................................................................................................................... 9
  2.2.1 - Governing Equations .......................................................................................................... 9
  2.2.2 - Boundary Conditions ......................................................................................................... 15
  2.2.3 - Initial Conditions .............................................................................................................. 19
  2.2.4 - Numerical Approach ....................................................................................................... 21
2.3 - Results and Discussion .......................................................................................................... 23
  2.3.1 - Validation ......................................................................................................................... 23
  2.3.2 - Performance Results and Parametric Studies ................................................................. 27
2.4 - Conclusions ........................................................................................................................... 37

Chapter 3: Effects of CO\textsubscript{2} on Electrospun Anion Exchange Membranes .............. 40

3.1 - Overview ............................................................................................................................... 40
3.2 - Theory .................................................................................................................................... 44
  3.2.1 - Discrete Morphology Model for Electrospun Membranes ............................................. 46
  3.2.2 - CO\textsubscript{2} Model ...................................................................................................... 51
3.3 - Experimental .......................................................................................................................... 54
3.4 - Results and Discussion .......................................................................................................... 55
  3.4.1 - Model Validation ............................................................................................................ 55
  3.4.2 - Simulation of the CO\textsubscript{2} Behavior of Electrospun AEMs ..................................... 58
3.5 - Conclusions ........................................................................................................................... 64

Chapter 4: Investigation into the Self-Purging Mechanism in AEMFCs ...................................... 67

4.1 - Overview ............................................................................................................................... 67
4.2 - Theory .................................................................................................................................... 71
  4.2.1 - Governing Equations ...................................................................................................... 71
  4.2.2 - Self-Purging Models ...................................................................................................... 77
  4.2.3 - Mixed Potential Theory ................................................................................................. 79
  4.2.4 - Numerical Methods ...................................................................................................... 83
4.3 - Results and Discussion ......................................................................................................... 94
  4.3.1 - Determination of an Appropriate Self-Purging Model .................................................. 94
  4.3.2 - Fundamental Simulation Results .................................................................................. 105
  4.3.3 - Effects of CO\textsubscript{2} on AEMFC Operation ............................................................. 114
4.4 - Conclusions .......................................................................................................................... 125
Chapter 5: Modeling Ionic Species Transport in Bipolar Membranes ......................... 129
  5.1 - Overview ............................................................................................................. 129
  5.2 - Theory .................................................................................................................. 132
    5.2.1 - Governing Equations ..................................................................................... 132
    5.2.2 - Numerical Methods ....................................................................................... 139
  5.3 - Results and Discussion ....................................................................................... 141
    5.3.1 - CO₂-free Space Charge Region Validation ................................................... 141
  5.4 - Conclusions and Next Steps ............................................................................... 144

Chapter 6: Conclusions and Remarks ........................................................................... 145
  6.1 - Key Findings and Contributions ......................................................................... 145
  6.2 - Recommendations for Future Work .................................................................... 149

References ................................................................................................................... 151
Chapter 1: Introduction

Anion exchange membrane fuel cells (AEMFCs) have garnered steadily increasing interest in recent years\(^1\). This attention is due in part to the prospect of using cheaper materials compared to proton exchange membrane fuel cells (PEMFCs), which is a key obstacle to the widespread implementation of low temperature fuel cells\(^2\). The development of highly conductive AEMs\(^1,3\) and an improved fuel cell water balance\(^4\) are important considerations for narrowing the performance gap between AEMFCs and PEMFCs.

Despite advantages such as more facile oxygen reduction reaction (ORR) kinetics\(^2\), even high performing AEMFCs still exhibit power densities many times lower than their proton exchange membrane (PEM) counterparts\(^2,5,6\). AEMs are inherently less conductive than PEMs, since their native charge carriers are hydroxide ions (OH\(^-\)), compared to protons (H\(^+\)) in PEMs. Therefore, it is important that their conductivity behavior is well understood in order to mitigate any factors that result in further decreased membrane conductivity.

In addition, AEMs and AEMFCs are subject to significant performance losses when exposed to carbon dioxide (CO\(_2\)). Many potential applications for AEMFCs involve operating in the presence of CO\(_2\). For example, for low temperature AEMFCs to be a convenient portable energy source they should be able to operate using ambient air as the oxidant, or other similarly convenient fuels such as methanol\(^2,7,8\). Other researchers have proposed to use AEMs to scrub CO\(_2\) from either the environment\(^9\) or flue gases from combustion processes\(^10\), creating energy and sequestering the CO\(_2\) in the process. These applications all expose the membrane to carbon dioxide, which degrades AEMFC performance by reacting with the native OH\(^-\) to form bicarbonate and carbonate ions (HCO\(_3^-\), CO\(_3^{2-}\) respectively), as depicted by Eqs. 1.1 – 1.2. These
ions are less mobile and therefore reduce the membrane’s conductivity relative to the pure hydroxide form$^{2,5,6,11-14}$.

\[ \text{CO}_2(\text{aq}) + \text{OH}^- \leftrightarrow \text{HCO}_3^- \]  
\[ \text{OH}^- + \text{HCO}_3^- \leftrightarrow \text{CO}_3^{2-} + \text{H}_2\text{O} \]  

Aside from Ohmic losses, the presence of (bi)carbonate species may also impact electrochemical processes (and hence activation/thermodynamic losses) in the AEMFC, a phenomenon which is still largely unexplored. Experimental studies can observe these effects, but it is difficult to get fundamental mechanistic insight about these processes because of how pervasive \( \text{CO}_2 \) is inside the AEMFC system. For example, at the cathode the absorption of \( \text{CO}_2 \) can decrease oxygen solubility and diffusivity in the electrolyte, and also lead to a decrease in the electrochemically active area$^{15}$. Similarly, \( \text{CO}_3^{2-} \) has been shown to decrease oxygen reduction reaction (ORR) activity on Pt/C and Pd/C electrodes$^{16}$. Lastly, Eqs. 1.1 – 1.2 reduce the pH in the membrane and catalyst layers, which can negatively affect both anode and cathode performance$^{6,17}$. For example, the Nernst equation predicts an overall cell voltage penalty of 59 mV per pH unit difference between the cathode and anode (at STP). This is an equilibrium phenomenon which is useful for predicting open circuit potentials, however it does not account for the coupling between Faradaic reactions and activation losses away from open circuit conditions. These processes all factor into the overall cell losses observed when AEMFCs are operated in the presence of \( \text{CO}_2 \), and are depicted in the schematic shown in Figure 1.
Figure 1 – A schematic of the carbonation, transport, and self-purging processes for an operating AEMFC exposed to carbon dioxide at the cathode.

Although AEMFC performance is certainly lower when operated in the presence of carbon dioxide, this can be mitigated during normal operation through an effect known as the self-purging mechanism. During operation, hydroxide ions are continuously supplied to the membrane via the ORR occurring at the cathode, Eq. 1.3.

$$\text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- \leftrightarrow 4\text{OH}^- \quad (1.3)$$

These incoming hydroxide ions mitigate some of the conversion of hydroxide in the membrane that occurs due to Eqs. 1.1 – 1.2. At the anode, hydroxide ions are consumed by the hydrogen oxidation reaction (HOR), Eq. 1.4 (referred to as the hydroxide HOR pathway),
\[ H_2 + 2OH^- \leftrightarrow 2H_2O + 2e^- \]  \hspace{1cm} (1.4)

In addition, (bi)carbonates are purged from the membrane at the anode due to an effect known as the self-purging mechanism. Several recent reviews and papers have noted that there remains a lack of consensus over the exact mechanism of the self-purging phenomenon\textsuperscript{1,15,17,18}. There are two prevalent theories, which can be described as (i) a chemical mechanism and (ii) an electrochemical mechanism. The chemical mechanism proposes that the local depletion of \( OH^- \) due to Eq. 1.4 shifts the equilibrium of Eqs. 1 – 2 back toward the reactants, thereby replenishing the \( OH^- \), reducing the AEM’s (bi)carbonate content, and releasing \( CO_2 \) into the anode gas stream via desorption. The electrochemical model proposes that (bi)carbonate ions are oxidized as a part of the HOR, e.g. via Eqs. 1.5 – 1.6 (referred to as the bicarbonate and carbonate HOR pathways, respectively). This theory would similarly explain the decrease in (bi)carbonate concentrations and \( CO_2 \) emission during operation.

\[ H_2 + 2HCIO_3^- \leftrightarrow 2CO_2 + 2H_2O + 2e^- \]  \hspace{1cm} (1.5)
\[ H_2 + CO_3^{2-} \leftrightarrow CO_2 + H_2O + 2e^- \]  \hspace{1cm} (1.6)

Due to the myriad ways in which \( CO_2 \) interacts with the AEMFC system, its effects are difficult to experimentally isolate. There is currently a gap in our understanding of how carbon dioxide affects the operation of AEMFCs. Dekel et al. recently reported that only 3% of experimental studies included the effects of ambient \( CO_2 \) on cell performance\textsuperscript{3}, even though the \( CO_2 \) problem is recognized as a key issue that must be addressed\textsuperscript{3,15,17}. A modeling approach can
prove very useful for this system because of the independent control over system properties and operating conditions, as well as the freedom to investigate very specific aspects of operation. To date, modeling approaches have typically focused on *ex situ* (non-operational/isolated) AEMs\textsuperscript{12,13,19} or have employed numerical and/or contextual simplifications\textsuperscript{20,21} that have made it hard to fully explain the carbonation and purging processes.

For example, Grew et al. developed a Dusty Fluid model\textsuperscript{22} to account for the morphological properties of AEMs in pure OH\textsuperscript{−} form, which they then extended to consider the effects of temperature and CO\textsubscript{2} on conductivity\textsuperscript{13}. Another take on morphology’s role on AEM conductivity was the Fiber Network model put forward by DeGostin et al.\textsuperscript{23} which was developed to study electrospun AEMs. The fiber network model was developed solely to characterize the membrane’s morphology: the effects of operating conditions and CO\textsubscript{2} absorption were not investigated.

A comprehensive description of HCO\textsubscript{3}− and CO\textsubscript{3}\textsuperscript{2−} formation in an *ex situ* AEM exposed to CO\textsubscript{2} was presented through the Ion Exchange model of Myles et al.\textsuperscript{12}. The Ion Exchange model solved spatial and time-varying diffusion equations for an isolated AEM, and utilized a detailed reaction mechanism to describe both HCO\textsubscript{3}− and CO\textsubscript{3}\textsuperscript{2−} formation and ion exchange with the fixed cationic functional groups.

The theoretical models listed above describe the behavior of isolated AEMs, that is, in the absence of polarization and electrochemical reactions. The polarization induced by the electrodes provides an extra driving force for transport across the membrane (in addition to diffusion), while the Faradaic ORR and HOR reduce and oxidize ions at the membrane boundaries. These reactions affect the concentrations of ionic species inside the membrane (and hence its
conductivity). Theoretical studies on the carbonation of in situ AEMs have been presented, again with varying degrees of simplifications.

For example, Siroma et al. developed a transport model to accompany their experimental AEMFC study. The model, which was developed for steady state operation, assumes that only \( \text{OH}^- \) & \( \text{CO}_3^{2-} \) or \( \text{CO}_3^{2-} \) & \( \text{HCO}_3^- \) ions can exist in the membrane at one time. This assumption is rooted in the dynamics of Eqs. 1.1 – 1.2, which proceed first through a carbonate accumulation period, and then to a carbonate depletion/bicarbonate accumulation period, as noted by Myles. Their model also prescribes that the flux of \( \text{CO}_3^{2-} \) and \( \text{HCO}_3^- \) through the membrane is negligible (zero), and that the \( \text{OH}^- \) concentration is fixed at zero at the anode. Under these assumptions they were able to reasonably predict the carbonate ion ratios of their operating fuel cell, although it was suggested that the two-ion assumption limited the accuracy and predictive capabilities of the model.

More recently, Shiau et al. developed a detailed 2-D AEMFC model that included varying water content, the relative humidity of the gas streams, and catalyst layer (CL) species concentration and current density distributions. They applied a chemical self-purging mechanism, which was able to demonstrate the membrane’s \( \text{OH}^- \) conductivity reclamation with increasing current density. However, detailed validation to \( \text{CO}_2 \)-focused AEMFC experiments was not presented. Also, the association/dissociation reactions with tethered cationic side groups (e.g. \( \text{TMA}^+ \)) were not considered. We believe these reactions should be included since these side groups can act as storage sites for the mobile anions and can take up and/or release ions as the local concentrations change, as demonstrated by Myles et al.

Krewer et al. developed a carbonation model for an operating AEMFC that investigated species transport and reactions through several AEMFC components, including flow channels,
They contend that it is not necessary to differentiate between chemical and electrochemical purging models, since in both cases identical amounts of carbon dioxide and electrons would be produced at the anode. The actual ionic species fluxes in their model were handled using a type of outflow boundary condition, in which any species reaching the Anode CL/membrane boundary are immediately consumed. This somewhat akin to the electrochemical mechanism, but does not account for varying reaction rates due to kinetics and concentration effects, which can result in both local consumption and accumulation. Furthermore, it is necessary to employ the correct mechanism in order to predict accurate electrode potentials and cell voltages.

Another similar approach was used by Nikonenko et al. to model CO$_3^{2-}$ and HCO$_3^-$ transport in an AEM electrodialysis cell. While their model included operational effects, the model assumed chemical equilibrium among ionic species, whereas it is known from Ref. [12] that the dynamics of the ion exchange process significantly affect the AEM’s behavior. Furthermore, it may not be the case that the reactions are in equilibrium during steady state operation of an AEMFC. Although their model can provide useful insight about AEM carbonation, the configuration of an electrodialysis cell is different from an AEMFC, which likely will lead to different behavior.

These theoretical studies are summarized in Table 1.1, which highlights the various features included in each model. In this dissertation, several models are presented that build upon the theory and insights gained in the aforementioned theoretical studies. Chapter 2 describes a transient, spatially averaged transport model that was developed to extend the work of Myles et al.$^{12}$ to an *in situ* AEM. Most significantly, this included the addition of operating effects such as current density and gas stream conditions. Chapter 3 extends the spatially averaged model to
electrospun AEMs, which have a unique morphology compared to conventional AEMs. Lastly, Chapter 4 refines the spatially averaged model by solving the spatially-resolved governing equations. Using this improved theory, a detailed investigation into the self-purging mechanism was performed. Until now, the self-purging phenomenon has only been employed using significant approximations. The results of the self-purging study can potentially lend useful insight to the design of new catalysts for AEMFCs, because of the mechanistic implications for the HOR in carbonated alkaline media.

Table 1.1

Review of AEM models that include CO₂ published in the literature

<table>
<thead>
<tr>
<th>Model (by author)</th>
<th>Current Density</th>
<th>Gas Channels</th>
<th>Transient</th>
<th>Spatially Varying</th>
<th>Chemical Kinetics/Equilibrium</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grew et al.¹³</td>
<td>No</td>
<td>No</td>
<td>No</td>
<td>No</td>
<td>Equil.</td>
</tr>
<tr>
<td>Siroma et al.²⁰</td>
<td>Yes</td>
<td>No</td>
<td>No</td>
<td>Yes</td>
<td>Equil.</td>
</tr>
<tr>
<td>Kiss et al.²⁵</td>
<td>No</td>
<td>No</td>
<td>No</td>
<td>No</td>
<td>Equil.</td>
</tr>
<tr>
<td>Myles et al.¹²</td>
<td>No</td>
<td>No</td>
<td>Yes</td>
<td>Yes</td>
<td>Kin.</td>
</tr>
<tr>
<td>Krewer et al.²⁴</td>
<td>Yes</td>
<td>Yes</td>
<td>No</td>
<td>Yes</td>
<td>Kin.</td>
</tr>
<tr>
<td>Shiau et al.¹⁸</td>
<td>Yes</td>
<td>Yes</td>
<td>No</td>
<td>Yes</td>
<td>Kin.</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Varying $T, P_{CO₂}$</th>
<th>Fixed Charge Interaction</th>
<th>Validation</th>
<th>$\sigma$</th>
<th>Activation Losses</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T, P_{CO₂}$</td>
<td>No</td>
<td>Yes</td>
<td>Yes</td>
<td>No</td>
</tr>
<tr>
<td>-</td>
<td>No</td>
<td>Yes</td>
<td>No</td>
<td>No</td>
</tr>
<tr>
<td>-</td>
<td>No</td>
<td>Yes</td>
<td>Yes</td>
<td>No</td>
</tr>
<tr>
<td>-</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td>No</td>
</tr>
<tr>
<td>-</td>
<td>No</td>
<td>No</td>
<td>No</td>
<td>From Nernst Equation</td>
</tr>
<tr>
<td>-</td>
<td>No</td>
<td>No</td>
<td>Yes</td>
<td>Yes (chemical model)</td>
</tr>
</tbody>
</table>
Chapter 2: Modeling the Conductivity of in situ Anion Exchange Membranes Exposed to Carbon Dioxide using a Spatially Averaged Model

This chapter is adapted from work originally published in *J. Electrochem. Soc.*, 164 (12) F1063-F1073 (2017).

2.1 - Overview

This study quantitatively describes the carbonate- and bicarbonate-forming reaction mechanism in an operating alkaline exchange membrane fuel cell that occurs as a result of carbon dioxide in the cathode gas stream. A transient, spatially-averaged theoretical model was created for this study and validated to experimental data from the literature. Results present the prediction of the membrane’s ionic conductivity as a function of operating conditions and membrane properties. The self-purging phenomenon was observed and studied, as well as the emission of carbon dioxide from the membrane during operation. Following the conductivity study, suggestions are made for optimal operating conditions and membrane properties to improve fuel cell performance in the presence of carbon dioxide.

2.2 - Theory

2.2.1 - Governing Equations

The basic structure of an AEM consists of a porous interwoven network of polymeric backbones with covalently tethered cationic groups. A common cationic side group is the trimethylammonium ion (TMA\(^+\), i.e. \(\text{N}(\text{CH}_3)_3^+\))\(^{26}\). In this work, TMA\(^+\) is used to denote the cationic side groups, although the results and analysis herein are can be generalized to AEMs employing alternative backbone and cation chemistries. The pores of the network are partially or
completely filled with water, and it is through these hydrated pores that the transport of ions takes place.

The transport of ionic species inside the membrane is governed by the one-dimensional Nernst-Planck (NP) equation with reactions

\[
\frac{\partial c_k}{\partial t} = \frac{\partial}{\partial x} \left( D_k \frac{\partial c_k}{\partial x} \right) + \frac{\partial}{\partial x} \left( \frac{z_k F D_k}{RT} c_k \frac{\partial \varphi}{\partial x} \right) + \dot{R}_k \tag{2.1}
\]

where \( c_k \) denotes molar concentration of species \( k \), and \( \dot{R}_k \) is the rate of generation of species \( k \). Due to the nonlinearity of the migration and source terms, and kinetic parameters which span several orders of magnitude, the resulting system of equations presents many numerical challenges. The system can be simplified by averaging across the membrane as follows

\[
\frac{1}{L} \int_0^L \frac{\partial c_k}{\partial t} \, dx = \frac{1}{L} \int_0^L \frac{\partial}{\partial x} \left( D_k \frac{\partial c_k}{\partial x} \right) \, dx + \frac{1}{L} \int_0^L \frac{\partial}{\partial x} \left( \frac{z_k F D_k}{RT} c_k \frac{\partial \varphi}{\partial x} \right) \, dx + \frac{1}{L} \int_0^L \dot{R}_k \, dx \tag{2.2}
\]

with the averaged form as

\[
\frac{\partial \bar{c}_k}{\partial t} = \frac{1}{L} \left[ J_{k,x=L} - J_{k,x=0} \right] + \bar{\dot{R}}_k \tag{2.3}
\]

Thus the spatially averaged NP equations can be solved for average concentrations within the membrane, \( \bar{c}_k \). The first and second terms on the right hand side of Eq. 2.1 are the fluxes due to diffusion and migration respectively, and are combined into \( J_k \) as shown in Eq. 2.3. The third
term becomes the average of the reaction source term for species $k$. The source terms, which are identical to those used in the Ref. [12], are listed in Table 2.1 and correspond to Eqns. 2.4 – 2.8.

**Table 2.1**

*Source terms necessary for the solution of the Nernst-Plank governing equations*

<table>
<thead>
<tr>
<th>Species</th>
<th>Source Term, $\dot{R}_k$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO$_2$</td>
<td>$-k_1^+ c_{CO_2} c_{OH} + k_1^- c_{HCO_3}$</td>
</tr>
</tbody>
</table>
| OH$^-$      | $-k_1^+ c_{CO_2} c_{OH} + k_1^- c_{HCO_3} - k_2^+ c_{HCO_3} c_{OH} + k_2^- c_{CO} c_{H_2O}$  
|             | $+ k_4^+ c_{TMA(OH)} - k_4^- c_{TMA} c_{OH}$                  |
| HCO$_3^-$  | $k_1^+ c_{CO_2} c_{OH} - k_1^- c_{HCO_3} - k_2^+ c_{HCO_3} c_{OH} + k_2^- c_{CO} c_{H_2O}$  
|             | $+ k_5^+ c_{TMA(HCO_3)} - k_5^- c_{TMA} c_{HCO_3}$             |
| CO$_3^{2-}$ | $k_2^+ c_{HCO_3} c_{OH} - k_2^- c_{CO} c_{H_2O}$               |
| TMA(OH)     | $-k_4^+ c_{TMA(OH)} + k_4^- c_{TMA} c_{OH}$                    |
| TMA(HCO$_3$) | $-k_5^+ c_{TMA(HCO_3)} + k_5^- c_{TMA} c_{HCO_3}$              |

The CO$_3^{2-}$ and HCO$_3^-$ forming reaction mechanism for an isolated membrane is assumed to remain valid for the bulk of an operating membrane under polarization since the interior of the membrane is isolated from the electrode surfaces. A schematic of the ion exchange process of an operating AEM is shown in Figure 2.1a: CO$_2$ and OH$^-$ enter the membrane at the cathode by absorption (defined later) and the ORR (Eq. 4) respectively, then Eqns. 2.5 – 2.9 proceed, and mobile species exit the membrane at the anode.

$$\frac{1}{2}O_2 + H_2O + 2e^- \leftrightarrow 2OH^-$$  \hspace{1cm} (2.4)
\[
\text{CO}_2(\text{aq}) + \text{OH}^- \leftrightarrow \text{HCO}_3^- \quad (2.5)
\]
\[
\text{HCO}_3^- + \text{OH}^- \leftrightarrow \text{CO}_3^{2-} + \text{H}_2\text{O} \quad (2.6)
\]
\[
(\text{TMA})\text{OH} \leftrightarrow (\text{TMA})^+ + \text{OH}^- \quad (2.7)
\]
\[
(\text{TMA})\text{HCO}_3 \leftrightarrow (\text{TMA})^+ + \text{HCO}_3^- \quad (2.8)
\]
\[
(\text{TMA})_2\text{CO}_3 \leftrightarrow 2(\text{TMA})^+ + \text{CO}_3^{2-} \quad (2.9)
\]

Averaging the source terms, i.e. expressing \( \overline{R_k} \), requires the same integration process as the diffusion and migration terms. However due to the nonlinearity of some of the terms, this is not always possible. To handle this, the model assumes that \( \overline{c_i c_j} = \overline{c_i} \overline{c_j} \) where \( c_i = c_i(x), c_j = c_j(x) \), the accuracy of which will be discussed later. In general, this assumption is more accurate when the magnitude of the gradients of \( c_i \) and \( c_j \) are smaller, which is likely more accurate for \( \text{CO}_3^{2-} \) and \( \text{HCO}_3^- \): transport of these species is sometimes assumed to be driven mainly by migration\(^5,^{21,27} \), which implies that their concentration gradients are small. To further simplify the calculations, it was assumed that the water concentration, \( c_{\text{H}_2\text{O}} \), is held constant at \( \left( \frac{\rho}{M} \right)_{\text{H}_2\text{O}} = 0.055 \text{ mol cm}^{-3} \), and is assumed to be in equilibrium with its self-dissociation products, i.e.

\[
\frac{[\text{H}^+][\text{OH}^-]}{[\text{H}_2\text{O}]} = K_W.
\]
Fixing the water concentration is a good approximation for the chemical reactions since the concentration of water in aqueous solutions is much larger than any of the other species.

Dissociated TMA, that is, \( \text{TMA}^+ \), and associated carbonate, \( \text{TMA}_2(\text{CO}_3) \), are found through the use of charge neutrality and conservation of mass, Eqns. 2.10 and 2.11 respectively:

\[
c_{\text{TMA}^+} = c_{\text{OH}^-} + c_{\text{HCO}_3^-} + 2c_{\text{CO}_3^{2-}} - c_{\text{H}^+} \quad (2.10)
\]
\[ c_{\text{TMA(CO}_3\text{)}} = \frac{1}{2} \left( c_0 - c_{\text{TMA}^+} - c_{\text{TMA(OH)}} - c_{\text{TMA(HCO}_3\text{)}} \right) \] (2.11)

Once the governing equations are solved, the average concentrations can be used to predict the ionic conductivity of the membrane, which is calculated using the Dusty-Fluid Model developed by Grew et al.\textsuperscript{22}, Eq. 2.12.

\[ \tilde{\sigma} = \frac{F^2}{RT} \sum_k \frac{z_k^2 D_k^{\text{eff}} (1 + \lambda)}{\lambda(1 + \delta_k)} \tilde{c}_k \] (2.12)

It can be seen that model predicts the total ionic conductivity (with contributions from OH\textsuperscript{-}, HCO\textsubscript{3}\textsuperscript{-}, and CO\textsubscript{3}\textsuperscript{2-}) of the membrane since all mobile charged species contribute in Eq. 2.12. The parameter \( \delta_k \) is the ion-solvent/ion-membrane diffusivity ratio, and its definition can be found in Ref. [13]. The effective diffusivity, \( D_k^{\text{eff}} \), is used to account for the morphological characteristics of the membrane. The results presented here use a Bruggeman model, \( D_k^{\text{eff}} = \varepsilon^q D_k \) with a Bruggeman exponent \( q = 1.5 \), but other models can be used, for example those presented in Ref. [23], which are specific to electrospun AEMs. The volume fraction of water in the membrane, \( \varepsilon \), is a function of the water uptake\textsuperscript{13,22}.

\[ \varepsilon = \frac{\lambda}{\left( \lambda + \frac{\rho_{H_2O}}{M_{H_2O} \rho_{\text{mem} IEC}} \right)} \] (2.13)

This effect is important and will be discussed further in the Results & Discussion section. In this work, the hydration state (and thus the porosity) is assumed to be constant and uniform. Future
work may consider the effect of electrode and species reactions on the hydration of the membrane.

Figure 2.1 – Schematic for a) membrane flux balance & reactions and b) macroscopic
anode/cathode approximations for free stream CO₂ concentrations

2.2.2 - Boundary Conditions

Boundary conditions are listed in Table 2.2 and are elaborated upon here. Fluxes for the fixed TMA groups must identically be zero (in the stationary Eulerian reference frame). The boundary conditions for CO₂ account for the anode and cathode gas feeds and the corresponding transfer of CO₂ into and out of the membrane by absorption and desorption; CO₂ is not assumed to be consumed by any electrochemical reactions (e.g. it is not reduced at the cathode). These processes are represented by convective boundary conditions on aqueous CO₂ according to the thin film model of Liss & Slater. This approach was used in Ref. [12], and it was found that the best agreement to experimental data was obtained when the mass transfer coefficient, $k_{abs}$, was large, that is, the transient aspects of CO₂ absorption are much faster than the transient periods associated with the ion exchange processes. Since this work considers gas feeds at standard conditions, it was assumed that the same mechanism is responsible for CO₂ absorption, thus the mass transfer coefficient was again chosen to ensure that $Bi \equiv \frac{k_{abs}L}{2D_{CO₂}} \geq 10^4$.

Table 2.2

Boundary conditions for species solved by the NP equation

<table>
<thead>
<tr>
<th>Species</th>
<th>$J_{k,x=0}$</th>
<th>$J_{k,x=L}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂</td>
<td>$J_{CO₂} = k_{abs}\left(\bar{c}<em>{CO₂,aq} - H</em>{CO₂}^{cc}c_{CO₂(g)}\right)$</td>
<td>$J_{CO₂} = k_{abs}\left(H_{CO₂}^{cc}c_{CO₂(g)} - \bar{c}_{CO₂,aq}\right)$</td>
</tr>
<tr>
<td>OH⁻</td>
<td>$J_{OH} = -t_{OH} \frac{i}{F}$</td>
<td>$J_{OH} = \frac{i}{F}$</td>
</tr>
<tr>
<td>HCO₃⁻</td>
<td>$J_{HCO₃} = -t_{HCO₃} \frac{i}{F}$</td>
<td>$J_{HCO₃} = 0$</td>
</tr>
<tr>
<td>CO₃²⁻</td>
<td>$J_{CO₃} = -t_{CO₃} \frac{i}{2F}$</td>
<td>$J_{CO₃} = 0$</td>
</tr>
<tr>
<td>TMA(OH)</td>
<td>$J_{TMA(OH)} = 0$</td>
<td>$J_{TMA(OH)} = 0$</td>
</tr>
<tr>
<td>----------------</td>
<td>------------------</td>
<td>------------------</td>
</tr>
<tr>
<td>TMA(HCO₃)</td>
<td>$J_{TMA(HCO₃)} = 0$</td>
<td>$J_{TMA(HCO₃)} = 0$</td>
</tr>
</tbody>
</table>

The absorption/desorption fluxes depend on the gas stream concentrations of CO₂ (in this case, the average concentrations) which, unlike isolated membranes, are not constant. A schematic of the process is shown in Figure 2.1b: as the gases flow over the anode and cathode membrane interfaces, their free stream CO₂ concentrations change as CO₂ is absorbed or desorbed (i.e. the free stream concentration is coupled with CO₂ flux). The average concentration of CO₂ in the anode and cathode gas streams (where the concentration boundary layer has been approximated as linear) can be found from continuity requirements, and lead to Eqns. 2.14a and 2.14b, respectively.

\[
c_{CO₂(\text{g})}^A \approx \frac{A \cdot J_{CO₂}^{TotA}}{2Q_{H₂}} \quad (2.14a)
\]

\[
c_{CO₂(\text{g})}^C \approx \frac{A \cdot J_{CO₂}^C}{2Q_{Air}} + \frac{p_{CO₂}^C}{RT} \quad (2.14b)
\]

The constant term in Eq. 2.14b, $\frac{p_{CO₂}^C}{RT}$, reflects the CO₂ concentration of the incoming gas. Eq. 2.14 assumes that the volume occupied by CO₂(g) in both gas streams is negligible compared to the volume of the feed gases. In Eq. 2.14a, the superscript ‘Tot’ indicates the total CO₂ flux, and reflects the fact that CO₂ can enter the anode gas stream by desorption of aqueous CO₂, or as the product of electrochemical reactions of CO₃²⁻/HCO₃⁻ with hydrogen³, which also form CO₂ (i.e.
$J_{\text{CO}_2}^{\text{Tot.A}} = J_{\text{CO}_2}^{\text{Des}} + J_{\text{CO}_2}^{\text{Elec}}$). These reactions are assumed to be simple, one-step recombinations according to Eqns. 2.15 and 2.16 (similar to, e.g., Refs. [11,14,27,29]).

\begin{align}
H_2 + 2\text{HCO}_3^- & \leftrightarrow 2\text{CO}_2 + 2\text{H}_2\text{O} + e^- \quad (2.15) \\
H_2 + \text{CO}_3^{2-} & \leftrightarrow \text{CO}_2 + \text{H}_2\text{O} + 2e^- \quad (2.16)
\end{align}

The HOR for this system, which is a mixed potential problem involving OH\(^-\), CO\(_3^{2-}\), and HCO\(_3^-\) in alkaline media, has not been extensively studied, and no mechanisms or rate determining steps have been proposed to the authors’ knowledge. More than one electron is rarely transferred during a single electrochemical step, however Eqns. 2.15 and 2.16 are only considered at a macroscopic level. Therefore according to species conservation requirements, the amount of CO\(_2\) produced will equal the sum of the amount of CO\(_3^{2-}\) and HCO\(_3^-\) consumed, i.e. $J_{\text{CO}_2}^{\text{Elec}} = (J_{\text{CO}_3} + J_{\text{HCO}_3})_{x=0}$. The free stream concentrations of Eq. 2.14, as well as the CO\(_3^{2-}\) and HCO\(_3^-\) fluxes (which are derived below) are substituted into the CO\(_2\) boundary conditions (see Figure 2.1b or Table 2.2 for the basic form), to obtain Eq. 2.17, which is the final form of the boundary conditions used in the governing equations (Table 2.4).

\begin{align}
J_{\text{CO}_2}^A &= k_{\text{abs}} \frac{H_{\text{CO}_2}^{cc} iA (t_{\text{HCO}_3} + t_{\text{CO}_3})}{2FQ_{\text{H}_2}} - \bar{c}_{\text{CO}_2,aq} \frac{1}{1 + k_{H} k_{\text{abs}} A} \quad (2.17a) \\
J_{\text{CO}_2}^\text{C} &= k_{\text{abs}} \frac{\bar{c}_{\text{CO}_2,aq} - H_{\text{CO}_2}^{cc} \beta_{\text{CO}_2}}{2Q_{\text{Air}}} \quad (2.17b)
\end{align}
The porosity of the gas diffusion layer, $\phi$, can also be incorporated to improve the accuracy such that $A_{\text{eff}} = \phi A$ is used since the CO$_2$ can only absorb/desorb through the pores. The boundary conditions shown in Eq. 2.17 allow for both absorption and desorption (as the case may be) of CO$_2$ at both boundaries. For instance, it may be the case that the CO$_2$ produced by electrochemical reactions raises the anode free stream concentration enough that there is a flux of CO$_2$ into the membrane via absorption.

The boundary conditions on the ionic species at $x = 0$ and $x = L$ prescribe the electrochemical reactions at the boundaries. A requirement of the model is that the number of electrons consumed at the cathode must equal the number of electrons produced at the anode. A common approach to model electrochemical reactions and their electrode potential dependency is using the Butler-Volmer equation. However due to the lack of detailed understanding of CO$_3^{2-}$ and HCO$_3^-$ based HOR reaction mechanism, and the sparse availability of kinetic and thermodynamic data, this is beyond the scope of this work. Instead, the flux of each ionic species at the anode will be modeled by the fraction of total charge it carries inside the membrane, dictated by its transference number, $t_k$:

$$t_k = \frac{z_k C_k u_k}{\sum_j z_j C_j u_j} \quad \text{for} \ k, j = \text{OH}^-, \text{HCO}_3^-, \text{CO}_3^{2-}$$

(2.18)

where the mobilities, $u_k$, are found through the Einstein relation: $u_k = \frac{F}{R T} D_k$. This allows the fluxes at the anode to be modeled by Eq. 2.19
\[ J_{k,x=0} = t_k \frac{i}{nF}, \text{ for } k = \text{OH}^-, \text{HCO}_3^-, \text{CO}_3^{2-} \]  

(2.19)

At the cathode, only Eq. 4 is assumed to take place, thus all of the current is carried by \text{OH}^-, i.e.

\[ J_{k,x=L} = \frac{i}{F}, \text{ for } k = \text{OH}^- \]  

(2.20a)

\[ J_{k,x=L} = 0, \text{ for } k = \text{HCO}_3^-, \text{CO}_3^{2-} \]  

(2.20b)

At high enough \( p^{C_{CO_2}} \), it’s possible that reduction of \text{CO}_2 (\text{CO}_2 \text{RR}) could occur at the cathode.

The \text{CO}_2 \text{RR} mechanism has not been extensively studied in alkaline media, so there is not enough information to include it in this study. More details regarding possible \text{CO}_2 \text{RR} mechanisms are needed to confirm this potentially important aspect of AEMFC operation.

It can be seen that \( \sum k t_k = 1 \), such that \( J_{\text{OH}^-,x=0} + J_{\text{HCO}_3^-,x=0} + \frac{J_{\text{CO}_3^{2-},x=0}}{2} = \frac{i}{F} \) so that the sum of charge coming into the membrane is equal to the sum of the charge going out. The boundary conditions in Eq. 2.19 imply that the kinetics of the HOR are the same regardless of which species is participating, the accuracy of which will be discussed in more detail in the Validation and Results & Discussion sections. The transference number representation is a type of constitutive relation that describes ion flux as a function of species concentration (while ensuring charge neutrality), but not overpotential or kinetic parameters. This representation allows for steady-state consumption of \text{CO}_3^{2-} and \text{HCO}_3^- which is a phenomenon implied by the steady state \text{CO}_2 emission at the anode observed experimentally in, e.g., Refs. [20,27,30].

2.2.3 - Initial Conditions
The initial conditions of the membrane in pure OH\(^-\) form are the same as in Ref [12] and are listed in Table 2.3 (they are simply a reflection of Eq. 2.7 in equilibrium; all other species are initially absent). The degree of dissociation is\(^{12}\)

\[
\alpha = \frac{1}{2} \left[ - \frac{k_4^+}{k_4^- C_0} + \frac{\left( \frac{k_4^+}{k_4^- C_0} \right)^2 + 4 k_4^+}{k_4^- C_0} \right] \tag{2.21}
\]

and the fixed charge concentration is

\[
C_0 = \frac{1}{\lambda} \left( \frac{\rho}{M} \right)_{\text{H}_2\text{O}} \tag{2.22}
\]

**Table 2.3**

*Initial conditions for the pure OH\(^-\) form*

<table>
<thead>
<tr>
<th>Species</th>
<th>Initial Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO(_2)</td>
<td>( \tilde{c}_{\text{CO}_2} = 0 )</td>
</tr>
<tr>
<td>OH(^-)</td>
<td>( \tilde{c}_{\text{OH}} = \alpha C_0 )</td>
</tr>
<tr>
<td>HCO(_3^-)</td>
<td>( \tilde{c}_{\text{HCO}_3} = 0 )</td>
</tr>
<tr>
<td>CO(_3^{2-})</td>
<td>( \tilde{c}_{\text{CO}_3} = 0 )</td>
</tr>
<tr>
<td>TMA(^+)</td>
<td>( \tilde{c}_{\text{TMA}} = \alpha C_0 )</td>
</tr>
<tr>
<td>TMA(OH)</td>
<td>( \tilde{c}_{\text{TMA(OH)}} = (1 - \alpha) C_0 )</td>
</tr>
<tr>
<td>TMA(HCO(_3))</td>
<td>( \tilde{c}_{\text{TMA(HCO}_3)} = 0 )</td>
</tr>
<tr>
<td>TMA(_2)(CO(_3))</td>
<td>( \tilde{c}_{\text{TMA}_2(\text{CO}_3)} = 0 )</td>
</tr>
</tbody>
</table>
To obtain initial conditions for a membrane in carbonate form, the simulation was performed at zero current until steady state was reached. The resulting steady state concentrations are then the initial conditions to be used in trials requiring the membrane to be in carbonate form.

2.2.4 - Numerical Approach

As a reference, the complete system of governing equations solved by the model is listed by species in Table 2.4. The system is solved in MATLAB using a numerical differentiation ordinary differential equation (ODE) solver with quasi-constant step size\textsuperscript{31}, which is suitable for the stiff governing equations encountered in this study. The numerical error is controlled by user inputs for relative, \( r \), and absolute, \( a \), error tolerances, which affect numerical parameters such as the time step. These properties were systematically decreased until they were observed to alter the concentration profiles by a maximum of 0.01%. Based on this study, \( r = 10^{-10} \) and \( a = 10^{-8} \) were chosen. The system was solved on a Dell Precision T7500 workstation with two Intel Xeon processors (2.66 and 2.67 GHz) and 24.0 GB of RAM.

### Table 2.4

**Governing equations for all species**

<table>
<thead>
<tr>
<th>Species</th>
<th>Governing Equation</th>
</tr>
</thead>
</table>
| \( \text{CO}_2 \) | \[
\frac{\partial c_{\text{CO}_2}}{\partial t} = \frac{k_{\text{abs}}}{L} \left( \frac{H_{\text{CO}_2}^c \, iA (t_{\text{HCO}_3} + t_{\text{CO}_3})}{2FQ_{\text{H}_2}} - \bar{c}_{\text{CO}_2, \text{aq}} \right) - \left( \bar{c}_{\text{CO}_2, \text{aq}} - H_{\text{CO}_2}^c \, \frac{p_{\text{CO}_2}^c}{RT} \right) \left( 1 + k_{\text{H}}^c \, \frac{k_{\text{abs}} A}{2Q_{\text{H}_2}} \right) \right)
- k_1^+ c_{\text{CO}_2} c_{\text{OH}} + k_1^- c_{\text{HCO}_3}
\] |
\[
\begin{align*}
\text{OH}^- & \quad \frac{\partial c_{\text{OH}}}{\partial t} = \frac{i}{FL} (1 - t_{\text{OH}}) - k_1^- c_{\text{CO}_2} c_{\text{OH}} + k_1^+ c_{\text{HCO}_3} - k_2^+ c_{\text{HCO}_3} c_{\text{OH}} + k_2^- c_{\text{CO}_3} c_{\text{H}_2\text{O}} + k_4^+ c_{\text{TMA(OH)}} - k_4^- c_{\text{TMA}} c_{\text{OH}} \\
\text{HCO}_3^- & \quad \frac{\partial c_{\text{HCO}_3}}{\partial t} = -t_{\text{HCO}_3} \frac{i}{FL} + k_1^+ c_{\text{CO}_2} c_{\text{OH}} - k_1^- c_{\text{HCO}_3} - k_2^+ c_{\text{HCO}_3} c_{\text{OH}} + k_2^- c_{\text{CO}_3} c_{\text{H}_2\text{O}} + k_5^+ c_{\text{TMA(HCO}_3)} - k_5^- c_{\text{TMA}} c_{\text{HCO}_3} \\
\text{CO}_3^{2-} & \quad \frac{\partial c_{\text{CO}_3}}{\partial t} = -t_{\text{CO}_3} \frac{i}{2FL} + k_2^+ c_{\text{HCO}_3} c_{\text{OH}} - k_2^- c_{\text{CO}_3} c_{\text{H}_2\text{O}} + k_6^+ c_{\text{TMA}_2(\text{CO}_3)} - k_6^- c_{\text{TMA}}^2 c_{\text{CO}_3} \\
\text{TMA}^+ & \quad c_{\text{TMA}} = c_{\text{OH}} + c_{\text{HCO}_3} + 2c_{\text{CO}_3} - c_H \\
\text{TMA(OH)} & \quad \frac{\partial c_{\text{TMA(OH)}}}{\partial t} = -k_4^+ c_{\text{TMA(OH)}} + k_4^- c_{\text{TMA}} c_{\text{OH}} \\
\text{TMA(HCO}_3) & \quad \frac{\partial c_{\text{TMA(HCO}_3)}}{\partial t} = -k_5^+ c_{\text{TMA(HCO}_3)} + k_5^- c_{\text{TMA}} c_{\text{HCO}_3} \\
\text{TMA}_2(\text{CO}_3) & \quad c_{\text{TMA}_2(\text{CO}_3)} = \frac{1}{2} \left( c_0 - c_{\text{TMA}} - c_{\text{TMA(OH)}} - c_{\text{TMA(HCO}_3)} \right)
\end{align*}
\]

In order to provide verification of the numerical method, the steady state limit of the equations shown in Table 2.4 was obtained by setting the partial derivatives with respect to time equal to zero. This resulted in a corresponding set of equations, but with the first four equations now decoupled from the last four equations. The first four equations are still nonlinear in their respective concentrations, but it was observed that they become linear if the denominator, \(B = \sum_k z_k c_k u_k\) of Eq. 2.18, and \(\bar{c}_{\text{OH}}\) are known. Note that the denominator is the same for all three species. This was used to develop a MATLAB code for the matrix solution of the first 4 equations by defining vectors having a span of values for \(\bar{c}_{\text{OH}}\) and \(B\). For each value of \(\bar{c}_{\text{OH}}\), a value of \(B\) was picked in turn, and the corresponding matrix solution for the concentrations was used to calculate an distinct output value of \(B\), called \(B_{\text{out}}\). The appropriate value of \(B\) for the selected \(\bar{c}_{\text{OH}}\) value occurred when \(B_{\text{out}} = B\). This was then repeated for each paired value of \(\bar{c}_{\text{OH}}\).
and $B$, resulting in many possible choices for the correct solution. The solution value of $c_{OH}$ was obtained by requiring the resulting total sum of associated and dissociated TMA groups to be equal to the fixed charge concentration of the membrane (similar to Eq. 2.11). The output solutions from the steady state MATLAB code compared well to the steady state limits from the transient code, as shown by the symbols in Figure 2.4.

2.3 - Results and Discussion

2.3.1 - Validation

The predicted resistance behavior due to the presence of $OH^-$, $CO_3^{2-}$, and $HCO_3^-$, $R = \frac{L}{\sigma A}$, of a Tokuyama A201 membrane as a function of operating current is shown below in Figure 2.2, compared to the experimental results of Suzuki et al.\textsuperscript{11} The group operated an in-house AEMFC with an A201 membrane across a range of current densities with different amounts of $CO_2$ in the cathode gas feed, and measured the membrane resistance using impedance spectroscopy. The experimental operating conditions provided were used in the model: $Q_{H_2} = Q_{Air} = 100 \text{ ml} \cdot \text{min}^{-1}$, $T = 50^\circ \text{C}$, $P_{CO_2}^C = 2,027 \& 5,066 \text{ Pa}$, $A = 5 \text{ cm}^2$, etc. Clearly the performance of the membrane is improved when operated at higher current densities, as will be explored in the following section.
Figure 2.2 – AEM ionic resistance comparison of the predicted results to the experimental results of Suzuki et al.\textsuperscript{11} for a) 2\% cathode CO\textsubscript{2} content and b) 5\% cathode CO\textsubscript{2} content

It can also be seen that the trend of experimental data is more closely matched at higher current densities, specifically beyond about 50 – 100 mA · cm\textsuperscript{−2}. During fuel cell operation, as the current is increased, the potential of the anode increases. This either shifts the potential of the anode closer to the equilibrium potential for some of the possible HOR reactions (decreasing the current provided by that reaction), and/or shifts other reactions further from equilibrium.
(increasing the current). The increased resistance in the experimental data below 50 – 100 mA·cm⁻² compared to the model suggests that at lower current densities, the anode potential is such that more participation of OH⁻ (the most conductive ion) or less participation of HCO₃⁻ or CO₃²⁻ is favored. Experimental studies⁷,³² have shown that the general trend of equilibrium potentials for the OH⁻, CO₃²⁻, and HCO₃⁻ HOR pathways is \( E_{\text{OH}}^\circ < E_{\text{CO}_3}^\circ < E_{\text{HCO}_3}^\circ \) which means that the open-circuit potential (the potential at which there is zero net current) at the anode in the presence of all three species is between \( E_{\text{OH}}^\circ \) and \( E_{\text{HCO}_3}^\circ \). In addition, CO₃²⁻ is more electrochemically active than OH⁻,⁷ which means that the open-circuit potential should be closer to \( E_{\text{CO}_3}^\circ \) to result in zero current. These two facts combined help explain the offset at low current densities: since consumption of CO₃²⁻ (the least conductive ion) is initially low, the resistance of the membrane is higher since OH⁻ has to react more to sustain the operating current. As the current and anode potential are increased, the resistance trend is matched more closely, implying that Eq. 2.19 becomes more accurate and suggesting that anode potential plays a lesser role in the relative consumption rates of the ions. This is further supported by the performance and overpotential curves presented in Ref. [14] which show that the anode potential in a similar system changes rapidly from 0 – 100 mA·cm⁻², but then subsides and increases linearly in a more gradual fashion. Outside of this regime (the activation overpotential regime) the performance decreases linearly, meaning that the anode potential is no longer as much of an influence on the relative reaction rates. The results in Figure 2.2 provide useful insight to the anode processes, including the self-purging mechanism, that occur in an operating AEMFC.

In addition to potential dependence, there are some other experimental considerations that may give rise to the initial discrepancy shown in Figure 2.2. For instance, the period of time between the removal of current and the conductivity measurement is an extremely important
factor. An isolated membrane begins converting to carbonate form as soon as the ORR stops. The AEM can be fully depleted of OH\(^{-}\) in a matter of minutes\(^{12}\), during the course of which its resistance increases which is not accounted for explicitly in the comparison shown in Figure 2.2. Also, physical AEM degradation phenomena such as damage from elevated temperature and ionic stability issues at high pH (nucleophilic attack; pH increases during operation), which would both increase the resistance of the membrane\(^{5,6}\), are not accounted for by this model.

Since the lumped model includes a detailed CO\(_2\) absorption/desorption mechanism, the anode gas stream CO\(_2\) concentration can be predicted and compared to the results of Watanabe et al.\(^{30}\) This experimental study operated an AEMFC with ambient air as the oxidant and monitored the CO\(_2\) in the anode exhaust via mass spectrometry. Their results show that as the current was increased stepwise, a characteristic spike in CO\(_2\) concentration was observed, followed by monotonic decay to a non-zero baseline value. The opposite effect was observed for decreasing current. The molar fraction of CO\(_2\) in the anode, \(\chi_{CO_2}^A\), can be predicted through a macroscopic mass balance as shown in Eq. 2.23:

\[
\chi_{CO_2}^A = \frac{\dot{n}_{CO_2}}{\dot{n}_{CO_2} + \dot{n}_{H_2} - \dot{n}_{H_2}^I}
\]  

(2.23)

where \(\dot{n}_{CO_2} = A \cdot J^{A,Tot}_{CO_2}\) is the molar flow rate of CO\(_2\) exiting the AEM, \(\dot{n}_{H_2} = \frac{PQH_2}{RT}\) is the molar flow rate of hydrogen entering the gas stream, and \(\dot{n}_{H_2}^I = \frac{iA}{2F}\) is the molar rate of hydrogen consumed at the electrode to supply the electrons necessary for operation. Using this definition the lumped model can be compared to experimental results, as shown in Figure 2.3. The spikes in CO\(_2\) emission are due to increased electrochemical consumption of HCO\(_3^-\) and CO\(_3^{2-}\) at the
anode when the current is stepped up. The model is able to capture some of this behavior as a result of the balance of Eqns. 2.4-2.9: the OH\(^-\) being introduced by the ORR initially reacts in Eqs. 2.5 and 2.6 before beginning to react at the anode, at which point consumption of CO\(_3^{2-}\) and HCO\(_3^-\) can subside. The spikes are larger in the experiment most likely due to spatial effects. The concentration of OH\(^-\) is locally lower at the anode, so the increase in current is supplied entirely by HCO\(_3^-\) and CO\(_3^{2-}\) until the incoming OH\(^-\) has been transported to the anode. The qualitative aspects of this phenomenon are replicated, specifically the characteristic time it takes for the CO\(_2\) emission to return to the baseline value. Thus the results in Figure 2.3 further validate the transient behavior of the model to be used in this study.

![Graph showing mole fraction of CO\(_2\) in anode gas stream predicted by this study compared to experimental data from Watanabe et al.\(^30\)](image)

**Figure 2.3 – Mole fraction of CO\(_2\) in anode gas stream predicted by this study compared to experimental data from Watanabe et al.\(^30\)**

2.3.2 - Performance Results and Parametric Studies
The transient results of the governing equations are shown in Figure 2.4. These results were obtained using the nominal parameters listed in Table 2.5 at three different current densities, and the circles on the plots are the concentrations obtained from the independent steady state model described in the Numerical Methods section.

Table 2.5
Nominal physical and operating parameters

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_k^+, k_k^-, K_k, D_k$</td>
<td>See Ref. [12], Table 2</td>
</tr>
<tr>
<td>$k_{abs}$ (cm s$^{-1}$)</td>
<td>Selected such that $Bi \geq 10^4</td>
</tr>
<tr>
<td>$A$ (cm$^2$)</td>
<td>5.0</td>
</tr>
<tr>
<td>$\phi$</td>
<td>0.78</td>
</tr>
<tr>
<td>$H_{CO_2}^{cc}$</td>
<td>$3.3 \times 10^{-4}RT \exp\left[(2400 + T)\left(\frac{1}{T} - \frac{1}{298.15}\right)\right]$</td>
</tr>
<tr>
<td>$Q_{H_2}, Q_{Air}$ (cm$^3$ s$^{-1}$)</td>
<td>1.667</td>
</tr>
<tr>
<td>$P_{CO_2}^C$ (Pa)</td>
<td>39</td>
</tr>
<tr>
<td>$T$ (K)</td>
<td>298</td>
</tr>
<tr>
<td>$\rho_{H_2O}$ (g cm$^{-3}$)</td>
<td>1.0</td>
</tr>
<tr>
<td>$M_{H_2O}$ (g mol$^{-1}$)</td>
<td>18</td>
</tr>
<tr>
<td>$IEC$ (mmol g$^{-1}$)$^{13}$</td>
<td>1.68</td>
</tr>
<tr>
<td>$L$ (cm)</td>
<td>0.0028</td>
</tr>
<tr>
<td>$\lambda$ $^{35}$</td>
<td>15</td>
</tr>
<tr>
<td>$\rho_{mem}$ (g cm$^{-3}$)$^{13}$</td>
<td>1.0</td>
</tr>
</tbody>
</table>
The initial conditions correspond to the carbonated state of the membrane, which refers to an isolated membrane with Eqns. 2.5-2.9 in equilibrium. Thus when a current is applied, there is an immediate effect on the species concentrations. The CO$_2$ concentration initially spikes since the HOR consumes CO$_3^{2-}$ and HCO$_3^-$ according to Eqs. 2.14 and 2.15 due to initially little OH$^-$ in the membrane. As discussed in the Validation section these reactions produce CO$_2$, some of which is then absorbed by the membrane according to Eq. 2.17a in order to establish equilibrium between the membrane and the anode gas stream. The OH$^-$ concentration, initially low, increases as ions are supplied by the ORR, Eq. 2.4. HCO$_3^-$ is initially abundant, but is depleted due to Eq. 2.15 (represented by Eq. 2.19). On the other hand, the CO$_3^{2-}$ concentration is initially low and increases as the increasing OH$^-$ concentration shifts Eq. 2.6 toward the products. The reason CO$_3^{2-}$ consumption doesn’t mimic HCO$_3^-$ consumption is because the electrochemical consumption of CO$_3^{2-}$ ions is less significant at first since Eq. 2.19 is proportional to concentration. Therefore CO$_3^{2-}$ briefly accumulates until Eq. 2.6 and Eq. 2.16 balance each other. Lastly, the concentrations of associated TMA groups (that is, anions bound to TMA$^+$ sites) generally mimic the behavior of their respective associated ion, since Eqns. 2.7-2.9 tend toward equilibrium. It can also be seen that increasing the current density decreases the transient period and changes the steady state concentrations. These effects will become important when observing the conductivity behavior. The transient period is a reflection of only the ion exchange and CO$_2$ absorption/desorption processes. The evolution of spatial concentration profiles could also affect the transient response, but the diffusion and migration (processes which are functions of concentration gradient and local concentration) time constants are generally on the order of just a few seconds$^{20}$. 
Figure 2.4 – Transient concentration profiles obtained using nominal operating parameters (Table 2.5) for a membrane initially in the carbonate state; open circles are obtained from independent steady state solutions.

The ion concentrations from Figure 2.4 can be used to predict the membrane’s ionic conductivity according to Eq. 2.12. Membrane conductivity is a function of operating current, as shown in Figures 2.2, 2.5, and 2.6. The increase in membrane conductivity with current is due to
the self-purging mechanism, whereby incoming \( \text{OH}^- \) (which is more the most mobile species) supplied by the ORR displaces \( \text{CO}_3^{2-} \) and \( \text{HCO}_3^- \) as they are consumed by reactions at the anode\(^{2,14,20,22}\). The self-purging mechanism is an important phenomenon unique to AEMs, and the model reported in this study can be used to investigate its response to operating conditions, as well as how it is affected by membrane properties. The following results, Figures 2.5 and 2.6 will demonstrate this. Herein when conductivity is plotted, the steady-state values obtained using the nominal parameters shown in Table 2.5 are shown unless otherwise noted.
Figure 2.5 – Conductivity vs. a) Time (membrane initially in carbonate state), b) Temperature, and c) $P_{CO_2}^C$ (shown as ppm of total gas), and d) pH vs. $P_{CO_2}^C$ of an A201 membrane at different operating currents ($i=100, 300, 500, 700, 900 \text{ mA} \cdot \text{cm}^{-2}$).

First, certain operating conditions like temperature, time, and $P_{CO_2}^C$ were investigated, as shown in Figure 2.5. The plots are normalized to the membrane conductivity for the pure OH$^-$ state when the cathode gas stream is free of CO$_2$: $\sigma_{0,298K} = 0.0184 \text{ S} \cdot \text{cm}^{-1}$ for Figures 2.5a and 2.5c (this value was calculated by the model described in this work, and compared well to the value presented in Ref. [12]), and $\sigma_{0,373K} = 0.0531 \text{ S} \cdot \text{cm}^{-1}$ for Figure 5b. The transient behavior of the membrane is investigated in Figure 2.5a. It can be seen that as current density increases, the conductivity rate of change increases as well. In addition, the maximum recovery compared to the pure OH$^-$ state (steady state value) is greater. Therefore, in the interest of maintaining high membrane conductivity, the cell should be operated at the highest possible current density. However, degradation aspects such as the membrane drying out are not considered, which may become important at high current densities. Figure 2.5b shows that the
conductivity is significantly affected by operating temperature. This is mostly due to the effects of temperature on the equilibrium constants for Eqns. 2.5 and 2.6, $K_1 = \frac{k_1^+}{k_1^-} = \frac{c_{\text{HC}O_3^-}}{c_{\text{CO}_2}\text{CO}_H}$ and 

$$K_2 = \frac{k_2^+}{k_2^-} = \frac{c_{\text{CO}_3^{2-}}c_{\text{H}_2\text{O}}}{c_{\text{HC}O_3^-}c_{\text{OH}}}$$

which are shifted to favor the reactants as temperature is increased. This increases the equilibrium value of OH$^-$ in the membrane, which increases the conductivity. Temperature also has the effect of lowering the Henry’s law constant, $k_{Hc}^{CC}$, which reduces both absorption and desorption of CO$_2$.

Figure 2.5c affirms the experimentally-observed trend$^{11,14,29}$ that membrane conductivity decreases as $P_{\text{CO}_2}^c$ is increased. Increasing $P_{\text{CO}_2}^c$ increases the free-stream CO$_2$ concentration in the cathode gas stream, $c_{\text{CO}_2}^c(g)$ (displayed as ppm of total gas in the figure), which shifts Eqns. 2.5 and 2.6 toward the products, thus favoring CO$_3^{2-}$ and HCO$_3^-$ in the membrane. The onset of conductivity loss occurs between $10 - 100$ ppm CO$_2$ in the cathode gas stream, depending on the current, which demonstrates the importance of maintaining CO$_2$-free gas streams. In the first regime, up to $10 - 100$ ppm CO$_2$ depending on the operating current, the ORR is able to supply enough OH$^-$ (especially at higher current densities) to displace the CO$_3^{2-}$ and HCO$_3^-$ produced by the relatively low levels of CO$_2$, so the conductivity drop is not as pronounced. As the incoming CO$_2$ concentration increases (the $> 10 - 100$ ppm regime), the CO$_2$ flux into the membrane is greater, and the concentrations of CO$_3^{2-}$ and HCO$_3^-$ rise accordingly, decreasing the conductivity of the membrane. Although there appears to be a third regime where the conductivity drop begins to plateau, free stream CO$_2$ concentrations greater than 10% were not investigated since some assumptions of the model may become invalid at high concentrations. For instance, reduction of CO$_2$ at the cathode may start to contribute to the total current if it is concentrated enough, which would decrease the flux of OH$^-$ ions due to the ORR (this may also contribute to
the offset initially seen in Figure 2.2; it is unknown at what concentration CO₂ begins contributing significantly to the cathode reaction). Furthermore, the accuracy of the Henry’s Law absorption model decreases for more concentrated gases.

In addition to conductivity, the pH of the membrane as a function of operating current and $P_{CO_2}^C$ is shown in Figure 2.5d. The pH is corrected for the ionic strength of the membrane using the Davies equation to find the hydrogen ion activity. The membrane’s pH drops as $P_{CO_2}^C$ increases since the resulting $CO_3^{2-}$ and $HCO_3^-$ ions displace $OH^-$ from the membrane. In addition, there is less of a pH drop at higher current densities due to the influx of $OH^-$ from the ORR. The results of Figures 2.5c and 2.5d combined present an interesting optimization problem for the use of AEMFCs. Clearly the presence of CO₂ in the cathode gas feed results in a drop in the membrane’s conductivity. However the drop in pH due to CO₂ interactions results in a less caustic environment, which leads to reduced electrolyte degradation and conductivity loss.⁳⁶

Although the results are not presented graphically here, it is worth discussing the effects of $Q_{Air}$ and $Q_{H_2}$ on CO₂ levels in the membrane. As $Q_{Air}$ and/or $Q_{H_2}$ are increased, the free stream concentrations of CO₂ (Eq. 2.14) approach the value at the entrance of the corresponding gas channel due to the decrease in boundary layer thickness. Therefore, the common practice of increasing the excess air as the fuel cell’s current is increased (to avoid concentration losses) would also have the effect of increasing $J_{CO_2}^C$. On the other hand, increasing $Q_{H_2}$ would increase the rate at which CO₂ is swept out of the gas stream, which would improve the self-purging effect.

Next, a parametric study was performed on membrane properties. Somewhat surprisingly, the ionic conductivity (normally an intrinsic property) is a function of the membrane’s thickness, as seen in Figure 2.6a, with conductivity decreasing with thickness. This
is mainly because the influx of $\text{OH}^-$ due to the ORR is independent of membrane thickness, so it has a greater effect on thinner membranes. In other words, in thinner membranes the ions introduced by the ORR constitute a greater percentage of the total ions, so the conductivity is reclaimed more easily.

Figure 2.6 – Ionic conductivity vs. current density of an AEM with nominal A201 properties as

- a) the membrane thickness ($L=14, 28, 56, 84, 112 \ \mu\text{m}$), b) the ionic exchange capacity
(IEC=1.2, 1.4, 1.6, 1.8 mmol · g⁻¹), and c) the hydration state (λ=5, 7, 9, 11, 13, 15, 17) are varied.

Figure 2.6b demonstrates the increase in conductivity with the membrane’s ion exchange capacity (IEC). The IEC acts like the inverse of a molecular weight for the functional groups of the membrane, i.e. \( IEC = \frac{c_{TMA^+}}{\rho_{mem}} \). Thus, with higher IECs, an increase in conductivity is expected, which is why some curves can surpass a normalized conductivity of unity (since the curves are normalized to the conductivity obtained with \( IEC = 1.68 \text{ mmol} \cdot \text{g}^{-1} \)).

Lastly, the effects of water uptake were investigated, shown in Figure 2.6c. The water uptake coefficient expresses the relative amount of water compared to the fixed cation concentration of the AEM, \( \lambda = \frac{c_{H_2O}}{c_{TMA^+}} \). The water uptake has a significant effect on the porosity of the membrane as discussed in the validation section, which in turn affects the diffusivities of the ionic species in the membrane. As the porosity is increased, the ions travel through the membrane more freely, which is reflected in the increase in \( D_{k}^{eff} \).

2.4 - Conclusions

A system of spatially averaged Nernst-Planck equations was developed to model the response of an AEM within an operating fuel cell. Solution of the system yields the average transient concentrations of aqueous species as a function of various operating conditions and membrane properties, which were used to calculate the membrane’s ionic conductivity. The self-purging mechanism was examined. It was observed that the ionic conductivity of the membrane can be partially recovered compared to that of the pure OH⁻ state during operation at even moderate current densities. Parametric studies were performed on operating conditions and
membrane properties in order to aid the design of more effective AEM fuel cell systems. The ionic conductivity of the AEM can be enhanced at higher temperatures, operating currents, and hydration states, and at the lowest CO$_2$ gas feed concentrations. In addition, it was found that thinner membranes with higher IECs are desirable in the interest of good conductivity. However, it is known that high IECs can adversely affect AEMs in other ways.$^{26}$ Thus these results should be considered in conjunction with existing fuel cell knowledge regarding water management, chemical/mechanical stability, etc. when designing AEM systems. To achieve the simplicity of the model described herein, some mathematical and physical assumptions were employed. Future work, some of which is already ongoing, could improve the accuracy of the model by accounting for spatial variation in concentrations, water management effects, and electrode polarization, however it is believed that the trends predicted are reasonable for operating AEMs.

List of Symbols

- $c$: Concentration, mol $\cdot$ m$^{-3}$
- $D$: Diffusion coefficient, m$^2$ $\cdot$ s$^{-1}$
- $z$: Ionic charge
- $F$: Faraday’s constant, C $\cdot$ mol$^{-1}$
- $R$: Universal gas constant, J $\cdot$ mol$^{-1}$ $\cdot$ K$^{-1}$
- $T$: Temperature, K
- $\dot{R}$: Reaction source term, mol $\cdot$ m$^{-3}$ $\cdot$ s$^{-1}$
- $J$: Molar flux, mol $\cdot$ m$^{-2}$ $\cdot$ s$^{-1}$
- $k^+$: Forward kinetic rate constant
- $k^-$: Backward kinetic rate constant
- $L$: Thickness of membrane, m
- $\bar{A}$: Spatial average of "A", where $A = A(x)$
- $p$: Partial pressure, N $\cdot$ m$^{-2}$
\( Q \) \hspace{0.5cm} \text{Volume flow rate, cm}^3 \cdot \text{s}^{-1} \\
\( k_{\text{abs}} \) \hspace{0.5cm} \text{Absorption coefficient, cm} \cdot \text{s}^{-1} \\
\( H_{\text{CO}_2}^c \) \hspace{0.5cm} \text{Dimensionless Henry solubility} \\
\( i \) \hspace{0.5cm} \text{Current density, A} \cdot \text{cm}^{-2} \\
\( A \) \hspace{0.5cm} \text{Geometric electrode area, cm}^2 \\
\( u \) \hspace{0.5cm} \text{Mobility, cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1} \\
\text{Greek} \\
\( \varphi \) \hspace{0.5cm} \text{Electrostatic potential, V} \\
\( \phi \) \hspace{0.5cm} \text{Gas diffusion layer porosity} \\
\( \lambda \) \hspace{0.5cm} \text{Water uptake coefficient} \\
\( \delta \) \hspace{0.5cm} \text{Solvent/membrane diffusivity ratio} \\
\( \varepsilon \) \hspace{0.5cm} \text{Membrane porosity} \\
\( \rho \) \hspace{0.5cm} \text{Density, g} \cdot \text{cm}^{-3} \\
\text{Superscripts} \\
\( A \) \hspace{0.5cm} \text{Anode} \\
\( C \) \hspace{0.5cm} \text{Cathode} \\
\( \text{Des} \) \hspace{0.5cm} \text{Desorption} \\
\( \text{Elec} \) \hspace{0.5cm} \text{Electrochemical} \\
\( \text{Tot} \) \hspace{0.5cm} \text{Total} \\
\( \text{eff} \) \hspace{0.5cm} \text{Effective} \\
\text{Subscripts} \\
\( k \) \hspace{0.5cm} \text{Species ‘}k\text{’} \\
\( (g) \) \hspace{0.5cm} \text{Gaseous} \\
\( aq \) \hspace{0.5cm} \text{Aqueous}
Chapter 3: Effects of CO₂ on Electrospun Anion Exchange Membranes

This chapter is adapted from work submitted to *J. Electrochem. Soc.* in Jan. 2019

3.1 - Overview

Electrospinning and radiation grafting are two processing methods that can be used to manufacture anion exchange membranes (AEMs) with good mechanical stability while also maintaining high conductivities. The unique properties of electrospun and radiation grafted AEMs may affect their response to carbon dioxide absorption, a process known to degrade the conductivity of traditional AEMs. In this study, we develop two models that allow us to predict the response of these membranes upon exposure to CO₂ in an operating fuel cell. In the first model, the morphological parameters of the electrospun membrane are analytically determined as a function of ionomer fiber content using a simplified picture of ion transport through the network of ionomer fibers. The results of this morphology model are then used in the second model, which numerically predicts the carbonation dynamics and ionic conductivity of the AEMs during fuel cell operation. The model predictions are validated to experiments performed on fuel cells employing radiation grafted AEMs. The results herein investigate the membranes’ conductivity loss/reclamation as a function of operating current, cathode gas CO₂ content, and ionomer fiber content.

The allure of using low-cost catalysts has sparked a steadily-increasing interest in anion exchange membrane (AEM) fuel cells over the last 10 years. However, a remaining challenge is to produce highly conductive AEMs with improved chemical and mechanical stability. AEMs are derived from polymeric materials with tethered cationic groups. The ionic (hydrophilic) nature of these groups result in the absorption (uptake) of solvents – typically water. Water
solvates the ionic group and facilitates anionic transport through the membrane. Strategies to improve AEM conductivity often focus on changing the cation chemistry, its attachment to the polymeric backbone, and/or increasing the ion exchange capacity (IEC) of the membrane\(^1\). Nevertheless, these modifications also affect other critical properties including the chemical and mechanical stability of the membrane\(^5,6\). In the context of AEMs, chemical stability refers to the ability of the film to resist a number of chemical reaction pathways that attack the positively charged side groups\(^6\). Mechanical stability refers to the apparent strength and stiffness of membranes during the changes in materials properties and/or dimensional changes from significant water uptake and swelling that occur as the membrane ages in the reacting environment (e.g. embrittlement due to degradation of the polymer backbone(s), plastication, creep, etc.).

As recently discussed by Gottesfeld et al.\(^17\), composite membranes employing an inert supporting phase can help achieve the goal of highly chemically and mechanically stable AEMs. Electrospinning is one technology that can introduce such a supporting phase, in order to decouple aspects of a membrane’s conductivity and stability. Specifically, this approach can enable membranes with increased IECs while also maintaining their mechanical integrity\(^26\). In addition, electrospun membranes can exhibit improved resistance to nucleophilic attack by forming a better microphase separated structure\(^37\). Previous electrospun membranes were typified as crosslinked polymer composites consisting of either a) a fiber network of hydrophilic ion-conducting phase embedded in an inert, supporting phase, or b) a hydrophilic ion-conducting phase supported by a fiber network of the hydrophobic phase. The hydrophobic phase can be used to control swelling, which enables a higher IEC for the ionomer phase while providing mechanical strength and stability. Ballengee and Pintauro studied both cases for proton exchange
membranes (PEMs) and found that although both structures exhibited comparable conductivities, case (a) resulted in stronger membranes. This was attributed to the greater connectivity of the inert phase when used as the supporting matrix. Park et al. studied case (a) for AEMs, and obtained similar findings.

Other methods for manufacturing composite membranes, like two-phase solution casting, can also control the swelling properties of the membrane, however good mechanical properties require a homogenous dispersion of the phases, which can be difficult to achieve. Electrospinning is a forced assembly technique that combines the dissimilar polymers into a well-dispersed mat, which can then be further processed into a fully dense membrane. The conductivity of electrospun AEMs strongly depends on the volume fraction of the ionomer phase, $f_I$, with pristine hydroxide ion ($\text{OH}^-$) conductivities up to 65 mS-cm$^{-1}$ having been reported for 65 wt. % ionomer fiber membranes in liquid water at 23°C. This is because the ionomer phase is responsible for most of the water uptake. At lower $f_I$, the decreased water content results in morphologies that are detrimental to conductivity, such as reduced cross-sectional area and increased tortuosity. Furthermore, the water uptake is a nonlinear function of ionomer content, meaning that the hydrophobic supporting phase also plays a role in this process, and so it can be difficult to predict the role of $f_I$ on conductivity a priori.

The transport of ions through electrospun AEMs has been explored by DeGostin et al. A fiber network (FN) model was devised in this study, which simulated the ionomer fibers as a network of randomly oriented resistor segments and accounted for inter- and intra-layer contacts. The FN model then solved Kirchhoff’s circuit laws across the discreet system to calculate the total conductivity of the network. It was also demonstrated that the electrospun membrane’s morphology could be considered using analytical homogenization approaches, e.g. based on the
Bruggeman relation, porous media theory, and others\textsuperscript{40,41}. These homogenized approaches do not offer as much small-scale detail as a direct simulation of the fibrous network, but they can quickly evaluate macro-scale morphological parameters of the system.

Both DeGostin\textsuperscript{23}, and Park et al.\textsuperscript{26} emphasized case (a) in their studies, and so the same types of membranes will be considered here. Because Ballengee et al. demonstrated similar conductivity performance (and hence morphology) between the two cases, it’s possible that the results herein could also be generalized to case (b). In addition, two-phase blended membranes, such as Nafion/poly(vinylidene fluoride) systems, appear to exhibit similar microstructures to electrospun membranes when the phases are well-dispersed\textsuperscript{39,42,43}, and therefore could also be described by the ensuing analysis. However, these remain topics to be verified in future work.

Existing electrospun membrane models do not consider the effects of carbon dioxide. It is known from previous work that CO\textsubscript{2} degrades membrane performance upon absorption by partaking in carbonate- and bicarbonate-forming reactions\textsuperscript{12,13} (CO\textsubscript{3}\textsuperscript{2−} and HCO\textsubscript{3}− respectively). The formation of these less mobile ions lowers the membrane’s conductivity. In the past we have developed a model\textsuperscript{44} to study the influence of operating conditions (such as current density, temperature, and cathode gas CO\textsubscript{2} content) on this effect. AEM carbonation and its effect on AEM conductivity has been extensively studied\textsuperscript{11–13,15,18,20,24,25,45}, but not yet applied to electrospun AEMs. Because the morphology and bulk material properties of electrospun AEMs can be considerably different from traditional AEMs, it is worthwhile to examine their susceptibility to CO\textsubscript{2}. Furthermore, the tunability of \( f_i \) is a key feature of these materials, but the influence of ionomer fraction on CO\textsubscript{2} absorption and reactions is yet unknown.

In the present study, we investigate the effects of CO\textsubscript{2} on \textit{in situ} electrospun AEM conductivity by building upon previously developed theory. An analytical electrospun
The morphology model is developed based on a simplified view of the layered fibrous structure, which is then integrated into a transient, spatially averaged CO$_2$ model. This approach provides independent control of key design/operation parameters, especially $f_I$, current density, and CO$_2$ content, which will be used to elucidate their specific role in the system’s response to CO$_2$. These results are then compared to selected single-phase AEMs, to put the electrospun membranes in context with more traditionally-structured materials. For example, the CO$_2$ response of the Tokuyama A201 AEM$^{46}$ and radiation-grafted (RG) vinylbenzyl chloride (VBC) – poly(ethylene-cotetrafluoroethylene) (ETFE) AEMs of Varcoe et al.$^{47}$ are presented. In addition, AEMFCs employing radiation-grafted VBC-ETFE AEMs manufactured using an improved procedure$^{48}$ were assembled for this study, to provide additional validation and comparison of the CO$_2$ model. These AEMs were used in recent AEMFC studies demonstrating very good performance ($1.4 – 1.9 \text{W} \cdot \text{cm}^{-2}$)$^{4,49}$, and should represent a new standard material for comparison of novel AEM designs.

### 3.2 - Theory

This section describes the theoretical models used in this work, namely, the analytical electrospun morphology (EM) model, and the CO$_2$ model developed previously$^{44}$. The EM model determines how $f_I$ affects the macro-scale morphological parameters like effective transport length and porosity, and is based on the analytical theory developed alongside the fiber network model of DeGostin et al.$^{23}$. The procedure is outlined in the flowchart shown in Figure 3.1, where the solid line indicates the path chosen in this work, and the dotted line indicates an alternate, equally effective approach. To begin, an electrospun AEM design is chosen (i.e. $f_I$ and ionomer fibers with given properties are selected), and the CO$_2$-free conductivity of the
membrane is measured (e.g. numerically or experimentally). This reference conductivity value is used to calibrate the EM model, which describes the homogenized electrospun morphology in a manner appropriate for use in the CO₂ model. It should be noted that the reference conductivity value must be obtained after all swelling takes place (for experimental data) or is simulated (for numerical data). The manner in which an electrospun membrane swells, i.e. isotropic vs. anisotropic, can strongly influence the resulting morphology, and in this work we consider already-swelled membranes. Lastly, the CO₂ model is run using these parameters, to simulate the effects of CO₂ on the membrane(s).
3.2.1 - Discrete Morphology Model for Electrospun Membranes

Most theoretical models describing the behavior of aqueous species in AEMs use a homogenized approach in which transport and reactions take place as though in ordinary water
(see, for example, Refs. [12, 15, 18–20, 25, 26]). The cross-sectional area and effective length of the membrane, as well as the species’ diffusion coefficients, are adjusted to account for the membrane’s morphology. A similar approach can be used to model transport in electrospun AEMs; however, it is first necessary to determine how $f_i$, a key design parameter unique to electrospun AEMs, influences these properties. Since the ionomer fibers are responsible for water uptake in the electrospun AEM, it is reasonable to expect that low $f_i$ membranes will have different properties and morphologies than membranes with a high $f_i$.

In the FN model approach, the tortuous, random, 3-D network of ionomer fibers was directly simulated, so expressions relating $f_i$, $\lambda$, $L_{eff}$, etc. were not needed. Herein we present an analytical procedure to map the fibrous morphology to the homogenized inputs used in the CO$_2$ model, especially their dependence on $f_i$. The benefit of the analytical approach is that it is fast and only needs to be performed once for a certain set of membrane properties, thus enabling the CO$_2$ model to predict electrospun AEM performance with almost no added computational cost.

**Figure 3.2** – Schematic representations of a) the electrospun membrane morphology model, and b) the CO$_2$ model.
The CO₂ model requires knowledge of the water volume fraction, \( \varepsilon \), the effective membrane thickness, \( L_{\text{eff}} \), and effective area, \( A_{\text{eff}} \). The morphology model used in this work is based on a simplified view of the electrospun fiber network, in which the layout of ionomer fibers is approximated by a uniform grid as demonstrated in Figure 3.2a. The density and spacing of the grid are dictated by the membrane and ionomer fiber dimensions, as well as the number of ionomer fibers, \( n \), necessary to achieve the chosen \( f_i \). In this representation, the volume fraction of ionomer phase is expressed as

\[
f_i = \frac{\left( \frac{\pi}{4} \right) d_i^2 n}{w \delta} \tag{3.1}
\]

where \( d_i \) is the diameter of the ionomer fibers, \( w \) is the geometric width of the membrane, and \( \delta \) is the thickness of one layer. At each chosen \( f_i \), Eq. 3.1 can be rearranged to solve for \( n \).

Once the number of ionomer fibers per layer is known, the transport path length through the entire membrane, \( L_{\text{eff}} \), can be approximated using Eq. 3.2, where \( N_{\text{layers}} \) is the total number of layers and \( k \) is a scaling constant that accounts for the tortuous nature of the electrospun membrane, and will be evaluated later. The number of layers is chosen at the user’s discretion to make thicker or thinner membranes.

\[
L_{\text{eff}} = k N_{\text{layers}} \left( \delta + \frac{w}{\frac{n}{2} - 1} \right) \tag{3.2}
\]
An assumption of this approach is that the ions will travel exactly one grid spacing in-plane before traversing to the next layer, as depicted by the red arrows in Figure 3.2a. This forgoes any direct modeling of the tortuosity, which is corrected by the scaling constant $k$.

The total number of transport paths is estimated as $N_{\text{paths}} = \alpha (n^2/4)$, where $n^2/4$ is the ideal number of intersections, and $\alpha$ is a scaling constant, bounded by zero and one, accounting for the possibility of incomplete and/or redundant transport paths. This allows the volume fraction of water to be calculated as the ratio of total water volume to membrane volume:

$$\varepsilon = \frac{N_{\text{paths}} L_{\text{eff}} A_I}{w^2 h} = \frac{\beta \frac{\pi n^2}{16} N_{\text{layers}} \left( \delta + \frac{w}{n} \right) f_{H_2O} d_I^2}{w^2 h}$$

(3.3)

where $A_I$ is the cross-sectional area of an ionomer fiber, $h = \delta N_{\text{layers}}$ is the geometric thickness of the membrane, $\beta = k \alpha$, and $f_{H_2O}$ is the water volume fraction within the ionomer phase. The value of $f_{H_2O}$ was calculated from the data of Park et al.\textsuperscript{26} and found to be approximately 0.63.

Eq. 3.3 describes the porosity, $\varepsilon$, in terms of known parameters, except for the scaling parameter $\beta$. In order to determine this parameter, we first implement a homogenized conductivity model, e.g. the Dusty Fluid model\textsuperscript{51} given by Eq. 3.4,

$$\sigma_{\text{eff}} = \frac{F^2}{RT} \sum_k z_k^2 D_k^{\text{eff}} (1 + \lambda) \frac{1}{\lambda (1 + \nu_k)} c_k$$

(3.4)

where $z_k$ is the valence of ionic species $k$, $D_k^{\text{eff}}$ is the effective diffusivity, $\lambda$ is the water uptake number, and $\nu_k$ is the ion-solvent/ion-membrane diffusivity ratio. In the absence of CO$_2$, $c_k$ is
simply the concentration of dissociated OH\(^-\). The conductivities found using Eq. 3.4 depend on membrane’s morphology according to the Bruggeman relation, \(D_k^{\text{eff}} = \varepsilon^q D_{k,\text{H}_2\text{O}}\), which has been successfully used to model the effective diffusivities of the aqueous species in the past\(^{12,22}\); where \(\varepsilon\) is the porosity (i.e. water volume fraction in the membrane), \(D_{k,\text{H}_2\text{O}}\) is the binary diffusion coefficient of species \(k\) in water, and \(q = 1.5\) is the Bruggeman exponent. The value of \(\varepsilon\) in the Bruggeman relation is replaced by Eq. 3.3, and the resulting effective diffusivity is substituted into Eq. 3.4, resulting in Eq. 3.5.

\[
\sigma_{0,f} = \frac{F^2}{RT} \sum_k \left( \beta \frac{\pi n^2}{16w^2h} N_{\text{layers}} \left( \delta + \frac{w}{n} \right) f_{\text{H}_2\text{O}a_i^2} \right)^q \frac{z_k^2 D_{k,\text{H}_2\text{O}}(1 + \lambda)}{\lambda(1 + n_k)} c_k \tag{3.5}
\]

Eq. 3.5 is then equated to the CO\(_2\)-free conductivities at each \(f_i\) previously calculated by the FN model (i.e. the FN result is treated as a “known”). Alternatively, \(\sigma_{0,f}\) results obtained through a different method, e.g. experimentally, could also be used although this is not done in this work. The only unknown in Eq. 3.5 is \(\beta\), which can now be solved for as a function of \(f_i\).

Finally, it is noted that the maximum number of transport paths should occur at the highest \(f_i\). Therefore \(\alpha\) at \(f_{i,\text{max}}\) is set equal to unity, which in turn gives \(k = \beta(f_{i,\text{max}})\) and \(\alpha = \frac{\beta(f_i)}{k}\). With these expressions, the parameters \(\varepsilon, L_{\text{eff}},\) and \(A_{\text{eff}} = \varepsilon w^2\) can all be determined analytically as functions of \(f_i\) and used in the CO\(_2\) model. Selected results of this procedure are presented in Table 3.1. One can see that as \(f_i\) increases, the porosity increases, which should be expected since the ionomer fibers are responsible for water uptake. This approach uses a similar methodology as the analytical conductivity models developed alongside the FN model in Ref.
[23], which were shown to compare very well to the FN predictions (see, e.g., Figure 4 in the mentioned reference).

Table 3.1

*Parameters found from the EM model for selected $f_i$*

<table>
<thead>
<tr>
<th>$f_i$</th>
<th>$\sigma_{0,\text{eff}}$ (mS/cm)</th>
<th>$\varepsilon$</th>
<th>$L_{\text{eff}}$ (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.4</td>
<td>7.70</td>
<td>0.183</td>
<td>65.0</td>
</tr>
<tr>
<td>0.5</td>
<td>13.00</td>
<td>0.259</td>
<td>55.7</td>
</tr>
<tr>
<td>0.6</td>
<td>19.74</td>
<td>0.342</td>
<td>49.6</td>
</tr>
<tr>
<td>0.7</td>
<td>28.65</td>
<td>0.439</td>
<td>45.2</td>
</tr>
<tr>
<td>0.8</td>
<td>42.08</td>
<td>0.567</td>
<td>41.9</td>
</tr>
<tr>
<td>0.9</td>
<td>64.81</td>
<td>0.756</td>
<td>39.4</td>
</tr>
</tbody>
</table>

The ionomer fiber properties are also necessary in the model, and can be found in the literature. In this study we use the nominal properties of the membranes made by Park et al.\textsuperscript{26} and simulated by DeGostin et al.\textsuperscript{23}, which are listed in Table 3.2.

Table 3.2

*Nominal ionomer fiber properties used in this study*

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$d_I$</td>
<td>700 nm</td>
</tr>
<tr>
<td>$\delta$</td>
<td>890 nm</td>
</tr>
<tr>
<td>$w$</td>
<td>2.24 cm</td>
</tr>
<tr>
<td>$N_{\text{layers}}$</td>
<td>14</td>
</tr>
</tbody>
</table>

3.2.2 - CO$_2$ Model

A transient, spatially-averaged CO$_2$ model has been developed to account for operating conditions of an AEMFC and their effect on the resistive losses incurred from the membrane
(i.e., changes in ionic conductivity of the AEM)\textsuperscript{44}. Specifically, the electrochemical reactions occurring at the electrodes during AEMFC operation result in ionic species fluxes into and out of the membrane, which affect the conversion of OH\textsuperscript{−} into HCO\textsubscript{3}\textsuperscript{−} and CO\textsubscript{3}\textsuperscript{2−}. By applying a species conservation approach, the transient conductivity of the membrane can be calculated as a function operating current, temperature, amount of CO\textsubscript{2} in the cathode gas stream, etc. As in Chapter 2, the governing equation for ionic species in the membrane is the Nernst-Planck equation, Eq. 3.6.

$$\frac{\partial c_k}{\partial t} = \frac{\partial}{\partial x} \left( D_k \frac{\partial c_k}{\partial x} \right) + \frac{\partial}{\partial x} \left( \frac{z_k F D_k}{RT} c_k \frac{\partial \varphi}{\partial x} \right) + \dot{R}_k$$  \hspace{1cm} (3.6)

where the subscript \( k \) denotes the species, i.e. Eq. 3.6 represents a system of 8 equations for the following species: CO\textsubscript{2(aq)}, OH\textsuperscript{−}, HCO\textsubscript{3}\textsuperscript{−}, CO\textsubscript{3}\textsuperscript{2−}, TMA\textsuperscript{+}, TMA(OH), TMA(HCO\textsubscript{3}), and TMA\textsubscript{2}(CO\textsubscript{3}). The source term, \( \dot{R}_k \), is the same as before, and its expression can be found in Table 2.1. The system of equations represented by Eq. 3.6 can be extremely numerically stiff. For electrospun membranes, we average these equations across the effective thickness of the membrane, \( L_{eff} \), to account for the tortuous nature of the electrospun morphology. This yields a much more tractable system, which is necessary for the large number of numerical experiments of interest (e.g. current sweep simulations). The spatially averaged governing equations are given by Eq. 3.7

$$\frac{\partial \bar{c}_k}{\partial t} = \frac{1}{L_{eff}} (J_{k,x=L} - J_{k,x=0}) + \bar{\dot{R}}_k$$  \hspace{1cm} (3.7)
where $\bar{c}_k$ is the average concentration of species $k$ in the membrane, and $J_{k,x=L}$ and $J_{k,x=0}$ represent the flux of species $k$ across the AEM-cathode and AEM-anode interfaces, respectively. In this work we consider considering an electrospun AEMFC fed by CO$_2$-containing air in the cathode and pure H$_2$ in the anode. Details regarding the complete system of equations, initial & boundary conditions, flow conditions, etc. for this configuration can be found in Chapter 2, and/or Ref. [44].

Following the solution of Eq. 3.7, the membrane’s conductivity is calculated with Eq. 3.4, using the values of $\bar{c}_{\text{OH}}$, $\bar{c}_{\text{HCO}_3}$, and $\bar{c}_{\text{CO}_3}$. The Dusty Fluid model provides a means to account for the effect of ion/membrane interactions when calculating the conductivity, as opposed to the simple Nernst-Planck conductivity that can be backed out from Eq. 3.6, $\sigma_{NP} = (F^2/RT) \sum_k z_k^2 D_k c_k$.

The inputs required to run the CO$_2$ model fall into two categories: operating conditions and material properties. The membrane property inputs include the membrane’s density, thickness, area, IEC, and $\lambda$. The effective thickness and porosity of electrospun membranes need to be adjusted to account for their morphological dependence on $f_I$. Radiation grafted AEMs, which possess no analogous ‘$f_I$’ parameter, are sufficiently described by their material/geometric properties, which can be determined experimentally. In their case the effective thickness is simply the measured swollen thickness, and the water volume fraction is related to the water uptake via Eq. 3.8.

$$\varepsilon = \frac{\lambda}{\lambda + \frac{\rho_{H_2O}}{M_{H_2O} \rho_{mem} IEC}}$$
3.3 - Experimental

AEMFCs for this study were assembled with a benzyl trimethylammonium functionalized ethylene tetrafluoroethylene (ETFE-BTMA) radiation grafted AEM\textsuperscript{48} and ionomer\textsuperscript{52}. Gas diffusion electrodes (GDEs) were prepared by successive grinding and sonication steps with the catalyst to create an ink. A detailed procedure of the GDE fabrication process was reported previously\textsuperscript{4,49}. PtRu(2:1)/C and Pt/C were used as the anode and cathode catalyst, respectively. The loading for both catalysts on the GDE were approximately 0.5 mg \cdot cm\textsuperscript{-2}. The GDEs and AEM were pressed together in-cell to form a membrane electrode assembly (MEA) with no prior hot pressing. The MEAs were secured in 5 cm\textsuperscript{2} Scribner Inc. hardware between two single pass serpentine flow graphite plates using 6 mil (152 \mu m) PTFE gaskets with 20\% pinch (5.1 N \cdot m torque). A Scribner 850e Fuel Cell Test Station was used for all testing with a cell temperature of 60\°C. H\textsubscript{2} and O\textsubscript{2} gas feeds were supplied to the anode and cathode, respectively, at 1.0 L \cdot min\textsuperscript{-1} and full humidity without back–pressurization (ca. 1 bar absolute). When CO\textsubscript{2} was fed to the cell, it displaced O\textsubscript{2} in the cathode supply, maintaining the total gas flow rate at 1.0 L \cdot min\textsuperscript{-1}.

Each assembled cell was first exposed to a break-in procedure described elsewhere\textsuperscript{4}, operating with H\textsubscript{2} and O\textsubscript{2} reacting gases, and then held at the current density of interest. Individual AEMFCs were operated at 200 mA\cdot cm\textsuperscript{-2}, 500 mA\cdot cm\textsuperscript{-2}, 1000 mA\cdot cm\textsuperscript{-2}, and 2000 mA\cdot cm\textsuperscript{-2}. After establishing a steady-state behavior at each current density, carbon dioxide was mixed into the cathode stream, starting at the lowest concentration (100 ppm) for 60 mins to equilibrate the fuel cell, then switched back to pure oxygen to fully purge the CO\textsubscript{2} from the cell with the aid of a temporary current increase. The area specific resistance (ASR) and operating voltage returned to the previous CO\textsubscript{2}-free values in each case, confirming complete reversibility.
of the carbonation effects upon purging with pure $O_2$. This process was repeated through each desired CO$_2$ concentration (100, 200, 400, 600, 800, 1600, and 3200 ppm). Throughout testing, the AEM resistivity was measured by the Scribner fuel cell test station, which was converted into ASR by multiplying the resistance and the cell active area.

### 3.4 - Results and Discussion

In this section, validation of the models and some key results will be presented. The results will be presented with two key questions in mind: a) How does CO$_2$ affect the *in situ* performance of electrospun and RG AEMs? and b) How does the performance these membranes compare to traditional AEMs? Nominal simulation parameters are listed in Table 3.3; unless specifically mentioned otherwise, the results presented here were obtained using these parameters.

**Table 3.3**

*Nominal physical and operating parameters*

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T$ (K)</td>
<td>323</td>
</tr>
<tr>
<td>$p_{CO_2}^c$ (Pa)</td>
<td>40</td>
</tr>
<tr>
<td>$P^A, P^C$ (Pa)</td>
<td>101325</td>
</tr>
<tr>
<td>$Q^A, Q^C$ (mL \cdot min$^{-1}$)</td>
<td>100</td>
</tr>
</tbody>
</table>

$k^+_k, k^-_k, D_k$ See Ref. [12], Table 2

### 3.4.1 - Model Validation

In their initial publications, the CO$_2$ model, as well as the analytical and fiber network models were validated to experimental data from the literature$^{23,44}$. The FN model accurately predicted the electrospun AEM conductivities measured by Park et al.$^{26}$, and the analytical model
(on which the present EM model is based) in turn agreed with the FN model. The CO$_2$ model was validated to experimental ASR data from Suzuki et al.$^{11}$, and was shown to capture the conductivity trends at moderate-high current densities (above $\sim$100 mA/cm$^2$). This effect is observed again in Figure 3.3, which compares the experimentally measured (symbols) and model-predicted (lines) ASR for the RG AEMs tested in this study. Relevant material properties and operating conditions for this validation experiment are listed in Table 3.4.

![Figure 3.3 – ASR vs. cathode CO$_2$ content and current density of an operating AEM; the ‘○’ symbols indicate experimental data, and the lines are from the simulations. Current densities shown: $i = 200, 500, 1000, 2000$ mA/cm$^2$.

At the moderate-high current densities tested, relatively small changes in the ASR were observed as a function of CO$_2$ content (although the overall penalty is substantial), whereas stepping up the current density had a much more significant effect. This is an important consideration for, e.g. cathode gas CO$_2$ sequestration techniques (as discussed in Ref. $^{17}$), because it implies that the onset of conductivity loss occurs at very low CO$_2$ contents: gas stream
CO₂ content should be reduced below ~10 ppm in order to see any appreciable conductivity benefits at low currents.

**Table 3.4**

*Membrane properties and operating conditions for the validation experiment*

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$L$ (μm)</td>
<td>60</td>
</tr>
<tr>
<td>$IEC$ (mmol · g$^{-1}$)</td>
<td>2.05</td>
</tr>
<tr>
<td>$\lambda$</td>
<td>18</td>
</tr>
<tr>
<td>$A$ (cm$^2$)</td>
<td>5.0</td>
</tr>
<tr>
<td>$T$ (K)</td>
<td>333</td>
</tr>
<tr>
<td>$P^A, P^C$ (Pa)</td>
<td>101325</td>
</tr>
<tr>
<td>$Q^A, Q^C$ (mL · min$^{-1}$)</td>
<td>1000</td>
</tr>
</tbody>
</table>

The model captures the trends of increasing ASR with increased CO₂ especially well at higher current densities, whereas at lower current densities the model slightly under-predicts the ASR. This is likely due to the model’s treatment of the hydrogen oxidation reaction (HOR) pathways at the anode, which probably over-predicts the involvement of (bi)carbonate species at low overpotentials. A more rigorous treatment of the Anode-AEM boundary would require a detailed description of the self-purging mechanism, i.e. the manner in which (bi)carbonates vacate the membrane. Several groups have modeled this recently$^{18,24}$, but the exact nature of the self-purging phenomenon is still debated$^{15,17}$. The CO₂ model used here employs an approximate constitutive model in which all three ionic species are consumed at a rate proportional to their concentrations to represent their direct participation in the HOR. This representation is somewhat similar to that used by Krewer et al.$^{24}$ who modeled anionic species consumption using a type of “outflow” boundary condition. Determining the mechanism by which self-purging occurs
remains an important challenge to be addressed for the field of AEMFC modeling\textsuperscript{15}. Despite this uncertainty, the agreement shown in Figure 3.3 gives confidence in using the CO\textsubscript{2} model to describe the behavior of \textit{in situ} AEMs.

### 3.4.2 - Simulation of the CO\textsubscript{2} Behavior of Electrospun AEMs

To observe the effect of CO\textsubscript{2} on electrospun AEMs, numerical simulations were performed for an electrospun AEMFC operating with varying amounts of CO\textsubscript{2} in the cathode gas stream. These results are presented in Figure 3.4 as the AEM ionic conductivity vs. operating current. In Figure 3.4, only a single membrane design is considered, \( f_I = 0.7 \), to focus on the effect of the CO\textsubscript{2} concentration.

![Figure 3.4 – Membrane ionic conductivity vs. current density at \( f_I = 0.7 \) with varying cathode CO\textsubscript{2} amounts; cathode CO\textsubscript{2} concentrations shown: 0, 200, 400, 800, 1200, 1600 ppm. The dashed line indicates the pristine (CO\textsubscript{2}-free) membrane conductivity.](image)
The pristine conductivity (pure OH\textsuperscript{−} form, 0 ppm CO\textsubscript{2}) in Figure 3.4 is indicated by the dotted line at the top, and one can see that the effect of adding CO\textsubscript{2} to the cathode stream is to decrease the conductivity of the membrane. One can also observe evidence of the self-purging effect on the electrospun membrane, indicated by the conductivity reclamation as current density is increased. The self-purging effect is a phenomenon observed\textsuperscript{11,20,45} in AEMFCs whereby the (bi)carbonate ions are purged from the membrane during normal operation, either by consumption in the electrochemical hydrogen oxidation reaction at the anode or through a shift in the equilibrium as OH\textsuperscript{−} is consumed – both pathways result in the emission of CO\textsubscript{2} gas at the anode. As the current is increased, the (bi)carbonate ions are displaced more and more by the incoming hydroxide ions supplied by the oxygen reduction reaction at the cathode, and the membrane’s conductivity increases as a result. The self-purging trend shown in Figure 3.4 is analogous to what has been observed before in conventional AEMs\textsuperscript{11,15,45}, meaning that the characteristics of this phenomenon are similar in electrospun AEMs.

Since electrospun membranes have a unique design parameter, \( f_I \), compared to conventional AEMs, it will be useful to observe how this parameter affects the CO\textsubscript{2} interactions. Figure 3.5a shows the effect of varying \( f_I \) on the conductivity of an operating electrospun AEM, \( \sigma_f \), with 400 ppm CO\textsubscript{2} in the cathode gas stream. It is clear that not only does increasing \( f_I \) increase the conductivity of the membrane, but it also increases the rate of conductivity reclamation as the current density is increased. For example, from 10 – 20 mA/cm\textsuperscript{2}, the conductivity of the membrane with \( f_I = 0.4 \) increases by about 1.5 mS/cm, while the conductivity of the membrane with \( f_I = 0.9 \) increases by about 11 mS/cm.
Figure 3.5 – a) Conductivity vs. current density for electrospun membranes with different ionomer phase volume fractions (solid lines), as well as RG ETFE and A201 membranes at 400 ppm cathode gas stream CO₂ content, and b) Normalized conductivity vs. current density for electrospun membranes. In both figures the following $f_i$ are shown: 0.4, 0.5, 0.6, 0.7, 0.8, 0.9.

The simulated conductivities of a Tokuyama A201 membrane⁴⁶ and a previously reported RG ETFE membrane⁴⁷ from Varcoe et al. are included in Figure 3.5a (denoted as A201 and ETFE-1, respectively) to put the model predictions in context with other well-known AEMs. The RG AEMs used in the fuel cells studied in this work (denoted as ETFE-2) are similar to those first presented by Varcoe et al.⁴⁷, but were manufactured using a modified procedure⁴⁸ that resulted in different membrane properties. Nominal properties for the non-electrospun membranes are listed in Table 3.5 (the properties of electrospun AEMs are calculated as a function of $f_i$ using the morphology model). Figure 3.5a demonstrates the important point that depending on the $f_i$ chosen, electrospun AEMs can perform better or worse than conventional
AEMs. This is because the fraction of ionomer phase dictates the amount of cationic side groups in the membrane, which in turn controls the number of mobile charge carriers present. In the limit as $f_I \to 1$, the electrospun membrane essentially becomes a conventional membrane with the properties of the ionomer fibers, which have very high IECs (much higher than the IECs of conventional single-phase AEMs\(^1\)). Therefore it’s worth noting that other kinds of composite membranes, e.g. two-phase solution cast membranes, would also perform similarly well as $f_I$ is increased. Likewise, the higher number of charge carriers is also likely the reason the new RG EFTE membrane, ETFE-2, outperformed ETFE-1, although this outcome was not guaranteed since ETFE-1 is thinner and had greater water uptake. These parameters were shown in the past to improve membrane conductivity\(^{44}\), however, the nearly doubled IEC of ETFE-2 can be seen to have the more significant effect. We can also see that ETFE-2 has a higher conductivity than most electrospun membrane designs (up to about $f_I \approx 0.75$). This may explain why previously reported electrospun AEMs\(^{26,53,54}\) were typified by $f_I$ between 0.8 – 0.9; future users should keep this in mind when balancing strength, stability, and conductivity.

**Table 3.5**

Nominal properties of non-electrospun AEMs

<table>
<thead>
<tr>
<th>Parameter</th>
<th>A201(^{35})</th>
<th>ETFE-1(^{47})</th>
<th>ETFE-2</th>
</tr>
</thead>
<tbody>
<tr>
<td>$IEC$ (mmol·g(^{-1}))</td>
<td>1.58</td>
<td>1.03</td>
<td>2.05</td>
</tr>
<tr>
<td>$L$ (μm)</td>
<td>28</td>
<td>80</td>
<td>60</td>
</tr>
<tr>
<td>$\lambda$ (liq. water)</td>
<td>18.5</td>
<td>22</td>
<td>18</td>
</tr>
</tbody>
</table>

It may be useful to determine the relative conductivity recovery attainable by a particular membrane design, for example to balance conductivity with chemical or mechanical stability. To observe this, we can normalize the results of Figure 3.5a to the pristine membrane conductivity

61
for each $f_I$ (denoted as $\sigma_f^0$). The effect is shown in Figure 3.5b, where it can be seen that the $\sigma_f/\sigma_f^0$ vs. current behavior for all $f_I$ is identical. This is a key insight into the performance of electrospun AEMs in operating fuel cells when operated in the presence of CO$_2$. Both the ion-exchange process and subsequent self-purging are unaffected, proportionally, by the volume fraction of ionomer fiber in the membrane. The explanation for this behavior is somewhat unclear from a physical point of view, but it is easy to see mathematically. Eq. 3.4 is used to predict $\sigma_f/\sigma_f^0$, as shown in Eq. 3.8, where it can be seen that any parameters that vary with $f_I$ (especially $\epsilon$) drop out. This means that regardless of the ionomer content in the electrospun AEM, the conductivity recovery due to self-purging will occur proportionally at the same rate.

\[
\frac{\sigma_f}{\sigma_f^0} = \frac{D_{OH^-}c_{OH^-}}{1 + \delta_{OH^-}} + \frac{D_{HCO_3^-}c_{HCO_3^-}}{1 + \delta_{HCO_3^-}} + \frac{4D_{CO_3^{2-}}c_{CO_3^{2-}}}{1 + \delta_{CO_3^{2-}}} + \frac{4D_{CO_2}c_{CO_2}}{c_{OH^-}}
\]  

(3.8)

A similar effect can be observed when varying the CO$_2$ content of the cathode gas stream. Figure 3.6 shows the normalized conductivity loss (the complementary metric of Figure 3.5b) of the membrane, $1 - \sigma_f/\sigma_f^0$, as the cathode CO$_2$ content is increased. The abscissa indicates the CO$_2$ content, and the curves are also grouped by different current densities ($i = 100, 300, 500$ mA/cm$^2$) as indicated by the labels. The results are banded in groups according to the current density, and within each band lies the $f_I$ simulated ($f_I = 0.4 - 0.9$). This demonstrates that the current density is a stronger influence on conductivity loss than the ionomer content of the membrane. As the current density is increased the bands become more tightly grouped which supports this idea.
Figure 3.6 – Normalized conductivity loss for different membranes as a function of cathode gas stream CO$_2$ and current density. Solid lines correspond to electrospun membranes, and each band of curves includes the following $f_I$: 0.4, 0.5, 0.6, 0.7, 0.8, 0.9.

It is also noteworthy that the A201 and ETFE membranes suffer a larger normalized conductivity loss than the electrospun membranes. This is because of the lower IECs of these membranes: lower IECs mean there are fewer native hydroxide ions in the membranes, which makes them more susceptible to CO$_2$ poisoning. The main advantage of electrospun AEMs stems from the support provided by the inert phase, which enables higher IECs and water uptakes without sacrificing mechanical properties. This implies that other composite AEM designs with a supporting phase should respond similarly well to CO$_2$ at higher $f_I$. Lastly, note that the A201 and ETFE curves approach the bands of electrospun membrane curves as the current density is
increased, further supporting the suggestion that morphological parameters in general become less relevant at higher operating currents.

3.5 - Conclusions

In this study, the effect of CO₂ on operational electrospun and radiation-grafted AEMs was investigated. Electrospun AEMs possess a unique design parameter, the volume fraction of ionomer fibers in the membrane, which affects their conductivity. It was found that CO₂ affects electrospun AEMs similarly to conventional AEMs, resulting in conductivity loss at low operating currents that is mitigated at higher currents due to the self-purging effect.

It was found that the relative conductivity (that is, a membrane’s conductivity normalized to its pristine conductivity) reclamation rate is identical for electrospun membranes with different $f_i$. This means that the operating current more significantly affects an electrospun membrane’s conductivity reclamation rate than $f_i$, which may be an important consideration when designing electrospun AEMFC systems.

Radiation-grafted AEMs synthesized using a new technique were also studied. It was shown that their high IEC results in higher conductivities than their predecessors’. These membranes performed well compared to electrospun AEMs, and only electrospun membranes with $f_i > ~0.75$ exhibited higher conductivities.

Future theoretical efforts should consider how the hydration state in the membrane varies during operation, and how the spatial variation of species concentrations affects the phenomena presented in this work. Both of these considerations were also identified in a recent review by Dekel et al.³ as important, but yet uninvestigated, aspects of AEMFC operation. In addition, experimental studies investigating the performance of electrospun AEMs used in an operating
fuel cell, especially one using ambient air, are still needed. Finally, AEM modeling efforts to
date suffer from a lack of understanding of the nature of the self-purging phenomenon in AEMs.
A better description of this phenomenon will enable more useful performance predictions in the
future, namely, the electrode overpotentials and overall cell voltage.

List of Symbols

\( c \) Concentration, mol cm\(^{-3}\)
\( D \) Diffusivity, cm\(^{2}\) s\(^{-1}\)
\( z \) Valence
\( F \) Faraday’s constant, 96485 C mol\(^{-1}\)
\( R \) Gas constant, 8.314 J mol\(^{-1}\) K\(^{-1}\)
\( T \) Temperature, K
\( A \) Area, cm\(^2\)
\( f \) Volume fraction of ionomer phase
\( \sigma \) Ionic conductivity, mS cm\(^{-1}\)
\( Q \) Gas stream flow rate, mL min\(^{-1}\)
\( p \) Partial pressure, Pa
\( P \) Total pressure in gas stream, Pa

Greek

\( \varepsilon \) Porosity/water volume fraction
\( \rho \) Density, g cm\(^{-3}\)
\( \lambda \) Hydration number
\( \delta \) Solvent/membrane diffusivity ratio

Superscript

\( s \) Anode
\( C \) Cathode
\( 0 \) Pristine (no CO\(_2\)) conditions
\( \text{eff} \) Effective
### Subscripts

- \( k \)  
  Species ‘\( k \)’

- \( f \)  
  Equivalent to \( f_1 \) when used as a subscript

- \( I \)  
  Ionomer phase

- \( aq \)  
  Aqueous

- \( mem \)  
  Membrane
Chapter 4: Investigation into the Self-Purging Mechanism in AEMFCs

This chapter is adapted from work submitted to *J. Electrochem. Soc.* in Jan. 2019

4.1 - Overview

In this study we investigate the commonly observed phenomenon whereby carbon dioxide (CO₂) in the cathode gas stream (e.g., air) is absorbed and released from the anion exchange membrane fuel cell (AEMFC). Often described as “self-purging” due to the emission of the CO₂ gas from the AEMFC with increased current, the mechanisms of this process are still largely unknown. Herein we provide evidence that this self-purging occurs through an electrochemical mechanism, in which bicarbonate and carbonate ions directly participate in the hydrogen oxidation reaction. After determining the nature of the self-purging mechanism, we present a series of parametric studies that investigate the fundamental effects of CO₂ on the AEMFC, and discuss certain operating parameters that can be manipulated to improve cell performance.

Carbon dioxide from ambient air (or other sources, such as flue gases⁷⁻⁵⁵) can degrade AEMFC performance by reacting with the native hydroxide ions (OH⁻) to form bicarbonate and carbonate ions (HCO₃⁻, CO₃²⁻ respectively), as depicted by Eqs. 4.1 – 4.2. These ions are less mobile and therefore increase ohmic losses in the fuel cell.

\[
\text{CO}_2(\text{aq}) + \text{OH}^- \leftrightarrow \text{HCO}_3^-
\]  \hspace{1cm} (4.1)

\[
\text{OH}^- + \text{HCO}_3^- \leftrightarrow \text{CO}_3^{2-} + \text{H}_2\text{O}
\]  \hspace{1cm} (4.2)
In addition, the presence of (bi)carbonate species may impact electrochemical processes (and hence activation/thermodynamic losses) in the AEMFC, a phenomenon which is still largely unexplored. Experimental studies can observe these effects, but it is difficult to get fundamental mechanistic insight about these processes because of how pervasive CO₂ is inside the AEMFC system. For example, at the cathode the absorption of CO₂ can decrease oxygen solubility and diffusivity in the electrolyte, and also lead to a decrease in the electrochemically active area. Similarly, CO₃²⁻ has been shown to decrease oxygen reduction reaction (ORR) activity on Pt/C and Pd/C electrodes. Lastly, Eqs. 4.1 – 4.2 reduce the pH in the membrane and catalyst layers, which can negatively affect both anode and cathode performance. For example, the Nernst equation predicts an overall cell voltage penalty of 59 mV per pH unit difference between the cathode and anode (at STP). This is an equilibrium phenomenon which is useful for predicting open circuit potentials, however it does not allow us to quantitatively model the dynamic combination of AEM carbonation and self-purging. These processes all factor into the overall cell losses observed when AEMFCs are operated in the presence of CO₂.

Although AEMFC performance is certainly lower when operated in the presence of carbon dioxide, this can be mitigated during normal operation through an effect known as the self-purging mechanism. During operation, hydroxide ions are continuously supplied to the membrane via the ORR occurring at the cathode, Eq. 4.3.

\[
O_2 + 2H_2O + 4e^- \leftrightarrow 4OH^- \quad (4.3)
\]
These incoming hydroxide ions mitigate some of the conversion of hydroxide in the membrane that occurs due to Eqs. 4.1 – 4.2. At the anode, hydroxide ions are consumed by the HOR, Eq. 4.4 (referred to as the hydroxide HOR pathway)

$$\text{H}_{\text{ad}} + \text{OH}^- \leftrightarrow \text{H}_2\text{O} + \text{e}^- \quad (4.4)$$

where $\text{H}_{\text{ad}}$ indicates adsorbed hydrogen. Also at the anode, (bi)carbonates are purged from the membrane due to the self-purging mechanism. Several recent reviews and papers have noted that there remains a lack of consensus over the exact mechanism of the self-purging phenomenon. There are two prevalent theories, which can be described as (i) a chemical mechanism and (ii) an electrochemical mechanism. The chemical mechanism proposes that the local depletion of $\text{OH}^-$ due to Eq. 4.4 shifts the equilibrium of Eqs. 1 – 2 back toward the reactants, thereby replenishing the $\text{OH}^-$, reducing the AEM’s (bi)carbonate content, and releasing $\text{CO}_2$ into the anode gas stream via desorption. The electrochemical model proposes that (bi)carbonate ions are oxidized as a part of the HOR, e.g. via Eqs. 4.5 – 4.6 (referred to as the bicarbonate and carbonate HOR pathways, respectively). This theory would similarly explain the decrease in (bi)carbonate concentrations and $\text{CO}_2$ emission during operation.

$$\text{H}_{\text{ad}} + \text{HCO}_3^- \leftrightarrow \text{CO}_2 + \text{H}_2\text{O} + \text{e}^- \quad (4.5)$$
$$2\text{H}_{\text{ad}} + \text{CO}_3^{2-} \leftrightarrow \text{CO}_2 + \text{H}_2\text{O} + 2\text{e}^- \quad (4.6)$$

Both proposed self-purging mechanisms can explain observed AEMFC responses to $\text{CO}_2$, such as anode gas stream emission and increased activation losses. However the distinction
between the two will improve our understanding of AEMFC operation, and may be useful in the design of improved HOR catalyst materials. Due to the myriad ways in which CO$_2$ affects the AEMFC, it is difficult to experimentally isolate. A modeling approach can prove very insightful for this system because of the independent control over system properties and operating conditions, as well as the freedom to investigate very specific aspects of operation. To date, modeling approaches have typically focused on ex situ (non-operational) AEMs$^{12,13,19}$ or have employed numerical/contextual simplifications$^{20,21}$ that have made it hard to draw conclusions about the underlying carbonation process.

Shiau et al. developed a detailed 2-D AEMFC model that included varying water content, the relative humidity of the gas streams, and catalyst layer (CL) species concentration and current density distributions. They applied the chemical self-purging mechanism, which was able to demonstrate the membrane’s OH$^-\text{ conductiv}y$ reclamation with increasing current density. However, detailed validation to CO$_2$-focused AEMFC experiments was not presented. Also, the association/dissociation reactions with tethered cationic side groups (e.g. TMA$^+$) were not considered. We believe these reactions should be included since these side groups can act as storage sites for the mobile anions and can take up and/or release ions as the local concentrations change, as demonstrated by Myles et al.$^{12}$.

Krewer et al. developed a carbonation model for an operating AEMFC that investigated species transport and reactions through several AEMFC components, including flow channels, gas diffusion layers (GDLs), CLs, and the AEM itself$^{24}$. They contend that it is not necessary to differentiate between chemical and electrochemical purging models, since in both cases identical amounts of carbon dioxide and electrons would be produced at the anode. The actual ionic species fluxes in their model were handled using a type of outflow boundary condition, in which
any species reaching the Anode CL/membrane boundary are immediately consumed. This somewhat akin to the electrochemical mechanism, but does not account for varying reaction rates due to kinetics and concentration effects, which can result in both local consumption and accumulation.

In this work we present a transient, spatially-varying AEM model to account for the carbonation process under operating conditions. Within this model we can individually simulate the chemical and electrochemical self-purging pathways, and compare the results to those observed experimentally. There are three characteristic features of the self-purging mechanism that will be investigated:

- The conductivity of the AEM increases as current density is increased (can be observed in several studies, including Refs. [11,29,36]).
- The anode overpotential increases with increasing CO$_2$ content, while the cathode overpotential is relatively unchanged (can be observed in Ref. [45]).
- During transient current step experiments, the CO$_2$ content of the anode gas stream exhibits “spikes” that correspond to the current steps (can be observed in Refs. [20,30]).

A proper self-purging model should be able to demonstrate these three phenomena. Following the determination of an appropriate self-purging model, we present a parametric investigation into this effect, and make suggestions on how it might be facilitated in order to improve AEMFC performance in the presence of CO$_2$.

4.2 - Theory

4.2.1 - Governing Equations
The flux of aqueous species inside the AEM is governed by the 1-D Nernst-Planck equation

\[ J_k = -D_k \left( \frac{\partial c_k}{\partial x} - \frac{z_k F}{RT} c_k E \right) \]  \hspace{1cm} (4.7)

where \( c_k \) is the local concentration of species \( k \), \( D_k \) is the diffusivity, \( z_k \) is the valence, and \( E \) is the electric field. The continuity equation, Eq. 4.8, gives the transient response

\[ \frac{\partial c_k}{\partial t} = -\frac{\partial}{\partial x} (J_k) + \dot{R}_k \]  \hspace{1cm} (4.8)

where \( \dot{R}_k \) is the reaction source term, which is expressed in Table 2.1. The source terms model the (bi)carbonate reactions, Eqs. 4.1 – 4.2, as well as the anion association/dissociation reactions, Eqs. 4.9 – 4.11, via mass action kinetics using the same rate constants used by Myles et al.\textsuperscript{12}. In this work, TMA\textsuperscript{+} is used to denote the tethered cationic side groups, although the results and analysis herein can be generalized to AEMs employing alternative backbone and cation chemistries.

\[ \text{TMA(OH)} \leftrightarrow \text{TMA}^+ + \text{OH}^- \]  \hspace{1cm} (4.9)
\[ \text{TMA(HCO}_3\text{)} \leftrightarrow \text{TMA}^+ + \text{HCO}_3^- \]  \hspace{1cm} (4.10)
\[ \text{TMA}_2\text{(CO}_3\text{)} \leftrightarrow 2\text{TMA}^+ + \text{CO}_3^{2-} \]  \hspace{1cm} (4.11)

Combining Eqs. 4.7 and 4.8 yields the overall governing equation.
\[
\frac{\partial c_k}{\partial t} = D_k \left( \frac{\partial^2 c_k}{\partial x^2} - \frac{z_k F}{RT} \left( E \frac{\partial c_k}{\partial x} + c_k \frac{\partial E}{\partial x} \right) \right) + \dot{R}_k
\] (4.12)

which can be applied to 8 unknown concentrations: \( k = \text{CO}_2, \text{OH}^-, \text{HCO}_3^-, \text{CO}_3^{2-}, \text{TMA}^+, \text{TMA(OH)}, \text{TMA(HCO}_3), \text{TMA}_2(\text{CO}_3) \), representing both mobile species and tethered complexes.

For uncharged species, \( z_k = 0 \) and Eq. 4.12 reduces to Fick’s second law. For tethered species, \( D_k \) is set to zero, and Eq. 4.12 represents only chemical reactions. The complete system of governing equations is presented in Table 4.1.

**Table 4.1**

Governing equations for aqueous species and the electric field

<table>
<thead>
<tr>
<th>Species</th>
<th>Governing Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{CO}_2 )</td>
<td>( \frac{\partial \text{c}_{\text{CO}<em>2}}{\partial t} = D</em>{\text{CO}<em>2} \frac{\partial^2 \text{c}</em>{\text{CO}<em>2}}{\partial x^2} + \dot{\text{R}}</em>{\text{CO}_2} )</td>
</tr>
<tr>
<td>( \text{OH}^- )</td>
<td>( \frac{\partial \text{c}<em>{\text{OH}}}{\partial t} = D</em>{\text{OH}} \left( \frac{\partial^2 \text{c}<em>{\text{OH}}}{\partial x^2} - \frac{z</em>{\text{OH}} F}{RT} \left( E \frac{\partial \text{c}<em>{\text{OH}}}{\partial x} + \text{c}</em>{\text{OH}} \frac{\partial E}{\partial x} \right) \right) + \dot{\text{R}}_{\text{OH}} )</td>
</tr>
<tr>
<td>( \text{HCO}_3^- )</td>
<td>( \frac{\partial \text{c}_{\text{HCO}<em>3}}{\partial t} = D</em>{\text{HCO}<em>3} \left( \frac{\partial^2 \text{c}</em>{\text{HCO}<em>3}}{\partial x^2} - \frac{z</em>{\text{HCO}<em>3} F}{RT} \left( E \frac{\partial \text{c}</em>{\text{HCO}<em>3}}{\partial x} + \text{c}</em>{\text{HCO}<em>3} \frac{\partial E}{\partial x} \right) \right) + \dot{\text{R}}</em>{\text{HCO}_3} )</td>
</tr>
<tr>
<td>( \text{CO}_3^{2-} )</td>
<td>( \frac{\partial \text{c}_{\text{CO}<em>3}}{\partial t} = D</em>{\text{CO}<em>3} \left( \frac{\partial^2 \text{c}</em>{\text{CO}<em>3}}{\partial x^2} - \frac{z</em>{\text{CO}<em>3} F}{RT} \left( E \frac{\partial \text{c}</em>{\text{CO}<em>3}}{\partial x} + \text{c}</em>{\text{CO}<em>3} \frac{\partial E}{\partial x} \right) \right) + \dot{\text{R}}</em>{\text{CO}_3} )</td>
</tr>
<tr>
<td>( \text{TMA}^+ )</td>
<td>( \text{c}<em>{\text{TMA}^+} = \text{c}</em>{\text{OH}^-} + \text{c}_{\text{HCO}<em>3^-} + 2\text{c}</em>{\text{CO}_3^{2-}} )</td>
</tr>
<tr>
<td>( \text{TMA(OH)} )</td>
<td>( \text{c}<em>{\text{TMA(OH)}} = \text{c}<em>0 - \text{c}</em>{\text{TMA}^+} - \text{c}</em>{\text{TMA(HCO}<em>3)} - 2\text{c}</em>{\text{TMA}_2(\text{CO}_3)} )</td>
</tr>
<tr>
<td>( \text{TMA(HCO}_3) )</td>
<td>( \frac{\partial \text{c}_{\text{TMA(HCO}<em>3)}}{\partial t} = \dot{\text{R}}</em>{\text{TMA(HCO}_3)} )</td>
</tr>
<tr>
<td>( \text{TMA}_2(\text{CO}_3) )</td>
<td>( \frac{\partial \text{c}_{\text{TMA}_2(\text{CO}<em>3)}}{\partial t} = \dot{\text{R}}</em>{\text{TMA}_2(\text{CO}_3)} )</td>
</tr>
</tbody>
</table>
By assuming local electroneutrality, such that $\sum_k z_k c_k(x, t) = 0$, we can replace the TMA$^+$ equation with Eq. 4.13

$$c_{\text{TMA}^+} = c_{\text{OH}^-} + c_{\text{HCO}_3^-} + 2c_{\text{CO}_3^{2-}}$$ (4.13)

In addition, the concentration of non-dissociated hydroxide, TMA(OH), can be calculated via a species balance on the tethered side groups, Eq. 4.14, to reflect that no TMA is entering or leaving the membrane

$$c_{\text{TMA(OH)}} = c_0 - c_{\text{TMA}^+} - c_{\text{TMA(HCO}_3^-)} - 2c_{\text{TMA}_2(\text{CO}_3)}$$ (4.14)

where $c_0$ is the total fixed charge concentration.

The concentration gradients that arise due to the chemical reactions in a carbonated AEM result in a diffusion current according to $i_{\text{diff}} = -F \sum_k z_k D_k \frac{dc_k}{dx}$. The total ionic current inside the membrane must satisfy $i_{\text{Tot}} = i_{\text{diff}} + i_{\text{Mlg}} = F \sum_k z_k J_k$, where $J_k$ is given by Eq. 4.7. Therefore the local electric field can be found using Eq. 4.15, as discussed by Newman et al.\textsuperscript{56}

$$E(x, t) = \frac{RT \left( \frac{i_{\text{Tot}}}{F} + \sum_k z_k D_k \frac{dc_k}{dx} \right)}{F \sum_k z_k^2 D_k c_k}$$ (4.15)
Equation 4.12 represents a system of 8 coupled initial-boundary value problems. Initial conditions for a pristine AEM (no carbonates) are uniform across the membrane at the values given in Table 2.3. Carbonated AEM initial conditions were obtained by simulating the carbonation of a pristine AEM under open-circuit (zero current) conditions until steady state.

Boundary conditions for the system are, in general, prescribed to account for the species fluxes at the membrane boundaries. The boundary conditions are summarized in Table 4.2, and will be briefly discussed here. The absorption/desorption of CO$_2$ into/from the membrane is modeled using convective mass transfer boundary conditions (as in Ref. [12]), which were modified to account for accumulation/depletion in the gas channels using a control volume approach (as in Ref. [44]). The fluxes of mobile ionic species at the boundaries reflect their participation in electrochemical reactions, and are modeled by Faraday’s law, $J_k = i_k/z_k F$, where $i_k$ is the partial current due to species $k$. The electrochemical reactions depend on the self-purging model being used, and will be discussed in more detail in the following section. Lastly, fluxes of all tethered groups are identically zero at the membrane boundaries.

These boundary conditions represent the membrane/electrode interface as a plane, similar to Krewer et al.$^{24}$. In reality, the anode and cathode are regions of finite volume, which provides additional space for species to diffuse/migrate, accumulate, and/or react, and it’s possible that this would influence the local species concentrations at the membrane/electrode interface. The simulations presented here use initial conditions corresponding to AEMs fully equilibrated with air. Since the electrodes are connected to the AEM via a percolated network of hydrated pores, their volume will also be equilibrated in the same manner. Therefore, the aqueous conditions inside the electrodes will be similar to those inside the membrane itself (see, e.g., the results of Shiau et al.$^{18}$), which means that the electrodes can be reasonably approximated as planar, and
having zero thickness. Regardless, including the electrode domains in our model remains an important focus of future work.

**Table 4.2**

*Boundary conditions at the anode \((x = 0)\) and cathode \((x = L)\) for species solved by the Nernst-Planck equation*

<table>
<thead>
<tr>
<th>Species</th>
<th>(J_{k,x=0})</th>
<th>(J_{k,x=L})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{CO}_2)</td>
<td>(J_{\text{CO}<em>2} = k</em>{\text{abs}}(c_{\text{CO}<em>2}(0) - H</em>{\text{CO}<em>2}^{\text{EC}} c</em>{\text{CO}_2}^{\text{AGC}}))</td>
<td>(J_{\text{CO}<em>2} = k</em>{\text{abs}}(H_{\text{CO}<em>2}^{\text{EC}} c</em>{\text{CO}<em>2}^{\text{AGC}} - c</em>{\text{CO}_2}(L)))</td>
</tr>
<tr>
<td>(\text{OH}^-)</td>
<td></td>
<td>(J_{\text{OH}} = -\frac{i}{F})</td>
</tr>
<tr>
<td>(\text{HCO}_3^-)</td>
<td><em>Boundary conditions for mobile charged species at the anode depend on the self-purging model being used; see Table 4.3</em></td>
<td>(J_{\text{HCO}_3} = 0)</td>
</tr>
<tr>
<td>(\text{CO}_3^{2-})</td>
<td></td>
<td>(J_{\text{CO}_3} = 0)</td>
</tr>
<tr>
<td>(\text{TMA(HCO}_3))</td>
<td>(J_{\text{TMA(HCO}_3}) = 0)</td>
<td>(J_{\text{TMA(HCO}_3}) = 0)</td>
</tr>
<tr>
<td>(\text{TMA}_2(\text{CO}_3))</td>
<td>(J_{\text{TMA}_2(\text{CO}_3}) = 0)</td>
<td>(J_{\text{TMA}_2(\text{CO}_3}) = 0)</td>
</tr>
</tbody>
</table>

The convective mass flux boundary conditions for carbon dioxide in Table 4.2 depend on the \(\text{CO}_2\) gas concentrations in the anode and cathode gas channels \((c_{\text{CO}_2}^A\) and \(c_{\text{CO}_2}^C\) respectively). These concentrations are found from the control volume approach detailed in Chapter 2, and are given by Eqs. 4.16 – 4.17. One can observe that the gas channel \(\text{CO}_2\) concentrations vary to account for depletion (as it is absorbed into the membrane), and accumulation (as it is released from the membrane by desorption and/or as the product of the (bi)carbonate HOR pathways).
\[ c_{CO_2}^A \approx -\frac{A}{2Q_A} \left( -D_{CO_2}^{eff} \frac{\partial c_{CO_2}}{\partial x} \bigg|_{x=0} - \frac{i_{CO_2}}{2F} - \frac{i_{HCO_3}}{F} \right) \]

\[ c_{CO_2}^C \approx \frac{A}{2Q_C} \left( -D_{CO_2}^{eff} \frac{\partial c_{CO_2}}{\partial x} \bigg|_{x=L} \right) + \frac{P_{CO_2}^C}{RT} \]

In Chapters 2 and 3, this system by spatially averaging Eq. 4.8 over the thickness of the membrane to arrive at a more tractable set of numerical equations. However, both the chemical and electrochemical reaction rates depend on the local concentrations, so a more accurate solution requires inclusion of spatial variation. Further assumptions employed in this work are as follows:

- **Constant water content** – Depending on the operating conditions (gas channel humidities, flow rates, membrane hydration, etc.), there may significant water flux from anode to cathode due to electrochemical reactions. The local hydration state affects the porosity of the membrane (which affects the species diffusivities), and there may also be significant electro-osmotic drag effects. Including a varying water concentration would greatly increase the numerical complexity of the system, and remains a challenge to be investigated in future work. In fully-humidified systems however, the water flux would not be as large.

- **Isothermal** – any heat generation from chemical and electrochemical reactions is not considered.

**4.2.2 - Self-Purging Models**
Implementing the two different self-purging mechanisms requires unique manipulations of the anodic boundary conditions. The chemical pathway is simulated by imposing that all of the current is supplied by the hydroxide HOR pathway. There is no flux of (bi)carbonate species across the anode boundary. The electrochemical pathway stipulates that the total current at the anode is distributed between the three HOR pathways. After determining the anode potential, which is common to all HOR pathways, the flux of each species is proportional to its respective HOR pathway’s rate via Faraday’s law. This constitutes a mixed potential problem. The general form of the anode boundary conditions for the two mechanisms are summarized in Table 4.3.

**Table 4.3**

*Anode Boundary conditions (x = 0) for the chemical and electrochemical self-purging mechanisms*

<table>
<thead>
<tr>
<th>Species</th>
<th>Chemical Pathway</th>
<th>Electrochemical Pathway</th>
</tr>
</thead>
<tbody>
<tr>
<td>OH⁻</td>
<td>( J_{OH} = \frac{i_{tot}}{z_{OH}F} )</td>
<td>( J_{OH} = \frac{i_{OH}}{z_{OH}F} )</td>
</tr>
<tr>
<td>HCO₃⁻</td>
<td>( J_{HCO_3} = 0 )</td>
<td>( J_{HCO_3} = \frac{i_{HCO_3}}{z_{HCO_3}F} )</td>
</tr>
<tr>
<td>CO₃²⁻</td>
<td>( J_{CO_3} = 0 )</td>
<td>( J_{CO_3} = \frac{i_{CO_3}}{z_{CO_3}F} )</td>
</tr>
</tbody>
</table>

A common approach to modeling Faradaic electrochemical currents at each electrode is by using a Butler-Volmer (BV) current-overpotential relation

\[
i = i_0 \left[ \frac{C_0}{C_0} e^{-\alpha_f \eta} - \frac{C_R}{C_R} e^{\alpha_a \eta} \right]
\]  

(4.18)
where $i_0$ is the exchange current density, $C_O = \prod_k c_{k,O}^{s_k}$ and $C_R = \prod_k c_{k,R}^{s_k}$ are the oxidized and reduced species concentrations at the electrode surface (the superscript $\theta$ denotes equilibrium conditions), $s_k$ are the stoichiometric coefficients, $\alpha_c$ and $\alpha_a$ are the cathodic and anodic transfer coefficients respectively, $f = F/RT$, $\eta = \phi - \phi^0$ is the overpotential, and $\phi^0$ is found using the Nernst equation at each time step. Using the Nernst equation to find $\phi^0$ ensures that Eq. 16 yields open circuit (zero current) conditions at the equilibrium potential corresponding to the local conditions. Therefore the BV equation includes overpotentials associated with concentration effects (e.g., pH shifts). The form of Eq. 4.18 without the concentration terms, i.e. with $c_{O,R}/c_{O,R}^0 \approx 1$ is only appropriate for well-mixed systems. In spatially finite, not-mixed systems (e.g. a carbonated fuel cell, multi-species electrolyzer, or microbial fuel cell), the concentration terms are important and must be included.

4.2.3 - Mixed Potential Theory

The current-overpotential relation, Eq. 4.18, describes the current provided by the reaction of a particular species at an electrode surface, referred to as the “partial” current from that species, $i_k$. With multiple electrochemically active species present at the electrode surface, there is a possibility that they all react concurrently; this type of electrode is known as a mixed electrode. An important conclusion from Wagner and Traud’s seminal work on mixed potential theory is that the partial currents from each species can be combined linearly to yield the total electrode current, $i_{tot}$, which they called “undistorted superposition”. Following this conclusion, the current-overpotential relation at a mixed electrode remains the same, and the kinetic and thermodynamic properties in Eq. 4.18 ($i, i_0, C_{O,R}, C_{O,R}^0, \alpha_{a,c}, \eta$) acquire an additional subscript $k$ to denote the $k^{th}$ electrode reaction. The total current at the electrode is then
\[ i_{tot} = \sum_k i_k \] (4.19)

The term “mixed potential” refers to the potential, \(E_m\), at which the net electrode current is zero, which can be thought of as a group equilibrium potential. This means that it’s likely that several of the individual reactions are not at equilibrium (i.e., implying both oxidation and reduction processes may be occurring simultaneously at the same electrode with zero net current). In the limiting case where all species are at their equilibrium concentrations, and all electrode reactions are equally facile, the mixed potential is simply equal to the average of the individual equilibrium potentials.

A complete and well-presented description of the mathematical treatment of mixed electrodes has been given by Gray and Cahill\(^{58}\). The superposition hypothesis allows us to use the same treatment away from equilibrium, i.e. for \(i_{tot} \neq 0\). Combining Eqs. 4.18 and 4.19 gives the mathematical formalization of the mixed potential problem:

\[ i_{tot} = \sum_k i_{0,k} \left[ \frac{C_{0,k}}{C_{0,k}^0} e^{-\alpha_{ck} f \eta_k} - \frac{C_{R,k}}{C_{R,k}^0} e^{\alpha_{ak} f \eta_k} \right] \] (4.20)

where \(\eta_k = \phi - \phi_{k}^0\), and \(\phi_{k}^0\) is found using the Nernst equation at each time step to reflect the changing local conditions. Therefore it’s important to note that some elements of the proposed chemical mechanism (i.e. concentration deviations and their effect on the equilibrium potentials) are still present in the electrochemical mechanism via the BV equation. In other words, Nernstian potential shifts are still present in a mixed potential problem.
The current-overpotential relation is not invertible outside of certain limiting conditions, so it must be solved iteratively. It is important to note that the concentration terms are coupled to the partial currents, since the partial currents are typically used to prescribe boundary conditions for the species fluxes at the membrane boundaries. Therefore, in systems where the pre-exponential concentration factors are expected to deviate significantly from unity, it is better to iterate on \( \phi \), and use \( i_{tot} \) as the constraint. This iteration must be performed simultaneously with any transport and/or reaction terms, which are also coupled with \( i_k \).

Equation 4.20 can be used to find the partial currents of the \( \text{OH}^- \), \( \text{HCO}_3^- \), and \( \text{CO}_3^{2-} \) HOR pathways listed in Table 4.3. A schematic of the AEMFC’s mixed potential anode is depicted in Figure 4.1. At open circuit under standard conditions, Figure 4.1a, the anode potential is such that some species are being oxidized and some are being reduced, all while \( i_{tot} = 0 \). Figure 4.1b depicts the process to drive a current at a mixed electrode: the anode potential increases, which increases the overpotential for some species (i.e., \( \text{OH}^- \) in Figure 4.1b) and changes the sign of the overpotential on others (i.e., \( \text{CO}_3^{2-} \) in Figure 4.1b). Species which were previously being reduced begin to be oxidized. We can see that the arrangement of the standard potentials favors oxidation of \( \text{OH}^- \), unless its kinetics are extremely sluggish compared to the other two species.

We expect that Eq. 4.4 should supply most of the current, since any (over)potential high enough to oxidize (bi)carbonates would drive large currents from the hydroxide pathway. Nevertheless, these simplified schematics do not take into account the shifts in equilibrium potentials due to concentration deviations. These deviations can be quite significant since, in the electrochemical self-purging model, species fluxes are directly proportional to the partial currents. There is likely a complicated balance between anode potential, partial currents, and local species concentrations.
Modeling the electrochemical pathway requires detailed knowledge of all three HOR pathways, especially kinetic data such as exchange current and transfer coefficients. Sheng et al. performed a thorough investigation of the hydroxide HOR pathway in alkaline media on carbon-supported platinum (Pt/C), a common fuel cell catalyst, however determining properties for the (bi)carbonate HOR pathways is much more difficult. St. John and coworkers studied the HOR in carbonated alkaline media, but mainly focused on the effects of the resulting drop in pH. Although they could not discount direct carbonate participation in the HOR, they did suggest that water’s ability to rapidly self-dissociate made it an active proton shuttle to hydroxide ions. Vega et al. suggested that the carbonate ion is an active proton acceptor in the HOR, and even proposed exchange current densities for Eq. 4.6. These experimental studies suggest that the HOR pathway in carbonated alkaline media is somewhat complicated, and still in need of clarification. Rather than approach this issue from another experimental electrochemistry perspective, the present work was designed to investigate the topic using reactive transport.
theory, and observe whether these results support a particular mechanism through indirect observations.

Thus, to date, the exchange currents and transfer coefficients for the bicarbonate and carbonate HOR pathways are mostly unknown for a realistic AEMFC anode/membrane interface. However, in the absence of experimental data, we can still simulate the electrochemical self-purging mechanism by parameterizing the exchange currents in Eqs. 4.5 – 4.6. The exchange current for the hydroxide HOR pathway reported by Sheng et al. will be used as a reference value for the (bi)carbonate pathways, and sensitivity studies can be performed on $i_{0,\text{HCO}_3}$ and $i_{0,\text{CO}_3}$ to observe their effect on the three characteristic features of self-purging mentioned in the Introduction.

### 4.2.4 - Numerical Methods

The chemical kinetics of Eqs. 4.1 – 4.2 and 4.9 – 4.11 are very fast compared with the diffusion and migration transport processes inside the membrane, which means that Eq. 4.12 represents a very stiff system of PDEs. One expected application of the model was to simulate current sweep experiments, which represent hundreds of transient simulations with different boundary conditions. In order to reduce the simulation time, it would be beneficial to have a numerical solution procedure that can use the largest time steps possible. Therefore an implicit time integration scheme was initially developed for the solution of Eq. 12 because of the good stability properties of implicit methods – for linear problems they are unconditionally stable. The derivation shown below is adapted from Kee, Coltrin, and Glarborg.

The simplest implicit method is the Backward Euler method, which can be used to solve first order ordinary differential equations of the form
\[ \frac{dy}{dt} = f(t, y) \]  

(4.21)

where \textbf{bold} notation indicates vector quantities. In the Backward Euler method, Eq. 4.21 is discretized as

\[ \frac{y_{n+1} - y_n}{\Delta t} = f(t_{n+1}, y_{n+1}) \]  

(4.22)

where the subscripts represent the discreet time step \( n \), \( \Delta t \) is the (constant) time step, and \( f(t_n, y_n) \) represents the function \( f \) evaluated at \( (t_n, y_n) \). For the purposes herein, the function \( f \) will be shown to represent the right hand side of Eq. 12, which does not depend on \( t \), and so the \textquoteleft t \textquoteright will be omitted from now on. To perform the time march (integration), Eq. 4.22 can be rearranged to solve for \( y_{n+1} \)

\[ y_{n+1} = \Delta t f(y_{n+1}) + y_n \]  

(4.23)

However, when \( f(y) \) is nonlinear with respect to \( y \), iterative methods must be used to solve for \( y_{n+1} \). The Newton-Raphson (or “modified Newton”) method is one technique that can be used to solve such equations. First, Eq. 4.23 is written in residual form

\[ y_{n+1} - y_n - \Delta t f(y_{n+1}) = 0 \]  

(4.24)
Iteration begins at an initial guess for \( y_n \), and the \( m^{th} \) guess for \( y \) is denoted as \( y^{(m)}_n \). At each iteration, the correction vector, defined as \( \Delta y^{(m)} = y^{(m+1)}_{n+1} - y^{(m)}_{n+1} \), is found using

\[
(I - \Delta tJ)\Delta y^{(m)} = y^{(m)}_{n+1} - y_n - \Delta t f(y^{(m)}_{n+1})
\]  

(4.25)

where \( I \) is the identity matrix and \( J = \frac{\partial f}{\partial y} \) is the Jacobian matrix. It can be seen that the only unknown in Eq. 4.25 is \( \Delta y^{(m)} \) which can be found by solving the linear matrix equation. Finally, the solution at the next iteration step is found using \( y^{(m+1)}_{n+1} = \Delta y^{(m)} + y^{(m)}_{n+1} \), and the process is repeated until \( \Delta y^{(m)} \) becomes sufficiently small, as determined by some user-defined metric.

At this point, it is useful to define \( y \) and \( f(y) \) for the solution of Eq. 4.12. First, the Implicit Euler method is a solution method for ODEs, not PDEs, so Eq. 4.12 must first be discretized. The simplest way to do this is by applying the 2\(^{nd}\) order centered difference operators, which approximate the spatial derivatives as

\[
\frac{\partial y}{\partial x}|_{j\Delta x} \approx \frac{y_{j+1} - y_{j-1}}{2\Delta x}
\]  

(4.26a)

\[
\frac{\partial^2 y}{\partial x^2}|_{j\Delta x} \approx \frac{y_{j-1} - 2y_j + y_{j+1}}{\Delta x^2}
\]  

(4.26b)

where the subscript \( j \) indicates the \( j^{th} \) spatial grid point, and \( \Delta x \) is the (constant) grid spacing.

Applying Eq. 4.26 to 4.12 turns the PDEs into a system of ordinary difference equations, O\( \Delta \)Es. For example, for \( \text{OH}^- \), Eq. 4.12 becomes
\[ \frac{\partial \text{[OH}^-\text{]}_j}{\partial t} = D_{\text{OH}} \left( \frac{[\text{OH}^-]_{j-1} - 2[\text{OH}^-]_j + [\text{OH}^-]_{j+1}}{\Delta x^2} \right) \]

\[ - \frac{F}{2RT\Delta x} \left( ([\text{OH}^-]_{j+1} - [\text{OH}^-]_{j-1})E_j + [\text{OH}^-]_j(E_{j+1} - E_j) \right) \]

\[ - k_1^+ [\text{CO}_2][\text{OH}^-] + k_1^- [\text{HCO}_3^-] - k_2^+ [\text{HCO}_3^-][\text{OH}^-] + k_2^- [\text{H}_2\text{O}][\text{CO}_3^{2-}] \]

\[ + k_4^+ [\text{TMA}(\text{OH})] - k_4^- [\text{TMA}^+][\text{OH}^-] \]

where bracket notation for concentrations, \( \text{[OH}^-\text{]} = c_{\text{OH}^-} \), is used for clarity.

Eq. 4.27 could now be solved using the Implicit Euler method, since it represents a system of ODEs. However since all the species are coupled to each other, the integrations for the entire system must be performed simultaneously. Therefore the solution vector \( \mathbf{y} \) is defined as

\[
\mathbf{y} = \begin{bmatrix}
    c_{\text{CO}_2} \\
    c_{\text{OH}^-} \\
    c_{\text{HCO}_3^-} \\
    c_{\text{CO}_3^{2-}} \\
    c_{\text{TMA}^+} \\
    c_{\text{TMA}(\text{OH})} \\
    c_{\text{TMA}(\text{HCO}_3)} \\
    c_{\text{TMA}_2(\text{CO}_3)} \\
    E
\end{bmatrix} \approx \begin{bmatrix}
    [\text{CO}_2]_1 \\
    \vdots \\
    [\text{CO}_2]_N \\
    [\text{OH}^-]_1 \\
    \vdots \\
    [\text{OH}^-]_N \\
    [\text{HCO}_3^-]_1 \\
    \vdots \\
    [\text{HCO}_3^-]_N \\
    [\text{CO}_3^{2-}]_1 \\
    \vdots \\
    [\text{CO}_3^{2-}]_N \\
    [\text{TMA}(\text{HCO}_3)]_1 \\
    \vdots \\
    [\text{TMA}(\text{HCO}_3)]_N \\
    [\text{TMA}_2(\text{CO}_3)]_1 \\
    \vdots \\
    [\text{TMA}_2(\text{CO}_3)]_N
\end{bmatrix}
\] (4.28)
Where $N$ is the total number of grid points, including ghost/boundary points. The right hand side function, $dy/dt$, is found by similarly concatenating the time derivatives of the individual species.

At this point, all of the information has been presented to implement Eq. 4.28 into Eq. 4.25 and start the iteration procedure. However there are some challenges associated with the procedure, especially regarding the Jacobian matrix. The Jacobian may be difficult or impossible to evaluate analytically, however it can be calculated numerically by applying Eq. 4.26a to the definition of the Jacobian matrix

$$J_{i,j} = \frac{\partial f_i}{\partial y_j} \approx \frac{f_i(y_j + \delta) - f_i(y_j - \delta)}{2\delta}$$

(4.29)

where tensor notation has been used and $\delta$ is a small perturbation magnitude to numerically approximate the derivative. The value of $\delta$ must be chosen with care to make sure that the approximate derivative is adequately close to the exact one, which does not always entail making $\delta$ infinitesimally small (especially when iterating through intermediate solutions for $y_{n+1}^{(m)}$). As we can see from Eq. 4.28, the problem statement in Eq. 4.12 represents a system of $6 \times N$ equations, which means that calculating Eq. 4.29 consists of $(6 \times N)^2$ calculations, which can quickly become prohibitively large as $N$ increases.

Fortunately, Eq. 4.26 prescribes a stencil over the spatial domain. For example, the diffusion term $D \frac{\partial^2 c}{\partial x^2}$ is only nonzero at three discreet grid points in the domain, namely $j$, $j + 1$, and $j - 1$, and likewise for the migration and reaction terms. This results in a sparsity pattern, or “mask” in the Jacobian that can either be derived a priori, or quickly obtained by observation.
For instance the sparsity pattern can be visualized by the Matlab function ‘spy’, which is shown in Figure 4.2. As demonstrated in Figure 4.2, the classic 2\textsuperscript{nd} order “tridiagonal” banding of the diffusion terms. In addition, there are singular bands associated with the tethered complexes, since these have no diffusion or migration (which depend on adjacent cells), and only depend on the local concentrations of reacting species. Lastly we can also see the effects of the electric field on the sparsity pattern, since all anionic species are affected by local and adjacent changes in the other anionic species.

The Jacobian only needs to be evaluated at indices corresponding to nonzero entries, which can be obtained in a number of ways upon observation of Figure 4.2. This reduces the number of calculations required from the aforementioned \((6 \times N)^2\), to \(64N\); this represents a reduction of \(1 - \frac{16}{9N} = 98\%\) for \(N = 100\). If the Jacobian was calculated without exploiting the sparsity pattern, this method would not be viable.
Figure 4.2 – Sparsity pattern of the Jacobian matrix for the system of OΔEs derived after discretizing the spatial derivatives in Eq. 4.12.

Implicit methods are known for their good stability properties, which usually enables longer time steps. Although this would imply that the time integration can be performed quickly, it’s often noted that implicit methods require more “work” at each time step\(^6\), which refers to not only calculating the Jacobian, but then solving the matrix equation represented by Eq. 4.25. Another technique that can be used to improve the computational time is to calculate the Jacobian less frequently during the iteration process within each time step. It is often the case that many iterations can be performed using an “old” Jacobian while still converging. Although this does mean that convergence will be slower (i.e. more iterations will be needed), the actual computational time is often faster. One criteria for convergence is that the correction vector, \(Δy^{(m)}\), approaches zero, which can be quantified by user-defined tolerances for absolute
convergence error, \( \max(|\Delta y^{(m)}|) \leq \alpha \), or relative error, \( \max\left(\frac{|\Delta y^{(m)}|}{y^{(m-1)}_{n+1}}\right) \leq r \) (using element-wise division). The user can also use these metrics to choose when to update the Jacobian. Several options are shown below, some or all of which can be used at one time:

- \( m = 0 \); The Jacobian should usually be calculated at the start of each time step.
- \( \max(|\Delta y^{(m)}|) \geq \max(|\Delta y^{(m-1)}|) \); If any entry in the correction vector becomes larger than the previous iteration, this is taken as a sign that the iteration is diverging, and the Jacobian should be updated.
- \( \max\left(\frac{|\Delta y^{(m)}|}{y^{(m)}_{n+1}}\right) \geq \max\left(\frac{|\Delta y^{(m-1)}|}{y^{(m-1)}_{n+1}}\right) \); Same as the above, but for relative error.
- \( m \geq B \); \( B \) is a user-defined “safety net” that tells the program to calculate the Jacobian after an arbitrary number of iterations has been reached.

Implementing these shortcuts usually requires some trial and error, and it’s not guaranteed that they will always work. The user should always perform proper verification/validation, check the steady-state residuals, etc.

This “Backward Time, Central Space (BTCS)” method was implemented for Eq. 4.12, and returned stable and fast short-time integrations of the system. However difficulties were often encountered during the time period where the physics of the system shift from the “hydroxide depletion” regime to “bicarbonate accumulation” (see Myles et al.\(^ {12} \), Figure 2). At this point the Newton-Raphson algorithm often converged (or, more aptly, stalled) at “solutions” that were still characterized by large residuals. It is believed that the algorithm was either converging to a local minimum of Eq. 4.24, and not the absolute minimum, or the problem has
multiple roots. To verify this, and in an attempt to improve the algorithm, we implemented the Matlab nonlinear solver ‘fsolve’, which solves nonlinear systems like Eq. 4.24 using the more sophisticated trust-region\textsuperscript{62} and Levenberg-Marquardt\textsuperscript{63} algorithms. The ‘fsolve’ routine was introduced to the code to solve Eq. 4.24, but unfortunately ran into similar problems. Therefore, due to project time constraints, alternate solution methods were explored, and the BTCS code was sidelined.

Time integration of the Eq. 4.12 was performed using the Matlab program ‘pdepe’, which discretizes the governing equations and solves the resulting system of ordinary differential equations using the stiff ODE solver ‘ode15s’\textsuperscript{31}. The maximum relative and absolute error are controlled by user inputs. In order to assess the accuracy of the method, a series of studies were performed. First, a mesh refinement study was performed to determine the grid spacing required for good results. We performed several simulations with varying grid spacing, using the nominal parameters listed in Table 4.4. The results of the refinement study are presented in Figure 4.3, in the form of steady state spatial concentration profiles for the four mobile species: CO\textsubscript{2}, OH\textsuperscript{−}, HCO\textsubscript{3}\textsuperscript{−}, and CO\textsubscript{3}\textsuperscript{2−}. Although many different grid spacings were investigated, only N = 30, 70, and 100 are shown (except for CO\textsubscript{2}), to maintain clarity, where N is the number of grid points. In general, the steepest gradients in the domain occur in the CO\textsubscript{2} profile near \(x = L\). Therefore the grid must be fine enough to eliminate the types of numerical instabilities observed in Figure 4.3a. Grid convergence is achieved fairly rapidly in the bulk of the membrane once these instabilities are resolved, as demonstrated by the indistinguishable profiles in Figures 4.3b-d. Therefore, all results presented herein use a grid of \(N = 200\) was used unless otherwise mentioned.

Table 4.4

*Nominal parameters for the grid refinement study*
<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>T</td>
<td>323 K</td>
</tr>
<tr>
<td>i</td>
<td>100 mA/cm²</td>
</tr>
<tr>
<td>([i_{0,\text{OH}}, i_{0,\text{HCO}<em>3}, i</em>{0,\text{CO}_3}])</td>
<td>([79, 0.79, 0.79]) A/m²</td>
</tr>
<tr>
<td>(p_{\text{CO}_2})</td>
<td>40.5 Pa (400ppm)</td>
</tr>
<tr>
<td>L</td>
<td>10 μm</td>
</tr>
</tbody>
</table>

We can also determine the observed order of accuracy of the numerical method, which should be close to 2, since this is a 2\(^{\text{nd}}\) order method. Consider the numerical concentration profiles \(c_1(x), c_2(x),\) and \(c_3(x)\), at three different meshes, \(\Delta x_1, \Delta x_2,\) and \(\Delta x_3\) as detailed by Roy\(^{64}\).

Using the series expansion for a solution of arbitrary order \(p\), we can solve for \(p\) as

\[
p = \frac{\ln \left( \left\| c_3 - c_2 \right\| \right)}{\ln(r)} \tag{4.30}
\]

Where the brackets \(\| \|\) indicate a norm (e.g. \(L_\infty, L_1, L_2\), etc.), and \(r = \frac{\Delta x_3}{\Delta x_2} = \frac{\Delta x_2}{\Delta x_1} > 1\). To observe the order of accuracy, we chose \(r = 2\) and \(\Delta x_1 = L/320\), and performed simulations using the conditions in Table 4.4. These results are shown in Table 4.5 for the four mobile species. The values near 2 give confidence that the discretization error is appropriate for the method used.

**Table 4.5**

*Observed order of accuracy for the four mobile species in this study*
<table>
<thead>
<tr>
<th>Species</th>
<th>$L_\infty$</th>
<th>$L_1$</th>
<th>$L_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO$_2$</td>
<td>2.249</td>
<td>2.144</td>
<td>2.207</td>
</tr>
<tr>
<td>OH$^-$</td>
<td>2.073</td>
<td>2.086</td>
<td>2.086</td>
</tr>
<tr>
<td>HCO$_3^-$</td>
<td>2.133</td>
<td>1.993</td>
<td>1.997</td>
</tr>
<tr>
<td>CO$_3^{2-}$</td>
<td>2.235</td>
<td>1.840</td>
<td>1.881</td>
</tr>
</tbody>
</table>

Lastly, the time integration error is controlled by user inputs for the absolute and relative error tolerances, $a$ and $r$ respectively. At each time step the error of component $k$, $e_k$, is made to satisfy

$$e_k \leq r|c_k| + a_k$$

(4.31)

where $c_k$ is the solution of component $k$ at the time step in question. The default values are $r = 10^{-3}$ and $a = 10^{-6}$. In this study, we found that reasonable computation times were obtainable with $r = a = 10^{-9}$, and that diminishing returns were gained upon refinement of these values. These tolerances ensure that the discretization error in the time derivatives are on the order of $\sim 10^{-12}$ M (since the simulations use mol/m$^3$ for concentrations) and/or below $10^{-7}$ % of the local concentration value.
4.3 - Results and Discussion

4.3.1 - Determination of an Appropriate Self-Purging Model

Figure 4.3 – Grid convergence investigation using steady-state spatial concentration profiles for a) $\text{CO}_2$ (inset is just a zoomed in view), b) $\text{OH}^-$, c) $\text{HCO}_3^-$, and d) $\text{CO}_3^{2-}$
The first goal of this work is to determine which self-purging model can accurately replicate the characteristic responses (identified in section 4.1) of an operating AEMFC during the carbonation process. To accomplish this, simulations were performed using the experimental conditions of Inaba et al.\textsuperscript{45} (to investigate membrane resistance and anode overpotential trends) and Watanabe et al.\textsuperscript{30} (to investigate CO\textsubscript{2} emission into the anode gas stream). The AEM’s area-specific resistance (ASR) is calculated using a Dusty Fluid model\textsuperscript{22} using the average steady-state concentrations. The relevant experimental and operating parameters of these studies are listed in Table 4.6.

Table 4.6

*Relevant experimental conditions of the studies used to investigate the self-purging models*

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Inaba et al.\textsuperscript{45}</th>
<th>Watanabe et al.\textsuperscript{30}</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Operating conditions</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( T ) (K)</td>
<td></td>
<td>323</td>
</tr>
<tr>
<td>( i ) (mA \cdot cm\textsuperscript{-2})</td>
<td>0 – 800</td>
<td>250 – 400</td>
</tr>
<tr>
<td>( p_{CO_2} ) (Pa)</td>
<td>10, 100, 500</td>
<td>39.5</td>
</tr>
<tr>
<td>( P_C ) (Pa)</td>
<td></td>
<td>101325</td>
</tr>
<tr>
<td>( P_A ) (Pa)</td>
<td></td>
<td>101325</td>
</tr>
<tr>
<td>( Q_C ) (mL \cdot min\textsuperscript{-1})</td>
<td>100</td>
<td>200</td>
</tr>
<tr>
<td>( Q_A ) (mL \cdot min\textsuperscript{-1})</td>
<td>200</td>
<td>100</td>
</tr>
<tr>
<td><strong>Membrane Properties</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( L ) (μm)</td>
<td>10</td>
<td>28</td>
</tr>
<tr>
<td>( A ) (cm\textsuperscript{2})</td>
<td></td>
<td>5.0</td>
</tr>
</tbody>
</table>
The results of implementing the chemical pathway are shown in Figure 4.4. First, as Figure 4.4a demonstrates, the decrease in ASR as a function of current density is nowhere near what is observed experimentally. The equilibrium shifts in Eqs. 4.1 – 4.2 are not sufficient for replicating the significant conductivity reclamation that is experimentally observed. Perhaps even more telling is that the chemical pathway produces a limiting current effect, as demonstrated in Figure 4.3b. The curves in Figures 4.4a and 4.4b terminate at 250 mA/cm², 16 mA/cm², and 3 mA/cm² (for 100 ppm, 1000 ppm, and 5000 ppm, respectively), even though Inaba et al. investigated current densities up to 500 mA/cm². The limiting current effect is a result of the extremely low OH⁻ concentration in the membrane near open circuit. In the chemical self-purging model, all of the anode current must be supplied by Eq. 4.4, which eventually depletes all of the local OH⁻. This effect is shown in Figure 4.4c, at the denoted limiting current densities for the corresponding CO₂ concentrations. For this reason, it was impossible to replicate the anode gas stream CO₂ concentrations at the conditions used by Watanabe et al., who studied the AEMFC at 395 ppm and current densities between 250 – 400 mA/cm².

<table>
<thead>
<tr>
<th>λ</th>
<th>8.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>( IEC ) (mmol \cdot g^{-1})^{46}</td>
<td>1.58</td>
</tr>
<tr>
<td>( \rho_{mem} ) (g \cdot cm^{-3})</td>
<td>1.0</td>
</tr>
</tbody>
</table>
Figure 4.4 – Effects of implementing the chemical self-purging pathway on a) ASR vs. current density, b) anode overpotential, and c) hydroxide ion concentration profiles at the limiting current densities.

In the chemical model, the flux of OH$^-$ at the anode is automatically prescribed by the operating current; the BV equation, Eq. 4.4, is only used to find the overpotential. Therefore, the concentration depletion observed in Figure 4.4c is an intrinsic feature of the chemical self-purging model. It is independent of any kinetic parameters and their associated uncertainties.
For this reason, the results of Figure 4.4 provide strong evidence that the chemical mechanism cannot adequately model the self-purging phenomenon.

Next, the electrochemical self-purging mechanism was investigated using the same sequence of tests. Because of the noted experimental difficulties in obtaining accurate electrochemical data for the (bi)carbonate HOR pathways, simulations were performed using a parametric study for the values for the exchange currents. Sheng et al. reported a hydroxide pathway exchange current density of $i_{0,\text{OH}} = 7.98 \text{ mA/cm}^2_{\text{geo}}$ in 0.1 M KOH, at 50°C on TKK 46 wt. % Pt/C electrodes (4.3 cm$^2_{\text{Pt}}$/cm$^2_{\text{geo}}$)$^{59}$, which will be used as the nominal value in this work. Exchange currents for Eqs. 4.5 – 4.6 can be varied relative to this benchmark, and the AEMFC’s characteristic responses can be analyzed. This investigation is presented in the form of a parametric study, which is presented in Figure 4.5. The conditions listed in Table 4.6 are again used, and the exchange currents used in each simulation are displayed at the top of each sub-figure, using a shorthand bracket notation defined as $i_0 = [i_{0,\text{OH}}, i_{0,\text{HCO}_3}, i_{0,\text{CO}_3}]$ A/m$^2$.

It is worth emphasizing that the purpose of the present work is not to fit the model to experimental data. There are too many variables and the available experimental studies are not ideal for this type of analysis; kinetic parameters should be fit from data obtained in carefully designed experiments that isolate the physics under investigation. Rather, we aim to find a set of exchange currents that enable the electrochemical self-purging model to replicate experimentally observed phenomena so as to support our hypothesis that it is indeed the pathway which is observed. The mixed potential modeling framework developed herein can be refined in the future if more accurate electrochemical data becomes available.
Figure 4.5 – Investigation of varying $i_{0,HCO_3}$ and $i_{0,CO_3}$ on the ASR and anode polarization of an operating AEMFC. Experimental data obtained by Inaba et al.\textsuperscript{45} are superimposed onto the ASR figures to facilitate validation, and to choose appropriate exchange currents to use in the electrochemical self-purging model (simulations were performed using experimental parameters listed in Table 4.6). The exchange currents used are listed at the top of each plot using the shorthand $i_0(A/m^2) = [i_{0,OH}, i_{0,HCO_3}, i_{0,CO_3}]$. 
Quantitative comparisons are difficult for the anode overpotentials, since there are several processes that contribute to this type of loss that are not accounted for here. Most significantly, the flow through the serpentine gas channels is not modeled due to lack of information about the experimental setup. Flow through the gas channels, catalyst layer resistances, and water and gas transport through the GDL, MEA, etc. all contribute to the shape of the current-overpotential curve (See Ref. [18], Figure 2 for a good visualization of the breakdown of these losses). This study focuses mainly on the HOR activation losses, so validation to experimental polarization data is limited to semi-quantitative observations. In addition, the pre-conditioning and hydration of the AEMs in the study are somewhat unknown, which significantly affect the magnitude of the ASR. For the results in Figure 4.5 we use a hydration number of $\lambda = 8.0$ which was obtained by fitting the Dusty Fluid conductivity model\textsuperscript{51} to the pure-O\textsubscript{2} ASR data of Inaba et al. Clearly the hydration of the membrane varies during operation, but in these studies it was treated as a constant, which we believe explains some of the offsets observed in the numerical ASR results.

Here we will highlight a few of the major observations from Figure 4.4. First, the case where $i_{0,OH} = i_{0,HCO_3} = i_{0,CO_3} = 79 \text{ A/m}^2$ (Figure 4.5a-b) greatly increased the computational time, taking several days to simulate the 100 ppm case. Since the 100 ppm results already showed significant deviation from the experiment, the 1000 ppm and 5000 ppm cases were not attempted. Next, we ruled out certain cases with particularly abnormal behavior (compared to experiments), namely:

- $i_{0,HCO_3} = i_{0,CO_3} = 7.9 \text{ A/m}^2$ (Figure 4.5c-d, ASR drop too steep for 100 ppm)
- $i_{0,HCO_3} = i_{0,CO_3} = 0.079 \text{ A/m}^2$ (Figure 4.5g-h, not enough ASR drop)
• $i_{0,\text{HCO}_3} = 0$, $i_{0,\text{CO}_3} = 0.79 \text{ A/m}^2$ (Figure 4.5k-l, unique “turnover” in anode overpotential curves near 100 – 200 A/m$^2$)

• $i_{0,\text{HCO}_3} = 7.9$, $i_{0,\text{CO}_3} = 0.79 \text{ A/m}^2$ (Figure 4.5m-n, too steep ASR drop at 100 ppm)

After reviewing all of the cases, we have chosen the set of parameters $i_0(50^\circ\text{C}) = [79, 0.79, 7.9] \text{ A/m}^2$, shown in Figure 4.5o-p, to simulate the electrochemical self-purging mechanism. These exchange currents have been shown to account for realistic ASR and anode overpotential behavior, and, as is shown in the main text, CO$_2$ emission into the anode gas stream.

From the studies in Figure 4.5, we found that exchange currents of $i_{0,\text{HCO}_3}(50^\circ\text{C}) = 0.079 \text{ mA/cm}^2$ and $i_{0,\text{CO}_3}(50^\circ\text{C}) = 0.79 \text{ mA/cm}^2$ were able to reproduce the characteristic AEMFC responses identified in the introduction. These values were then used in the simulations whose results are shown in Figure 4.6. Not only did the electrochemical self-purging mechanism allow for simulation of all the current densities under investigation (unlike the chemical mechanism), but the trends of ASR (Figure 4.6a) and anode overpotential (Figure 4.6b) vs. current density are consistent with those observed by Inaba et al.$^{45}$ Although the ASR results can be quantitatively validated, comparisons to experimental anode overpotentials should be more qualitative. This is because, as noted by Zeng et al.$^{65}$, there are many experimental challenges associated with the placement of reference electrodes, which could introduce additional biases.

Using the electrochemical mechanism, the purging of CO$_2$ into the anode gas stream is much more realistic, as demonstrated by Figure 4.6c. It should be noted that the transient aspects in Figure 4.6c are considerably longer (~5x longer) that what Watanabe et al. observed$^{30}$, which is most likely due to experimental aspects that are unable to be implemented in the present model, like gas channel geometry and time lag associated with the mass spectrometer.
implementation (used for experimental CO$_2$ detection). In addition, we would like to identify species transport through the electrodes as an important target for future work. The anodes of AEMFCs are often partially or completely flooded with the water generated by the HOR, which introduces an additional barrier to gas phase and aqueous species transport.

Figure 4.6 – Effects of implementing the electrochemical self-purging pathway on a) ASR vs. current density (symbols are adapted from the experimental results of Inaba et al.$^{45}$), b) anode overpotential, and c) anode gas stream CO$_2$ content (dashed line indicates current density).
Simulations were performed using the parameters in Table 2, and using $i_{0,\text{OH}} = 7.9 \text{ mA/cm}^2$, $i_{0,\text{HCO}_3} = 0.079 \text{ mA/cm}^2$, and $i_{0,\text{CO}_3} = 0.79 \text{ mA/cm}^2$.

4.3.2 - Fundamental Simulation Results

In this chapter we explore the fundamental results obtained by the solution of Eq. 4.12. The results in this section are all obtained using the nominal parameters listed in Table 4.7, unless specifically noted. In general, we chose the nominal parameters to simulate an AEMFC operating at 50°C, using pure H$_2$ as the fuel and normal air (21% O$_2$, 400 ppm CO$_2$) as the oxidant, at reasonable flow rates and no back-pressure.

Table 4.7

Nominal simulation parameters for AEMFC investigation.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Operating conditions</td>
<td></td>
</tr>
<tr>
<td>$T$ (K)</td>
<td>323</td>
</tr>
<tr>
<td>$p_{\text{O}_2}$ (Pa)</td>
<td>$(0.21)P_c$</td>
</tr>
<tr>
<td>$p_{\text{CO}_2}$ (Pa)</td>
<td>$(400 \times 10^{-6})P_c$</td>
</tr>
<tr>
<td>$P_c$ (Pa)</td>
<td>101325</td>
</tr>
<tr>
<td>$P_A$ (Pa)</td>
<td>101325</td>
</tr>
<tr>
<td>$Q_c$ (mL · min$^{-1}$)</td>
<td>200</td>
</tr>
<tr>
<td>$Q_A$ (mL · min$^{-1}$)</td>
<td>200</td>
</tr>
<tr>
<td>Membrane Properties</td>
<td></td>
</tr>
<tr>
<td>$L$ (μm)</td>
<td>28</td>
</tr>
<tr>
<td>$A$ (cm$^2$)</td>
<td>5.0</td>
</tr>
</tbody>
</table>
\[ \lambda \]
\[ IEC \text{ (mmol} \cdot \text{g}^{-1}) \]
\[ \rho_{\text{mem}} \text{ (g} \cdot \text{cm}^{-3}) \]
\[ 15 \]
\[ 1.58 \]
\[ 1.0 \]

First we present a series of curves that detail the transient carbonation of an AEM operating at a current density of 100 mA \cdot cm^{-2}, initially in the pure OH\textsuperscript{−} form. Note that where possible, the scale of the ordinate (y) axis is kept the same, but it might change from frame to frame in order to best illustrate the process. The evolution of the spatially-varying CO\textsubscript{2} concentration profiles is shown in Figure 4.7. The concentration at \( x = L \) is always \( \sim 6.93 \times 10^{-6} \text{ mol/L} \), which corresponds to the Henry’s law value at these conditions, although this is not always kept “in-frame”, in order to observe the finer features of the profile for locations \( x \leq L \).

The most striking feature is the very steep dropoff near \( x = L \), which corresponds to the rapid consumption of CO\textsubscript{2} due to Eqs. 4.1 – 4.2 as it is absorbed into the pure OH\textsuperscript{−} membrane. As the (bi)carbonate concentrations gradually increase, the forward rate of Eq. 4.1 slows, and CO\textsubscript{2} likewise starts to build up and diffuse towards the anode (e.g., \( t = 10 \text{s} \)). Since the anode is nominally CO\textsubscript{2}-free, any accumulation near \( x = 0 \) is enough to make the CO\textsubscript{2} desorb into the gas stream; this is the reason for the steep positive gradients observed in, e.g., \( t = 50 \text{s} \) and onwards.

The reason this “shoulder” near \( x = 0 \) exists is because of the accumulation of (bi)carbonates there. When the concentrations of (bi)carbonates are “high” and hydroxide is “low”, Eqs. 4.1 – 4.2 allow for some accumulation of CO\textsubscript{2}, even though the prevailing intuitive wisdom is that CO\textsubscript{2} is immediately and completely converted inside the membrane. This serves to highlight the utility of a model that can directly simulate these reactions.
Next, we can observe the similar evolution of the OH\textsuperscript{−} profiles. The initial response of OH\textsuperscript{−} shows the effect of Eq. 4.1: up to about $t = 1$s there is a relatively local consumption of hydroxide near $x = L$, while the rest of the membrane is unaffected. In this unaffected region, there are no concentration gradients or other ionic species, meaning that the current inside the membrane is supplied entirely by OH\textsuperscript{−} migration. In the $t = 10$s snapshot, we see the first development of the positive gradient near $x = 0$. This corresponds to both (bi)carbonate accumulation, and consumption of OH\textsuperscript{−} in the HOR. Once the positive gradient is established across the entire membrane, little else changes except for the gradual depletion of OH\textsuperscript{−} in the membrane as a whole, i.e., the shape of the profile remains similar but is shifted lower and lower as $t \to \infty$. 

Figure 4.7 – Transient snapshots of the spatially-varying CO\textsubscript{2} concentration profiles.
Figure 4.8 – Transient snapshots of the spatially-varying $OH^-$ concentration profiles.

Bicarbonate is initially absent in the pure $OH^-$ membrane, although it quickly accumulates near the cathode due to Eq. 4.1, as demonstrated by Figure 4.9. Due to the higher standard potential of the bicarbonate HOR pathway, Eq. 4.5, $HCO_3^-$ begins to accumulate at the anode at intermediate times (e.g., $t = 10s$); an effect that remains until steady state. This “bicarbonate enrichment zone” has been noted by other researchers before\textsuperscript{24}, and was used as evidence that bicarbonates don’t participate in the HOR. The results of Figure 4.9 show that the electrochemical mechanism can still result in bicarbonate “enrichment” near the anode. The constant participation (consumption) of $OH^-$ in the HOR allows for accumulation of $HCO_3^-$, which is why its gradient is negative across the membrane from roughly $t = 50s$ onward.
Figure 4.9 – Transient snapshots of the spatially-varying $HCO_3^-$ concentration profiles.

The last mobile species, $CO_3^{2-}$, initially exhibits a similar behavior to $HCO_3^-$. This is because Eq. 4.2 proceeds even more rapidly than Eq. 4.1 when all the reactants are present; Myles et al.\textsuperscript{12} have referred to this as the “carbonate accumulation” regime. In the isolated membrane that they studied, this was followed by a “bicarbonate accumulation” regime, during which time carbonate is depleted. We don’t observe quite the same phenomenon here, due to the consumption of $OH^-$ in the HOR, which prohibits the levels of $HCO_3^-$ necessary to observe “bicarbonate accumulation”. The positive gradient that develops near the anode at longer times reflects the increasing participation of $CO_3^{2-}$ in the HOR, Eq. 4.6, that becomes necessary as $OH^-$ is depleted. Note that carbonate is consumed in the HOR more preferentially than bicarbonate due to its lower standard potential (see Figure 4.1).
Figure 4.10 – Transient snapshots of the spatially-varying $CO_3^{2-}$ concentration profiles.

These results were presented to give the reader an idea of the transient evolution of the species concentrations at given operating conditions. These characteristics would likely change slightly at different current densities or temperatures for example, but it is worth examining the basic principles for a nominal case. The next section will focus on the effects of these operating conditions, but in general only for steady state operation. This is because common practice (current sweep experiments for example) is to run the fuel cell at what amounts to steady state conditions.

4.3.3 - Effects of CO$_2$ on AEMFC Operation

Following the determination of appropriate kinetic parameters for the electrochemical self-purging mechanism in section 4.3.1, various effects of CO$_2$ on AEMFC operation were explored. Again the parameters in Table 4.7 were used unless otherwise noted. As yet, the model does not include water transport throughout the cell, and so the relative humidities of the gas streams are not needed as inputs (not to diminish this very important aspect of AEMFC operation).

First, the steady-state spatial profiles of some key properties were investigated at several different current densities, as shown in Figure 4.11. It’s clear that the operating current has a
significant effect on the mobile species’ concentration profiles. At open circuit ($i = 0$), aqueous carbon dioxide (Fig. 4.11a) is relatively abundant in the membrane. The steep drop in CO$_2$ concentration near $x = L$ is indicative of the rates of Eqs. 4.1 – 4.2, which consume CO$_2$ quite rapidly. The similar drop near $x = 0$ is due to the constant desorbing of CO$_2$ into the anode gas channel, which occurs because we are simulating the flow of CO$_2$-free gas (if we were simulating an isolated AEM, the concentration profile would be symmetrical, as observed by Myles et al.$^{12}$). As the current density increases, the membrane’s CO$_2$ content steadily decreases, as is expected because of the self-purging mechanism. Near $x = 0$ we also see that the gradient changes signs after $i = 500$ mA/cm$^2$, due to the buildup of CO$_2$ in the anode gas stream. At low current densities, the gas stream CO$_2$ content is low enough that CO$_2$ desorbs from the membrane (positive gradient inside the membrane), but at higher currents there is actually enough CO$_2$ produced by Eqs. 4.5 – 4.6 (the (bi)carbonate HOR pathways) that there is a net flux of CO$_2$ into the membrane (negative gradient).

![Graphs showing CO$_2$ and OH$^-$ concentration profiles](image)
Figure 4.11 – Numerical steady-state, spatially-varying solutions for a) $CO_2$ concentration, b) $OH^-$ concentration, c) $HCO_3^-$ concentration, d) $CO_3^{2-}$ concentration, e) the electric field (solid lines correspond to a carbonated AEM, dashed lines are the reference electric field for a pristine AEM), and f) ionic current transport numbers for the three ionic species in the membrane. The arrows in each figure indicate the trend of increasing current, with $i = 0, 10, 20, 50, 100, 200, 500, 1000 \text{ mA/cm}^2$ shown in each figure.
The \( \text{OH}^- \) variation in the membrane follows the opposite trend of \( \text{CO}_2 \): while its concentration is initially low due to the complete carbonation at \( i = 0 \), it is gradually replenished as the operating current is increased and hydroxide ions are supplied to the membrane by Eq. 4.3 (the ORR). The open circuit, fully-carbonated state of the membrane favors \( \text{HCO}_3^- \), as evidenced by Fig. 4.11c and predicted/observed by other researchers before\(^{12,46} \). Again, as the current density is increased, the \( \text{HCO}_3^- \) content in the membrane decreases due to self-purging. At higher current densities there exists some curvature in the \( \text{HCO}_3^- \) concentration profile, which some have called the (bi)carbonate “enrichment” zone\(^{20,24} \), which is also observed in the \( \text{CO}_3^{2-} \) profile, Fig. 4.11d. In general, the \( \text{CO}_3^{2-} \) concentration in the membrane is much lower than the other two ions (note the difference in scale of the ordinate axis). As the current density is increased, the \( \text{CO}_3^{2-} \) concentration rises slightly due to the balance of Eqs. 4.1 – 4.2. More significantly, there is a change in curvature of the \( \text{CO}_3^{2-} \) profile after \( i = 500 \text{ mA/cm}^2 \). This is likely tied to the change in the gradient of the \( \text{CO}_2 \) profile at \( x = 0 \) discussed before: since \( \text{CO}_2 \) is effectively being supplied to the anode side of the AEM at high currents, Eq. 4.2 is more likely to produce \( \text{CO}_3^{2-} \) (moderate local concentrations of \( \text{CO}_2, \text{OH}^-, \) and \( \text{HCO}_3^- \) encourage Eq. 4.1, and subsequently Eq. 4.2, to favor their products).

The net anionic species flux through the membrane must be negative, meaning they move from cathode to anode, according to direction of electron flow. However due to the combined forces of diffusion and migration, it is not clear from the concentration gradients alone which direction the individual ions move. The spatial variation in the electric field required to drive the ionic current is shown in Figure 4.11e. At low currents the variation is fairly linear, however at higher currents the electric field changes shape in order to balance the combined effects of the local diffusion current (due to concentration gradients) and reactions. Also note the value of the
electric field with carbonates (solid lines) compared to that of a pristine AEM (dashed lines, shown only for \(i = 100, 200, 500, 1000\) mA/cm\(^2\) for clarity). In the pristine AEM, ion transport is driven entirely by migration and the electric field obtained from the Nernst-Planck equation is 
\[ E = \frac{iRT}{F^2D_{\text{eff}}^{\text{OH}} c_{\text{OH}}} \]
. At lower current densities, the electric field inside the carbonated membrane is larger than the pristine value, because the conductivities of (bi)carbonates are much lower than \(\text{OH}^-\). At higher current densities, the electric field inside the carbonated membrane becomes weaker compared to the pristine case, since the steeper concentration gradients (especially for \(\text{OH}^-\)) produce more significant diffusion currents.

The breakdown of the individual species’ shares of the total ionic current are shown in Figure 4.11f, in the form of ionic transport numbers (also sometimes called the transference numbers, i.e. the fraction of the total ionic current provided by a single species). Even at low current densities, when the membrane is fully carbonated, \(\text{OH}^-\) carries most of the ionic current. Interestingly, the negative transport number for \(\text{HCO}_3^-\) indicates a positive species flux, meaning that the diffusion from anode to cathode is stronger than the migration from cathode to anode. This is one of the reasons why the electric field in the carbonated AEM is larger than the pristine AEM at low currents. However it should be noted that the transport numbers are normalized to the total ionic current. Therefore, even though the bicarbonate transport number is large (\(\approx -0.15\)) at low currents, this doesn’t mean that there is a large bicarbonate flux from anode to cathode. As the current density increases, the self-purging of the membrane means that the contributions of both \(\text{HCO}_3^-\) and \(\text{CO}_3^{2-}\) to the ionic current diminish, as indicated by their transport numbers approaching zero.

Next, current sweep experiments were simulated at various cathode gas stream \(\text{CO}_2\) concentrations, to observe the influence of \(\text{CO}_2\) on fuel cell performance. The individual electrode
potentials are shown as a function of current density in Figure 4.8a. To simulate the cathode potential we use Eq. 4.18 to describe the ORR, using the exchange current $i_{0,\text{ORR}} = 9.0 \times 10^{-4} \text{mA/cm}^2_{\text{geo}}$ obtained by Perez et al.\textsuperscript{66} at 25°C, and adjusted to 50°C by assuming an Arrhenius dependence on temperature (this will be described in more detail shortly). As Figure 4.8a demonstrates, the cathode performance is hardly affected by the carbonation process, which has been observed experimentally by Inaba et al.\textsuperscript{45}. This is because the cathode overpotential is already high due to relatively sluggish ORR kinetics. The concentration variations hardly have any effect, although the performance does improve very slightly due to local OH\textsuperscript{−} replenishment near the cathode. On the other hand, the anode behavior is significantly affected by the presence of CO\textsubscript{2}, not only due to the higher potentials required to drive the (bi)carbonate HOR pathways (Eqs. 4.5 – 4.6), but also due to concentration effects (OH\textsuperscript{−} depletion) in the hydroxide HOR pathway (Eq. 4.4). The contributions of the different HOR pathways are shown in Figure 4.8b, where a log scale is used for the abscissa in order to better observe the low current behavior. Because Eq. 4.4 is much more facile than Eqs. 4.5 – 4.6, almost all of the current is supplied by the hydroxide HOR pathway as long as there is any OH\textsuperscript{−} near the anode. Only at very low current densities are Eqs. 4.5 – 4.6 significantly active; for intermediate-high currents Eq. 4.4 dominates because it features the lowest standard potential.
Figure 4.12 – Numerical current sweep simulations showing the steady-state solutions of a) cathode and anode electrode potential, and b) HOR transference number for the three different HOR pathways. The arrows in each figure indicate the trend of increasing \( \text{CO}_2 \) content, with \( \chi_{\text{CO}_2} = 100, 200, 300, 400, 500, 1000, 2000 \) ppm shown in each figure.

The results of Figure 4.12 elucidate just how electrochemical (bi)carbonate activity affects the anode performance. Just because both \( \text{HCO}_3^- \) and \( \text{CO}_3^{2-} \) may be active HOR participants does not necessarily mean they significantly contribute to the current produced at the anode. They do however raise the anode overpotential to prevent the reverse of Eqs. 4.5 – 4.6, which would occur if the anode potential is lower than their respective equilibrium potentials, \( \phi_A < \phi_k^0 \). Furthermore, note that low (bi)carbonate HOR participation does not necessarily mean a low \( \text{CO}_2 \) flux: 0.1 mA/cm\(^2\) from either (bi)carbonate pathway translates to a \( \text{CO}_2 \) flux of \( 1.03 \times 10^{-3} \) \( \mu\text{mol} \cdot \text{cm}^{-2} \cdot \text{s}^{-1} \) which in turn gives a rough estimate of the anode \( \text{CO}_2 \) mole fraction of \( \chi_{\text{CO}_2} \approx AJ_{\text{CO}_2}RT/Q_A P_A = 82 \) ppm (using the parameters in Table 4.7).

The current sweep experiments in Figure 4.12 were performed with all other parameters constant, to isolate the effect of current density and to gain insight into the AEMFC’s response.
However we can also observe the interplay between multiple operating parameters simultaneously, to get an idea of the “design space” of AEMFC operation. To this end, we simulated the variation of cathode and anode gas stream flow rates simultaneously with a current sweep experiment, to get the cell voltage contours shown in Figures 4.13a and 4.13b respectively. As Figure 4.13a demonstrates, increasing the anode flow rate can slightly improve the cell performance because higher flow rates sweep purged CO$_2$ from the gas stream more quickly. On the other hand, in Figure 4.13b we see that lower cathode gas flow rates offer slightly better performance, because higher flow rates introduce CO$_2$ to the system at a faster rate. This effect was identified by Rigdon et al.$^{10}$ to improve CO$_2$ removal from the gas stream electrochemical CO$_2$ separators. We should emphasize that the cell voltage, calculated as $V = \phi_c - \phi_A$, includes only activation losses from ORR and HOR pathways, concentration losses due to ion depletion at the membrane/electrode interfaces, ohmic losses due to ion migration across the membrane, and concentration losses due to the transport of gas phase reactants to the membrane/electrode interfaces. A more detailed description of the gas channels that includes pressure drop, and concentration variations along the length of the channel might refine these results further.
Figure 4.13 – Cell voltage contours, where $V = \phi_C - \phi_A$, as a function of current density and a) anode gas flow rate, b) cathode gas flow rate, and c) temperature, using the parameters in Table
A log scale for current density is used to better visualize both low and high current regimes.

We also wanted to observe the effect of changing the cell’s temperature, since temperature affects several aspects of AEMFC operation, such as the exchange currents, diffusion coefficients, chemical reaction rate constants, Henry’s law solubility, and migration. For example, the dimensionless Henry solubility, \( c_{aq}/c_g \), of \( \text{CO}_2 \) decreases from 0.82 at 25\( ^\circ \text{C} \), to 0.32 at 80\( ^\circ \text{C} \) which should greatly reduce the amount of absorbed \( \text{CO}_2 \) in the system. Similarly, the diffusivities of the ionic species increase by factors of 2.5 — 3 over the same temperature interval. Sheng et al. found that the exchange current of the hydroxide HOR pathway obeyed an Arrhenius relationship with \( \mathit{i}_{0, \text{OH}}(T) = 4.66 \times 10^5 e^{−29500/RT} \) mA/cm\(^2\)geo. Unfortunately, activation energies for the (bi)carbonate HOR pathways are not known. Until these values become known, we can assume consistent activation energies and Arrhenius forms of the (bi)carbonate pathways as the \( \text{OH}^- \) pathway, on the basis of the the 50\( ^\circ \text{C} \) values determined in Figure 4.4. Although this procedure is speculative, it will allow us to predict trends in cell performance providing that the three HOR pathways obey similar temperature dependencies. We can follow a similar procedure for the ORR as well by combining the values \( \mathit{i}_{0, \text{ORR}}(25^\circ \text{C}) = 9.0 \times 10^{-4} \) mA/cm\(^2\)geo obtained by Perez et al.\(^{66}\) and \( E_a = 42000 \) J/mol obtained by Schmidt et al.\(^{67}\) to yield \( \mathit{i}_{0, \text{ORR}}(T) = 2072 e^{−42000/RT} \) mA/cm\(^2\)geo.

Using these values, we obtained the voltage vs. temperature and current density contour shown in Figure 4.13c. The relationship between voltage and temperature is not monotonic, as it was with \( Q_A \) and \( Q_C \). At lower current densities (up to \( \sim 10 \) mA/cm\(^2\)), higher temperatures result in higher cell voltages, due to the improved electrochemical kinetics and lower \( \text{CO}_2 \) solubility.
However, at moderate to higher currents the performance is actually worse at higher temperatures. This result is somewhat surprising, since higher temperatures lead to higher diffusivities, exchange currents, and lower CO₂ solubility, which should all lead to better performance. The cell performance mostly depends on the conditions at the anode/membrane interface, where there exists a complicated interplay between the oxidation of the different ionic species participating in the HOR, recirculation of CO₂ into and out of the membrane, and the chemical reactions converting CO₂, OH⁻, HCO₃⁻, and CO₃²⁻ (Eqs. 4.1 – 4.2). We find that the net result of these processes is that at high temperatures and current densities, HCO₃⁻ is the predominant species at the anode/membrane interface. The equilibrium potential for the HCO₃⁻ HOR pathway is the highest of all three pathways, which leads to increased anode overpotentials and the decrease in cell voltage seen in the upper right region of Figure 4.13c.

Because the implications of Figure 4.13c were so unexpected to us, we searched the literature for some experimental evidence of this effect. For instance, Krewer et al.²⁴ also observed that higher temperature equilibrium shifts result in higher (bi)carbonate concentrations, especially near the anode and at higher current densities, which supports our explanation. In a different study, Topal et al.⁶⁸ observed the effects of temperature on AEMFC performance curves while using ambient air in the cathode. They did not observe any performance drop at higher temperatures, however only current densities up to 60 mA/cm² were investigated. According to the trends in Figure 4.13c, high temperature performance decreases are more likely to occur at higher current densities (> 300 mA/cm²). In addition, the aforementioned study used extremely low anode flow rates, ~25 mL/min, which would reduce the self-purging mechanism and cause the temperature to have a purely beneficial effect.
4.4 - Conclusions

A numerical model of the carbonation of an operating AEMFC was developed based on the solution of coupled, 1-D Nernst-Planck equations with chemical reactions. We developed two sets of boundary conditions at the anode/membrane interface, in order to simulate the chemical and electrochemical self-purging mechanisms. We found that only the electrochemical mechanism was able to reproduce experimentally-observed trends in ASR, anode overpotential, and anode gas stream CO\(_2\) content. The electrochemical model is based on mixed-potential theory, and uses exchange currents determined from a parametric investigation on the effects of CO\(_2\) on ASR and anode overpotential.

Using the electrochemical self-purging model, we also observed the aqueous species concentration profiles across the membrane as a function of current density. As expected, the (bi)carbonate content in the membrane decreases as current density is increased and OH\(^-\) is supplied by the ORR. Concentration gradients develop in the membrane due to the balance of transport and reactions, which result in diffusion currents that are compensated by an increase in the electric field. We found that although HCO\(_3^-\) and CO\(_3^{2-}\) are modeled as active HOR participants, most of the anode current is still supplied by the hydroxide HOR pathway. This indicates that the observed increase in anode potential is to prevent the reduction of CO\(_2\) at the anode. The model also predicts that the cathode overpotential is not significantly affected by carbonation, which is consistent with experimental observations. Lastly, the cell voltage was predicted as a function of anode & cathode gas flow rates, temperature, and current density, to gain practical insight into AEMFC operation. It was found that higher anode flow rates can increase the self-purging effect by removing CO\(_2\) from the gas stream more quickly, while higher cathode flow rates can degrade performance by introducing CO\(_2\) into the system more quickly.
Temperature was found to have a strong, yet unexpected, influence on cell performance and was strongly correlated to the current density. At low temperatures and current densities (up to ~10 mA/cm²) performance is improved due to improved electrochemical kinetics. However, at higher current densities (~100 – 1000 mA/cm²), higher temperatures shift the chemical equilibria to favor HCO₃⁻ near the anode, which decreases the cell performance. Unexpectedly, the operational temperature generally did not have nearly the significance on cell performance that current density did.

Although the model presented herein provides strong evidence that an electrochemical self-purging mechanism occurs, there is still a need for detailed experimental studies to verify this effect. Exchange currents and mechanistic descriptions for both bicarbonate and carbonate HOR pathways, including temperature dependence, would greatly refine our results. Future models could improve upon our work by including water transport throughout the system, and including direct simulation of additional fuel cell components, like catalyst layers, gas diffusion layers, and gas channels.

**List of Symbols**

- $c$: Concentration, $mol \cdot L$
- $E$: Electric field, $V \cdot m^{-1}$
- $D$: Diffusion coefficient, $cm² \cdot s^{-1}$
- $z$: Ionic charge
- $F$: Faraday’s constant, $C \cdot mol^{-1}$
- $R$: Universal gas constant, $J \cdot mol^{-1} \cdot K^{-1}$
- $T$: Temperature, $K$
- $\dot{R}$: Reaction source term, $mol \cdot L^{-3} \cdot s^{-1}$
- $J$: Molar flux, $mol \cdot cm^{-2} \cdot s^{-1}$
\[ k^+ \] Forward kinetic rate constant
\[ k^- \] Backward kinetic rate constant
\[ L \] Membrane thickness, \( m \)
\[ P \] Total pressure, \( N \cdot m^{-2} \)
\[ p \] Partial pressure, \( N \cdot m^{-2} \)
\[ Q \] Volume flow rate, \( cm^3 \cdot s^{-1} \)
\[ k_{abs} \] Absorption coefficient, \( cm \cdot s^{-1} \)
\[ H^{cc} \] Dimensionless Henry solubility
\[ i \] Current density, \( A \cdot cm^{-2} \)
\[ A \] Geometric electrode area, \( cm^2 \)
\[ u \] Mobility, \( cm^2 \cdot V^{-1} \cdot s^{-1} \)

**Greek**

\[ \phi \] Electrode potential, \( V \) vs. ref.
\[ \chi \] Mole fraction
\[ \lambda \] Water uptake coefficient
\[ \delta \] Solvent/membrane diffusivity ratio
\[ \epsilon \] Membrane porosity
\[ \rho \] Density, \( g \cdot cm^{-3} \)
\[ \alpha \] Transfer coefficient
\[ \eta \] Overpotential, \( V \)

**Superscripts**

\[ 0 \] Denotes equilibrium or standard conditions
\[ Des \] Desorption
\[ Elec \] Electrochemical
\[ Tot \] Total
\[ eff \] Effective

**Subscripts**

\[ k \] Species ‘\( k \)’
\[ C \] Cathode (cathodic)
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Anode (anodic)</td>
</tr>
<tr>
<td>g</td>
<td>Gaseous</td>
</tr>
<tr>
<td>aq</td>
<td>Aqueous</td>
</tr>
<tr>
<td>ad</td>
<td>Adsorbed</td>
</tr>
<tr>
<td>geo</td>
<td>Geometric</td>
</tr>
</tbody>
</table>
Chapter 5: Modeling Ionic Species Transport in Bipolar Membranes

5.1 - Overview

Bipolar membranes (BPMs) are laminate structured composite membrane materials consisting of anion-exchange (AEM) and cation-exchange (CEM) layers, as well as a transition region. Traditionally BPMs have found use in water electrolysis, transporting the produced protons and hydroxide ions to separate electrodes. However, recent work has demonstrated their applicability to fuel cells\textsuperscript{69–71}, microbial fuel cells\textsuperscript{72}, photoelectrochemical cells for e.g. solar driven water-splitting, CO\textsubscript{2} reduction, desalination\textsuperscript{73,74}, and electrochemical transistors for artificial synapses and neuromorphic computing\textsuperscript{75,76}. BPM devices can be quite complex, involving several simultaneous chemical and electrochemical reactions, as well as the associated transport of their reactants and products. Optimizing the performance of these devices requires a fundamental understanding of the local transport and reaction processes, especially near the BPM interface. In the vicinity of the interface, rapid acid-base recombinations occur which result in a space charge region (SCR) and generate a very strong electric field.
Figure 5.1 – Schematic of BPM domain with acidic anode and alkaline cathode for a) CO$_2$-free gas feeds, and b) CO$_2$-containing cathode feed.

Designs for improved BPM fuel cells (BPMFCs) consisting of an alkaline layer on the cathode side and an acid layer on the anode side have been demonstrated$^{70,77,78}$. This configuration, which is sketched in Figure 5.1a, is referred to as “forward-bias”, and enables water formation at the AEM|CEM junction, which can mitigate performance losses associated with membrane dry-out. BPMs can also be employed for enhanced electrolysis, including
photoelectrochemical water-splitting, which puts the membrane in “reverse-bias”\textsuperscript{79}. These configurations make use of the different pH on either side of the interface to reduce activation losses: the ORR is more facile in alkaline environments while the HOR is more facile in acid. Other versions of these types of devices feature a custom-tailored interface for enhanced ionic conductivity\textsuperscript{69}, and transparent BPM materials to enable photoelectrocatalysis at the interface\textsuperscript{80}. Additionally the design of BPMs allows for control over the relative thicknesses of the CEM and AEM layers, which is advantageous since H\textsuperscript{+} ions are more mobile than OH\textsuperscript{−}, and so the AEM side should be thinner.

These features make a promising case for the future of BPMFCs, however it has been observed\textsuperscript{81} that the transport of native species, OH\textsuperscript{−} and H\textsuperscript{+}, to and from the interface, is the main driver of BPM performance. In addition, it is known from previous AEM work\textsuperscript{2,5,11–13} that exposing anion exchange membranes to air can introduce carbon dioxide into the system, which initiates a (bi)carbonate-forming reaction mechanism that can significantly lower the membrane’s conductivity. It is known from past work on ion exchange membranes\textsuperscript{2,11,12,82} that the CO\textsubscript{2} present in ambient air dissolves into both CEMs and AEMs. This process does not significantly affect CEM performance because the amount of CO\textsubscript{2} dissolved is small, and the resulting chemical reactions proceed to a negligible extent. However in AEMs this initiates a (bi)carbonate-forming reaction mechanism, which degrades performance in a number of ways, as discussed in Chapters 2-4 of this dissertation. BPMs will likely suffer similar losses due to CO\textsubscript{2} because of the (bi)carbonate reactions occurring on the AEM side. In a BPMFC, it is yet unknown if the self-purging mechanism occurs since carbonates and bicarbonates may not reach the anode to participate in the HOR. However, there may be an analogous mechanism in which they are purged from the AEM side upon accepting protons from the CEM and forming carbonic
acid (H\textsubscript{2}CO\textsubscript{3}) and/or hydrated CO\textsubscript{2}. This proposed mechanism is demonstrated in Figure 5.1b. The reactions in Figure 5.1b, which correspond to Eqs. 5.1 – 5.5, are modeled after the hydration and dehydration mechanism of aqueous CO\textsubscript{2}, which has been extensively studied for oceanic applications\textsuperscript{83-85}.

$$\text{H}^+ + \text{OH}^- \leftrightarrow \text{H}_2\text{O} \quad (5.1)$$

$$\text{H}^+ + \text{HCO}_3^- \leftrightarrow \text{CO}_2^+ + \text{H}_2\text{O} \quad (5.2)$$

$$\text{H}^+ + \text{CO}_3^{2-} \leftrightarrow \text{HCO}_3^- \quad (5.3)$$

$$\text{CO}_2(\text{aq}) + \text{OH}^- \leftrightarrow \text{HCO}_3^- \quad (5.4)$$

$$\text{OH}^- + \text{HCO}_3^- \leftrightarrow \text{CO}_3^{2-} + \text{H}_2\text{O} \quad (5.5)$$

By modeling these reactions we can observe the ion exchange processes that occur at the interface to see if there is any self-purging phenomenon (i.e. consumption of (bi)carbonates from the AEM side). Operating effects, especially operating current, should also be considered since the resulting ionic fluxes at the boundaries strongly influence the behavior of Eqs. 5.1 – 5.5.

5.2 - Theory

5.2.1 - Governing Equations

The model proposed herein will include the effects of both small and large length scales by employing a species conservation approach, i.e. the balance of species flux and reactions. This approach is known as the Poisson-Nernst-Planck (PNP) system, in which the governing equations are the 1-D Nernst-Planck,
\[ J_k = -D_k \left( \frac{\partial c_k}{\partial x} + \frac{z_k c_k F}{RT} \frac{\partial \phi}{\partial x} \right) \]  \\
(5.6)

continuity,

\[ \frac{\partial c_k}{\partial t} = - \frac{\partial J_k}{\partial x} + \dot{R}_k \]  \\
(5.7)

and the Poisson equation

\[ \frac{\partial^2 \phi}{\partial x^2} = - \frac{\rho}{\varepsilon} = - \frac{F}{\varepsilon} \sum_k z_k c_k \]  \\
(5.8)

The inclusion of the Poisson equation eliminates the need to impose charge-neutrality, which is a common assumption in theoretical ion exchange membrane models. More importantly, the Poisson equation is necessary to solve for the potential distribution across the BPM interface. A schematic of the BPM domain is shown in Fig. 5.1, with \( x = -L \) corresponding to the Anode|CEM interface and \( x = L \) corresponding to the AEM|Cathode interface. This configuration is the most useful to consider since the hydrogen oxidation reaction (HOR) is more facile in acidic environments, and the oxygen reduction reaction (ORR) is more facile in alkaline. The coupled Eqs. 5.7 – 5.8 can be used to solve for 4 unknowns: \( c_{H^+}, c_{OH^-}, c_{H_2O}, \) and \( \phi \). The feature of BPMs that creates the space charge region (SCR) is that the sign of the tethered charges (e.g. \( SO_3^- \) and/or \( TMA^+ \), or others) changes when crossing the interface. This
can be readily implemented manually in the numerical solution procedure. The complete system of equations, for the pristine (CO$_2$-free) case are presented in Table 5.1.

**Table 5.1**

*Governing equations for aqueous species and the electrostatic potential*

<table>
<thead>
<tr>
<th>Species</th>
<th>Governing Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>OH$^-$</td>
<td>$\frac{\partial c_{OH}}{\partial t} = D_{OH} \left( \frac{\partial^2 c_{OH}}{\partial x^2} + \frac{z_{OH} F}{RT} \left( \frac{\partial \phi}{\partial x} \frac{\partial c_{OH}}{\partial x} + c_{OH} \frac{\partial^2 \phi}{\partial x^2} \right) \right) + \dot{R}_OH$</td>
</tr>
<tr>
<td>H$^+$</td>
<td>$\frac{\partial c_H}{\partial t} = D_H \left( \frac{\partial^2 c_H}{\partial x^2} + \frac{z_H F}{RT} \left( \frac{\partial \phi}{\partial x} \frac{\partial c_H}{\partial x} + c_H \frac{\partial^2 \phi}{\partial x^2} \right) \right) + \dot{R}_H$</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>$\frac{\partial c_{H_2O}}{\partial t} = D_{H_2O} \frac{\partial^2 c_{H_2O}}{\partial x^2} + \dot{R}_{H_2O}$</td>
</tr>
<tr>
<td>$\phi$</td>
<td>$\frac{\partial^2 \phi}{\partial x^2} + \frac{F}{\varepsilon} \sum_k z_k c_k = 0$</td>
</tr>
</tbody>
</table>

Boundary conditions are prescribed to account for operating conditions, especially current density. Operating an electrochemical BPM device will result in species fluxes across the outside boundaries corresponding to the Faradaic processes, both oxidation and reduction, occurring at the membrane/electrode interfaces. The familiar current-overpotential relation of the form of Eq. 5.9 will be used to describe the electrochemical reaction rates at the electrode surfaces, which are coupled to the species concentrations at the membrane boundary:

$$i_k = i_0 \left( \frac{c_O}{c_0} e^{-\alpha_f \eta_k} - \frac{c_R}{c_R^0} e^{\alpha_f \eta_k} \right)$$

(5.9)
where \( i_0 \) is the exchange current density, \( C_O \) and \( C_R \) are the oxidized and reduce species products respectively, \( \alpha_a \) and \( \alpha_c \) are the anodic and cathodic transfer coefficients respectively, \( f = F/RT \), and \( \eta_k \) is the overpotential for electrochemical reaction \( k \). Eq. 5.9 can then be translated into species fluxes via Faraday’s law, \( J_k = \pm i_k/z_k F \). At \( x = -L \) under forward bias, reaction \( k \) refers to the HOR, and at \( x = L \) under forward bias, reaction \( k \) refers to the ORR. Equation 5.9 can handle reverse bias operation (indicative of, e.g., electrolysis) as well, with the left and right boundaries’ electrochemical reactions switching to the hydrogen and oxygen *evolution* reactions. The Faradaic reactions can be turned into boundary conditions by noting that the sum of ionic species fluxes is related to the total current by \( J_{H^+} - J_{OH^-} = i_{tot}/F \).

The electrostatic potential can be “grounded”, e.g. \( \phi_{x=-L} = 0 \), since only the potential gradient is used in Eq. 5.6. The potential gradient at \( x = L \) can be found as a function of the operating current and local diffusion currents, similarly to Eq. 4.15, as given by Eq. 5.10.

\[
\frac{d\phi}{dx}\bigg|_{x=L} = -\frac{RT \left( i + F \sum_k z_k D_k \frac{dc_k}{dx}\bigg|_{x=L} \right)}{F^2 \sum_k z_k D_k c_k \bigg|_{x=L}}
\]

Similar approaches have been used to solve for the concentrations and potential drop across electrolytes with coupled electrochemical reactions and species transport in the past\(^{50,86,87}\). These boundary conditions are summarized in Table 5.2.

**Table 5.2**

*Boundary conditions at the anode \((x = -L)\) and cathode \((x = L)\) for species in the PNP system*

| Species | \( x = -L \) | \( x = L \) |
\[
\begin{align*}
\text{H}^+ & \quad J_H - \frac{i_{tot}}{F} - D_{OH} \left( \frac{\partial c_{OH}}{\partial x} - \frac{F}{RT} c_{OH} \frac{\partial \phi}{\partial x} \right) = 0 \quad \text{H}^+ - \frac{i_{tot}}{F} - D_{OH} \left( \frac{\partial c_{OH}}{\partial x} - \frac{F}{RT} c_{OH} \frac{\partial \phi}{\partial x} \right) = 0 \\
\text{OH}^- & \quad J_{OH} - \frac{i_{tot}}{F} - D_H \left( \frac{\partial c_H}{\partial x} + \frac{F}{RT} c_H \frac{\partial \phi}{\partial x} \right) = 0 \quad \text{OH}^- - \frac{i_{tot}}{F} - D_H \left( \frac{\partial c_H}{\partial x} + \frac{F}{RT} c_H \frac{\partial \phi}{\partial x} \right) = 0 \\
\text{H}_2\text{O} & \quad J_{\text{H}_2\text{O}} = 0 \quad J_{\text{H}_2\text{O}} = 0 \\
\phi & \quad \phi = 0 \quad \frac{\partial \phi}{\partial x} = \frac{RT \left( \frac{i_{tot}}{F} - D_{OH} \frac{\partial c_{OH}}{\partial x} + D_H \frac{\partial c_H}{\partial x} \right)}{F^2 (D_H c_H - D_{OH} c_{OH})}
\end{align*}
\]

The source terms in Eq. 5.7 represent the chemical reactions taking place inside the hydrated channels of the BPM. In the absence of CO\textsubscript{2}, this refers solely to the auto-ionization reaction of water, which occurs mainly at the BPM interface, according to Eq. 5.1. The rate of this reaction can be represented using traditional mass-action kinetics\textsuperscript{79,88}

\[
\hat{R}_{\text{H}_2\text{O}} \left[ \text{M} \cdot \text{s}^{-1} \right] = k_f (c_{\text{OH}^-} - c_{\text{H}^+} - K_W)
\] (5.11)

where \(k_f\) is the rate constant (M\textsuperscript{-1} \cdot s\textsuperscript{-1}) of OH\textsuperscript{-} and H\textsuperscript{+} recombination, and \(K_W = k_f/k_b\) is the auto-ionization constant of water. These rate constants can be affected by water auto-ionization catalysts embedded at the interface\textsuperscript{89}, which may be beneficial for water splitting applications. However to use the mass-action law there are some additional physics that need to be included which arise from the unique nature of the BPM interface. The large electric fields found at the interface, on the order of 10\textsuperscript{8} V \cdot m\textsuperscript{-1}\textsuperscript{79}, can affect the kinetic rate constants according to Onsager’s Second Wien Effect (SWE)\textsuperscript{90}. This effect can be represented by a power series as
\[
\frac{k(E)}{k(E = 0)} = 1 + b + \frac{b^2}{3} + \frac{b^3}{18} + \frac{b^4}{180} + \frac{b^5}{2700} + \frac{b^6}{56700} \ldots
\]  

(5.12)

where \( k(E) \) is the rate constant under the influence of the electric field, \( b = 0.09636E/\varepsilon_r T^2 \), \( E \) is the electric field in \( V/m \), and \( \varepsilon_r \) is the relative permittivity. This expression provides a means of coupling the rate constants with the electric field.

Under forward bias, the water formation reaction occurs very rapidly due to \( k_f = 1.1 \times 10^{11} \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1} \). The water splitting reaction is much slower, with \( k_b = 2 \times 10^{-5} \text{ s}^{-1} \), such that even the SWE is not enough to account for the high water-splitting rates attainable in BPMs\(^91\). It has been suggested\(^{92-95}\) that protonation of the tethered anionic and cationic groups can occur, which presents an additional mechanism for rapid water splitting. This has been referred to as the chemical reaction model (CRM)\(^89\). The reactions included in this mechanism can be expressed by additional mass-action expressions\(^89,91\) to be used in the PNP formalism, whose rate constants can be found in the literature\(^96\). The CRM is a robust mechanism for describing water splitting because it is capable of modeling the water dissociation with any number of acid/base groups that have been included in the interface region to act as catalysts; it is simply a matter of finding the appropriate rate constants for the proton-transfer reactions. However for forward bias operation, the water forming reaction dominates, and these effects are not as prevalent.

The carbonation of a BPM can be modeled using similar theory to Chapters 2 – 4, resulting in additional Nernst-Planck equations, which are summarized in Table 4.3. The source terms for these species are identical to those used in the preceding chapters, and so will not be reproduced here (see Table 2.1 for a reference).
Table 5.3

_Governing equations for CO₂-related species_

<table>
<thead>
<tr>
<th>Species</th>
<th>Governing Equation</th>
</tr>
</thead>
</table>
| CO₂     | \[
\frac{\partial c_{\text{CO}_2}}{\partial t} = D_{\text{CO}_2} \frac{\partial^2 c_{\text{CO}_2}}{\partial x^2} + \dot{R}_{\text{CO}_2}\]
| HCO₃⁻   | \[
\frac{\partial c_{\text{HCO}_3}}{\partial t} = D_{\text{HCO}_3} \left( \frac{\partial^2 c_{\text{HCO}_3}}{\partial x^2} + \frac{z_{\text{HCO}_3} F}{RT} \left( \frac{\partial \phi}{\partial x} c_{\text{HCO}_3} \frac{\partial^2 \phi}{\partial x^2} \right) \right) + \dot{R}_{\text{HCO}_3}\]
| CO₃²⁻   | \[
\frac{\partial c_{\text{CO}_3}}{\partial t} = D_{\text{CO}_3} \left( \frac{\partial^2 c_{\text{CO}_3}}{\partial x^2} + \frac{z_{\text{CO}_3} F}{RT} \left( \frac{\partial \phi}{\partial x} c_{\text{CO}_3} \frac{\partial^2 \phi}{\partial x^2} \right) \right) + \dot{R}_{\text{CO}_3}\] |

Boundary conditions for CO₂-related species will also be prescribed as before. The absorption/desorption of CO₂ into and out of the membrane will be modeled by convective mass-transfer as in Chapters 2 – 4. This work will also include the effects of operating current, since the resulting ionic fluxes at the boundaries strongly influence the behavior of the ion exchange processes.

Some BPM applications involve the electrochemical reduction of CO₂, e.g. as a means to generate syngas. To model this, the boundary conditions on CO₂ would need to be modified to reflect the Faradaic processes instead of simple absorption/desorption. This would be accomplished in the same manner as for OH⁻ and H⁺, i.e. using Faraday’s law and applying mixed potential theory if necessary. In addition, with the appropriate kinetic parameters (namely, the exchange current density), the CO₂ electrode potential could be found.

The solution of the model will determine the species concentrations and potential distribution, and post-processing can yield, e.g., ionic species fluxes, overall cell voltage, and CO₂ gas formation (if any). The nature of the auto-ionization of water can also be explored.
Namely, the mechanisms for water formation and splitting (including both the Second Wien Effect and Chemical Reaction theories) at the interface will be incorporated into the BPM model to elucidate BPM performance under forward and reverse bias.

### 5.2.2 - Numerical Methods

The Matlab program ‘pdepe’, which was used in Chapter 4, will not suffice for the system of BPM PNP equations outside of open circuit conditions, due to the limitations on user-defined boundary conditions. Therefore a numerical algorithm was developed from scratch to perform the time integration of Eq. 5.7.

As described in section 4.2.4, we again employ 2nd order centered differences, given by Eq. 5.13.

\[
\frac{\partial y}{\partial x}\bigg|_{j\Delta x} \approx \frac{y_{j+1} - y_{j-1}}{2\Delta x} \quad (5.13a)
\]

\[
\frac{\partial^2 y}{\partial x^2}\bigg|_{j\Delta x} \approx \frac{y_{j-1} - 2y_j + y_{j+1}}{\Delta x^2} \quad (5.13b)
\]

Applying Eq. 5.13 to Eqs. 5.6 – 5.7 yields the system of OΔEs, depicted for \( \text{OH}^- \) in Eq. 5.14.

\[
\frac{\partial [\text{OH}^-]_j}{\partial t} = D_{\text{OH}} \left( \frac{[\text{OH}^-]_{j-1} - 2[\text{OH}^-]_j + [\text{OH}^-]_{j+1}}{\Delta x^2} + \frac{z_{\text{OH}} F}{RT} \left( \frac{([\text{OH}^-]_{j+1} - [\text{OH}^-]_{j-1})(\phi_{j+1} - \phi_{j-1})}{\Delta x^2} + [\text{OH}^-]_j \frac{\phi_{j-1} - 2\phi_j + \phi_{j+1}}{\Delta x^2} \right) \right) - k_f([H^+]_j[\text{OH}^-]_j - K_W) \quad (5.14)
\]
Similarly, discretizing the Poisson equation, Eq. 5.8, yields

\[
\frac{\phi_{j-1} - 2\phi_j + \phi_{j+1}}{\Delta x^2} = -\frac{F}{\varepsilon} (z_{\text{OH}}[\text{OH}^-]_j + z_{\text{H}}[\text{H}^+]_j)
\]  

(5.15)

The time integration was performed using the 3rd order Runge-Kutta scheme developed by Spalart et al.\textsuperscript{98}, which solves ODEs of the form

\[
\frac{dy}{dt} = f(y)
\]  

(5.16)

The solution values at each Runge-Kutta sub-step \(m\) can be expressed as

\[
y^{m+1} = y^m + \Delta t (\alpha_m f(y^m) + \beta_m f(y^{m-1}))
\]  

(5.17)

for \(m = 1, 2, 3\), where \(y^1 = y(t)\), \(y^4 = y(t + \Delta t)\), and \(\alpha\) and \(\beta\) are the coefficients given by

\[
(\alpha_1, \alpha_2, \alpha_3) = (8/15, 5/12, 3/4)
\]  

(5.18a)

\[
(\beta_1, \beta_2, \beta_3) = (0, -17/60, -5/12)
\]  

(5.18b)

This scheme can be implemented to perform the time-integration for the system of equations represented by Eqs. 5.7 and 5.13 by defining the solution vector \(y\) as
\[ y = \begin{bmatrix} c_{\text{OH}^-} \\ c_{\text{H}^+} \\ c_{\text{H}_2\text{O}} \end{bmatrix} \approx \begin{bmatrix} [\text{OH}^-]_1 \\ \vdots \\ [\text{OH}^-]_N \\ [\text{H}^+]_1 \\ \vdots \\ [\text{H}^+]_N \\ [\text{H}_2\text{O}]_1 \\ \vdots \\ [\text{H}_2\text{O}]_N \end{bmatrix} \]  

(5.19)

Much like the pressure term in the numerical solution of the Navier-Stokes equations, the Poisson equation, Eq. 5.8, is solved every time the right hand side function \( f(y) \) is calculated. This requires the solution of the matrix equation represented by Eq. 5.15, which fortunately results in a tri-diagonal matrix, for which there exist fast solution methods such as the Thomas algorithm aka the “tridiagonal matrix algorithm”. These equations can be integrated to give the transient solution, and steady state conditions will be assumed when the right hand side of Eq. 5.14 becomes sufficiently close to zero for all species and grid points.

5.3 - Results and Discussion

5.3.1 - CO\textsubscript{2}-free Space Charge Region Validation

Using the “forward time, central space” (FTCS) integration scheme described in Section 5.2.2, the steady state solution of Eq. 5.7 was obtained for the conditions shown in Table 5.4. These values were used in a study by Grew et al.\textsuperscript{79}, so by using them we can verify & validate our numerical method to their results. Note that the properties in Table 5.4 are symmetrical (i.e. \( D_{\text{H}^+} = D_{\text{OH}^-} \)), which may not be realistic but allows for easier interpretation of the fundamental results. For similar reasons, we also limit the simulation to a small region around the interface, \( L = \pm 2.5 \text{ nm} \).
### Table 5.4

*Nominal simulation parameters for CO₂-free interface simulation*

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$i$ (mA \cdot cm^{-2})</td>
<td>0</td>
</tr>
<tr>
<td>$T$ (K)</td>
<td>300</td>
</tr>
<tr>
<td>$L$ (nm)</td>
<td>2.5</td>
</tr>
<tr>
<td>$D_{H^+}, D_{OH^-}$ (m² \cdot s⁻¹)</td>
<td>$6 \times 10^{-9}$</td>
</tr>
<tr>
<td>$c_{SO\text{–}}, c_{TMA^+}$ (M)</td>
<td>1.5</td>
</tr>
<tr>
<td>$\epsilon_r$</td>
<td>35</td>
</tr>
</tbody>
</table>

The steady state $H^+$ and $OH^-$ concentration profiles across the interface are shown in Figure 5.2a below, where the solid lines are from the FTCS scheme discussed in Section 5.2.2 and the symbols are from Grew et al.⁷⁹. The good agreement gives confidence that the numerical method is implemented correctly. The electrostatic potential and electric field are shown in Figure 5.2b and 5.2c respectively. Note the very large electric field, $\sim 6 \text{ V} \cdot \text{nm}^{-1}$ at the interface, which proves the migration forces that prevent complete acid-base neutralization of the acid/alkaline regions.
Figure 5.2 – Numerical solution of the space charge region in a CO₂-free BPM for a) native ionic species concentration profiles (symbols are adapted from Grew et al.⁷⁹), b) electrostatic potential, and c) electric field.
For the CO$_2$-free BPM it is only necessary to simulate the space charge region, since outside of this region the solutions are well known: they simply correspond to pristine PEMFC or AEMFC operation in which all transport is governed by migration and the concentration profiles are uniform.

5.4 - Conclusions and Next Steps

A 3$^{rd}$ order Runge-Kutta numerical integration scheme has been applied to a Poisson Nernst Planck system describing the ionic species in the vicinity of the acid-alkaline interface of a BPM at open circuit conditions. This represents an important verification of the numerical method, and gives confidence in using it moving forward. It still remains to extend the model to include the effects of an operating current, which would entail new boundary conditions on the electrostatic potential (e.g. as depicted in Table 5.2). This would allow the model to predict the junction potential during operation, which would be a key insight for operational BPMFCs. Another key feature to be included would be the effects of CO$_2$ absorption at the AEM side. It is expected that the AEM side of a BPM will behave similarly to standalone AEMFCs, but this effect needs to be verified, especially during operation. One effect to look for would be an analogous self-purging mechanism, whereby (bi)carbonates somehow migrate to the CEM side, and eventually release into the anode gas stream. These are important considerations to understand for practical implementation of BPMFCs.
Chapter 6: Conclusions and Remarks

6.1 - Key Findings and Contributions

The key findings of each chapter are summarized here.

Chapter 2: Spatially Averaged AEM Model

- The effects of operating current on an AEM exposed to carbon dioxide were modeled. This introduced initial concepts of self-purging, such as $\text{OH}^-$ replenishment at the cathode, and (bi)carbonate species participation in the HOR.

- At the time of publication (Wrubel et al. 2017), the rate of removal of anionic species at the anode was only approximately modeled. Although this is only somewhat rooted in the physics of the process (it neglects any kinetic differences in the three different HOR pathways), a version of it was used in AEMFC models a year later (see Krewer et al. 2018). This suggests that the community is aware of the complexities of self-purging, and that there is still need of further investigation.

- The effects of a gas stream with finite volume were also included. In \textit{ex situ} AEM models, the ambient air represents an infinite reservoir for CO$_2$. However, in operating fuel cells, there is a finite amount of CO$_2$ in the cathode stream, and its absorption depends on both gas stream and membrane conditions. Similarly, the effects of CO$_2$ buildup in the anode gas stream can affect the membrane conditions if its CO$_2$ content becomes high enough.

Chapter 3: Electrospun AEM Morphology Model

- A morphology model was developed that enabled the spatially-averaged CO$_2$ model to predict the response of electrospun AEMs, especially the role of $f_I$. This was accomplished by backing out the relevant morphological parameters from the swelled,
pristine conductivity values of different electrospun membrane designs. These pristine values, $\sigma_{0,f}$ can be obtained either numerically or experimentally to be used in the morphology model developed in this work.

- It was found that electrospun AEMs respond to CO$_2$ absorption similarly to conventional AEMs. In addition, the CO$_2$ penalty to the conductivities of the different electrospun designs exhibited a nearly linear relationship to $f_I$, which is evidenced by the collapse of the $\sigma_f$ vs. $i$ curves upon normalizing to their pristine conductivities. This means that there is no inherent improvement in the electrospun membrane’s CO$_2$ response upon increasing $f_I$. Potential users should bear in mind however that this is only a relative effect; the baseline conductivities are still higher at higher $f_I$.

- In the presence of CO$_2$, the conductivity of the AEM depends on both material/morphological properties (IEC, thickness, porosity, etc.) and operating conditions (current density, temperature, gas streams, etc.). The observation that the curves collapse when normalized to $\sigma_{0,f}$ (which represents all the material/morphological properties), but still change significantly as functions of operating current and CO$_2$ content, tells us that the operating conditions are very important to the performance of the AEM. Thus, in the interest of conductivity reclamation in the presence of CO$_2$, AEMFCs should be operated at the highest current densities reasonable for the application.

Chapter 4: Self-Purging Investigation

- A transient, spatially-varying transport model was developed to gain insight into the self-purging mechanism in AEMFCs operating in the presence of CO$_2$. Solving the spatially-varying governing equations (instead of the averaged form, as in Chapter 2) improves both the fidelity of the model, since many physical processes (electrochemical reactions,
gas-phase absorption, electric field, etc.) depend on the local concentrations, and also provides additional insight, through the observation of concentration gradients.

- The two leading theories describing self-purging, the chemical and electrochemical mechanisms, were implemented into the model via the anode boundary conditions. This resulted in two distinct models that were used to evaluate the two different theories by observing the transport properties of the membrane during operation. The outcome of this study was that the chemical self-purging model alone is not enough to explain observed AEMFC behavior, and it is likely that (bi)carbonates react directly in their own HOR pathways. It was hoped that this result will encourage more work in this area, since the topic is still not fully resolved, see Section 6.2.

- Further insight into the CO$_2$ recirculation mechanism at the anode was gained, which was enabled by the spatially-varying solutions. As hypothesized in Chapter 2, the anode gas stream CO$_2$ concentration does become large enough to be re-absorbed into the membrane. Therefore CO$_2$ is “shuttled” across the membrane as (bi)carbonate ions, which are converted into gaseous CO$_2$ by either chemical and/or electrochemical reactions. This can be observed by the negative concentration gradients in the CO$_2$ profile near the anode at certain current densities, indicating that the net flux at the anode/membrane interface is into the membrane.

Chapter 5: Ionic Transport in BPMs

- A transient, spatially-varying transport model was developed for ionic species to and across the BPM interface, resulting in a set of equations known as the Poisson Nernst-Planck system. This system was solved for a nominal set of conditions corresponding to
ex situ, CO₂-free operation, in order to verify the numerical implementation and compare to similar theoretical studies.

- It still remains to extend this model to include operating conditions (namely current density), CO₂-effects, and electrolysis configurations; see Section 6.2.

In addition, contributions to the literature are listed below:


6.2 - Recommendations for Future Work

Although the research efforts presented in this dissertation have improved our understanding of AEMFCs and their response to carbon dioxide, they have also uncovered even more key questions which still need to be addressed. Some suggestions for future research are presented here.

- System-level fuel cell components, such as catalyst layers, gas diffusion layers, and actual gas channels should be integrated into the AEMFC model. Such components were not included yet because we wanted to focus on the transport and electrochemistry inside the membrane and at its boundaries, which can be validated to membrane ASR results. However, other key performance metrics such as actual cell voltage and CO$_2$ emission quantitatively depend on these system-level components. The model developed in Chapter 4 can qualitatively replicate these processes, but it will certainly be useful to predict practical aspects of AEMFC performance. To accomplish this, we suggest starting with the analytical model developed by Das et al.$^{99}$, which is based on composite plane-wall theory. By introducing a tuning parameter to account for electrode flooding, this extra bit of theory will account for the transport losses necessary to model realistic cell voltages, not just the activation losses modeled in Chapter 4. In addition, this would enable realistic time constants for CO$_2$ emission into the anode gas stream.

- The water concentration should be included as a variable instead of being treated as a constant. Although the water concentration is effectively constant for the purposes of chemical reaction rates, including its variation could enable prediction of the local hydration state of the membrane (which in turn affects the membrane’s conductivity). Furthermore, one of the conclusions of St. John et al.$^{60}$ was that the rapid dissociation of
water can supply $\text{OH}^-$ for the HOR. Since the $\text{OH}^-$ concentration is usually high enough that water dissociation doesn’t matter, we didn’t include this reaction. But if $\text{OH}^-$ completely depletes, as the chemical self-purging mechanism predicts, there would be significant water dissociation. However, for now this is thought to be a secondary effect, i.e. it probably happens, but doesn’t discount (bi)carbonate participation in the HOR. This is because the ASR response of the membrane, e.g. Figure 4.6a, still relies on significant (bi)carbonate removal, which probably wouldn’t happen if just $\text{OH}^-$ reacts. In any case, including this extra facet of the mechanism would resolve any remaining doubt that (bi)carbonates participate in the HOR.

- The BPM transport model needs to be extended to include current densities, $\text{CO}_2$, and electrolysis (reverse bias) configuration.
References


57. C. Wagner and W. Traud, Electrochemistry, 44 (1938).


