Applicability of Effective Medium Theory and Transport Theories to Fuel Cell Materials

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Fuel cell technology has many promising characteristics which make it an attractive prospect for an environmentally friendly energy conversion device. Some of the benefits of using these devices include high efficiencies, diversity in applicability and scalability, high energy densities, and the ability to use a wide variety of fuels. However, continuing limitations which are a constant thrust in basic research include improving performance, system cost, and longevity. One promising fuel cell type, the polymer electrolyte fuel cell, is a low temperature fuel cell which generally scales from the portable power level up to small back-up power units or automobile engines. Two basic types of these cells are the proton and anion exchange membrane fuel cells (PEMFC and AEMFC). These fuel cells make use of a solid polymer membrane as the ion conducting electrolyte.

Like other fuel cells, polymer electrolyte membrane fuel cells are the subject of intensive research to improve their overall performance while reducing cost and degradation. The polymer membrane material itself is the subject of many studies since the membrane must have high ionic conductivity while maintaining durability for the fuel cell to function. The situation is further complicated because the ionic conductivity is linked intimately to the hydration state of the membrane. Keeping the delicate water balance of the system such that the membrane is hydrated but the electrodes are not flooded is a constant struggle. Naturally, the transport behavior occurring within the membrane in respect to water, ions, and gases are of great interest since this all contributes to the performance of the fuel cell. This work presents several studies of polymer
electrolyte membranes, both PEM and AEM, for each of the aforementioned species types. These studies include measuring water diffusivity and gas permeability as well as modeling transport during ion exchange processes and cell operation. Due to the complicated heterogeneous nature of not only the polymer electrolyte membranes, but also many other fuel cell materials, popular effective medium theories are investigated. These analytical theories are useful as they provide homogeneous approximations of transport properties in complicated systems. The theories are extended to allow for added complexity in the systems studied in the form of multiple material types and anisotropic behaviors.
Applicability of Effective Medium Theory and Transport Theories to Fuel Cell Materials

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Chapter 1: Introduction

1.1 Motivation for Fuel Cells

Fuel cell technology has received significant attention recently with a serious drive towards commercialization. There are a number of potential advantages fuel cells offer over competitive technologies which make them an attractive option for future use [1-3].

1. Since fuel cells convert fuel electrochemically they can offer improved efficiencies over traditional heat engines, which are limited by Carnot principles. This feature is scalable to all size power plants.

2. The diversity of the technology additionally allows for a wide range of scalability with fuel cells designed anywhere in size from portable power sources all the way up to stationary power plants.

3. Fuel cells typically exhibit higher energy densities than their battery counterparts. They also offer instant recharge characteristics since the device will operate so long as there is fuel flow through it.

4. Many fuel cells make use of hydrogen as a primary fuel. This limits the pollution production to the pollution produced in creating the hydrogen itself. Hydrogen can be produced many ways and the current number one method is methane reforming, which accounts for 95% of the production in the U.S., but the recent initiative by the federal government known as the National Hydrogen Energy Roadmap [4] seeks to lay out a plan for cleaner, more abundant, hydrogen production.

5. The use of hydrogen allows for an array of possible fuel sources to be tapped into such as coal, biomass, natural gas, or water electrolysis from renewable sources.
6. Aside from the balance of plant to operate them, fuel cells themselves have no moving parts and constant improvements to designs helps eliminate the need for extra pumps, compressors, or blowers. This also leads to a more quiet product.

Despite the numerous advantages of fuel cells there are a number of obstacles which must be overcome before the technology will become a widely commercially available, viable alternative, to more traditional energy delivery systems [1-3].

1. If hydrogen is the fuel to be used there are many difficulties in storage that require attention. Despite having a high energy density by weight, hydrogen is a light gas that does not have a high energy density by volume. Efforts to store large amounts of hydrogen include compression, cryogenics, and chemical storage (ex. metal hydrides). Each offers advantages and disadvantages in terms of cost, scale, and safety that are being continually researched.

2. System cost is a major issue for fuel cells. In order to be competitive in the market they must offer similar performance at a comparable or reduced cost to existing technologies.

3. Improved materials for better performance and increased longevity are needed. Not only do fuel cells need to have their performance continually improved to be competitive in the energy conversion market but continued use of these devices always leads to decay of performance. Decelerating this decay of performance is a key element of research in the community across the board.

The last two points are the major reason for much of the basic research done in the fuel cell community. The need to improve performance and reduce cost requires not only ingenious new ideas but also a firm grasp of the nature of the existing technology and how it works.
1.2 Polymer Electrolyte Membrane Fuel Cells

1.2.1 Basic Concepts

A popular class of fuel cells is the polymer electrolyte membrane fuel cell. As the name suggests, the main feature of these fuel cells is the polymer membrane material which is used as an ion conducting electrolyte. Two common types of these fuel cells are the proton exchange membrane (PEM) and the anion exchange membrane (AEM) fuel cells. Figure 1.1 shows the two side by side.

Overall Reaction

\[ H_2 + \frac{1}{2} O_2 \rightarrow H_2O \]
Both the PEM and AEM fuel cells operate on similar principles. Fuel is oxidized at the negative anode liberating electrons from the hydrogen fuel. It should be noted that both the AEM and PEM are the subject of research for alternative fuels such as methanol but the general principle is the same [5-9]. At the positive cathode, electrons traveling through the external circuit are consumed in the reduction half-cell reaction. As figure 1.1 shows, the major difference between the two fuel cell types has to do with the ion transport through the membrane. PEMs conduct positively charged protons from anode to cathode while AEMs conduct negatively charged anions from the cathode to the anode. This leads to different half-cell reactions as indicated in figure 1.1 but the overall cell reaction stays the same.

In terms of construction polymer electrolyte fuel cells typically consist of a membrane electrode assembly (MEA) contained between flow channels. The MEA has the membrane electrolyte at the middle with catalyst layers and diffusion media on either side. The catalyst layers are generally a mixture of the ionomer material and a catalyst such as platinum to facilitate the cell reactions. The flow channels and the diffusion media serve as a means of hydration control and fuel delivery as well as current collectors. As will be seen throughout this thesis, proper hydration is extremely important to polymer electrolyte fuel cell operation. Ion transport in the membrane is only possible at high levels of hydration but excessive hydration at either of the electrodes can lead to flooding where the fuel is unable to reach the catalyst site. These fuel
cells operate at lower temperatures; about 80 °C for the PEM and 60 °C for the AEM. Generally, their scale runs from portable power applications to small backup power generators or vehicle power plants [1-3].

1.2.2 PEMs vs. AEMs

Anion exchange membrane fuel cells (AEMFCs) and proton exchange membrane fuel cells (PEMFCs) are seen by many as competitive technologies where applications overlap. PEMFCs are the comparatively mature technology and many arguments for AEMFCs are made based on advantages which are offered over PEMFCs. A number of factors make AEMFCs attractive compared to PEMFCs. These include operation in an alkaline environment which makes kinetics more facile. This allows for the use of less expensive packaging materials as well as non-precious catalysts such as nickel. The nature of the ion transport, which facilitates water transport through electro-osmotic drag, also allows for the potential to simplify the balance of plant at the system level [10-14]. Furthermore, while alcohol fuels are also applied to PEMFC systems, the alkaline environment of the AEMFC allows for easier oxidation of the fuel [10,15-18].

AEM technology attempts to capitalize on the benefits of alkaline fuel cell technology while eliminating some of the problems with the technology such as solid carbonate precipitants forming in the presence of carbon dioxide and complications of dealing with a liquid electrolyte, e.g. electrolyte weeping, by introducing a polymer membrane in place of the liquid electrolyte [2,3,10]. Despite the advantages of the AEMFC there continues to be difficulties in producing membrane materials. A major advantage to PEMFCs over AEMFCs currently is the quality of
the membranes. One of the most popular PEMs, Dupont’s Nafion, has high mechanical durability and ionic conductivity. Competitive AEM technology, such as Varcoe and associates’ preformed fluorinated ethylene propylene (FEP) or ethylene tetrafluoroethylene (ETFE) based films [10,19-21] exhibit ionic conductivities of about 30 mS/cm vs. Nafion’s reported 90 mS/cm for fully hydrated conditions at 30 °C. Tokuyama A201 and A901 membranes are a mass produced and well-studied AEM which has reported conductivity of about 40 mS/cm [22-26]. This amounts to less than half the conductivity in the hydroxide form. These lower conductivities can be partly linked to the lower mobilities of the charge carriers in the AEM in water which acts as the conduit for ion transport in the membrane. Ions also do not dissociate as freely from the functional groups in the AEMs as they do in the sulfonic acid groups found in Nafion. A common method of improving the conductivity involves boosting the IEC of the membrane. Boosting the IEC comes at a price however, as it decreases the mechanical integrity of the membrane and leads to higher degree of swelling at fully hydrated conditions and brittleness in the dry state [27]. Aside from the issue of lower ionic conductivity there is the problem of stability for AEMs. Chemical degradation of the AEM materials is a common research topic in the literature where AEMs have been shown to be susceptible to nucleophilic attack or Hoffman elimination processes [10,27]. In addition to the lower ionic conductivity in the hydroxide form there is also the potential for an ion exchange process in the presence of carbon dioxide. If the AEMFC is run in the presence of carbon dioxide the composition of counter-ions will change from just hydroxide to a mixture of primarily carbonate and bicarbonate ions with minimal levels of hydroxide ions [22,23,25,26]. This can happen even at the low levels of carbon dioxide present in air (385 ppm). While the membrane is actually more stable in this form [28,29], it suffers from further reduction in ionic conductivity due to the poor mobility of the carbonates.
and bicarbonates. It has however, been reported that carbonate/bicarbonate ions can be displaced from the operating fuel cell via what is commonly referred to as the self-purging mechanism [23,25].

1.2.3 Membrane Characteristics

Current state of the art membranes in both the AEM and PEM category have similar characteristics. They consist of a polymer backbone material which has embedded functional groups (e.g. sulfonic acid groups for PEMs and benzyltrimethylammonium hydroxide for AEM are popular). As the membrane becomes hydrated, the ions dissociate from the fixed charge groups and act as charge carriers during operation. The model proposed by Gierke suggests that the ionic groups create clusters and bridges between clusters form at sufficiently high hydration states to provide connectivity for ionic transport [30-35]. It is worth mentioning that other models of the structure of Nafion exist such as the lamellar model proposed by Litt [36], the sandwich model detailed by Haubold et al. [37], and a rod-like model discussed by Rubatat et al. [38] to name a few. It is believed that the mechanisms for ion transport in the PEM and AEMs may be similar [39-43]. The overall transport is believed to be the combined effect of multiple components including en masse diffusion, migration, convection, Grotthuss behavior, and surface site hopping (i.e. hydroxide ions “hopping” between functional side chain groups). It is important to note that some of these behaviors are not only important in looking at ion transport but also for other species as well. Gas transport through the membrane contributes to cross over fuel losses and the water balance of the membrane is extremely important for optimal operation. As stated above, proper hydration is critical for ion conduction.
There have been a wide variety of membrane types synthesized. As alluded to previously, PEMs have several well established brands such as Nafion, Aciplex, Flemion, and Gore. Different classifications of PEMs exist such as perfluorinated, partially fluorinated, non-fluorinated membranes with aromatic backbones, non-fluorinated hydrocarbons, and acid–base blends [44]. It is generally believed however, that the perfluorinated membranes exhibit the most desirable qualities and the key membranes currently used are generally perfluorinated such as those listed above [44]. Even among the industry standards it’s safe to say that Nafion stands out as a popular membrane currently. Despite the well-established PEM technology there is still plenty of research being done on improvements to the technology such as, for example, the electro-spinning techniques [45,46] for improved durability and decreased gas permeation or modification for high temperature operation [47,48] (100-200 °C).

In contrast to PEMs, AEMs are still lacking in benchmark brands. Due to the reasons mentioned in section 1.2.2 there is still a wide variety of techniques being used to synthesize these membranes and the reviews of Hickner et al. [49] and Merle et al. [50] provide a general overview of the communities progression thus far. Production of AEMs is generally analogous to PEMs. A standard method of production for these membranes involves the functionalization of a polymer, such as polysulfone or polystyrene, via chloromethylation followed by a quaternization step using trimethylamine [27,51-56]. Other methods for AEM production exist however, such as the radiation grafted membranes developed by Varcoe and associates [10,19-21], the electro-spinning technique detailed by Park, Turley, and Pintauro [57-60], or the hybrid membranes produced by Unlu, Zhou, and Kohl [61-63] to name a few.
1.2.4 Modeling Transport

A fundamental understanding of species transport in polymer electrolyte membranes is critical towards predicting performance and designing improved materials. Models for membrane transport can generally be divided into the molecular level and macroscopic categories. Molecular level models include molecular dynamics simulations (MD) [42,43,64-66], quantum mechanical molecular mechanical (QM/MM) [67,68], multi-state empirical valence bond (MS-EVB) [39,41,43,69], and multi-scale coarse-graining (MS-CG) [70,71]. While these approaches gleam extremely useful information, the focus of this thesis on restricted to device level of macroscopic modeling efforts.

For macroscopic modeling Weber and Newman [72] described two major classifications: diffusive models and hydraulic models. Diffusion models stem from treating the membrane as a homogeneous phase where water and protons move by diffusion. The Nernst-Planck equation applied to infinite dilution mixtures is an example of a diffusive model when the convective velocity term is eliminated [72]. To account for all individual species interactions which may occur in the membrane concentrated solution theories may be applied such as the Stefan-Maxwell equations [73,74] or irreversible thermodynamics [75,76]. Conversely, hydraulic models used for membrane transport include Schologl’s equation [77] and Darcy’s law [34] which do not account for diffusive water transport. In an attempt to combine the diffusive and convective elements of the models other approaches have been utilized which generally amount to a linear combination of driving terms [78-80]. Alternatively, the dusty fluid model (DFM) can be used [40,81,82]. The DFM uses the Stefan-Maxwell formula as a starting point and attempts to add in the effect of convective flow by relating diffusive and convective species velocities through Schologl’s equation.
1.3 Characterization of Heterogeneous Transport Parameters

1.3.1 Overview of Methodologies

The modeling techniques mentioned in section 1.2.4 often make use of effective properties such as effective diffusivities. This practice is not restricted to modeling membrane transport in fuel cells or just diffusion. It is very common across many disciplines, even outside of fuel cells, to encounter complex heterogeneous materials where it is desirable to assign a single characteristic value to the transport coefficients such as the thermal and electrical conductivity or the diffusivity. A number of means of estimating these effective parameters exist. Three of the most common approaches which show up in many studies include percolation theory [83-85], parallel capillary modeling [86,87], and effective medium theory [88-91].

Percolation theory is generally applied to systems which have a conducting and non-conducting material type. Generally, the process of describing that system’s effective parameter relies on numeric simulations. If the simple scenario of a 2-D grid is considered that has a volume fraction, f, of conductive material then the volume fraction is taken to be the probability that any given square in the 2-D grid is occupied by the conductive material instead of the non-conductive material. Randomly generated grids are then used to calculate the observed behavior of the effective parameter as f is changed. A powerful feature of percolation theory is the percolation threshold, $f_0$, which is predicted. This percolation threshold is the volume fraction below which there exists no connected pathway through the material. Typically, a power law behavior is reported for percolation theory results.

\[
D = D_0 (f - f_0)^n
\]

(1.1)
The effective parameter (eq. 1.1 considers the diffusivity) of the system is related to the structurally uninhibited parameter multiplied by the difference between the volume fraction and the percolation limit raised to the \( n \) power. The parameter \( n \) is typically fitted and ranges between 1.3-1.7 for 3-D structures [83].

Parallel pore models are another common modeling frame used to describe effective parameters in heterogeneous materials. The approach is quite simple. In considering a material similar in nature as the percolation theory material, i.e. a mixture of conductive and non-conductive types, the structure is imagined as a non-conductive matrix with capillary pores running through it of the conductive material. These capillary pores are imagined to be uniform in cross section and run through the entire matrix from end to end. Performing straightforward substitutions of pore references to bulk references in a Fick’s law relationship leads to the correction of eq. 1.2.

\[
D = D_0 \frac{f}{\tau^2}
\]  

(1.2)

This result leads to the complicated task of determining a suitable value of the tortuosity, \( \tau \), of the material of interest where the tortuosity represents the effective length of the conductive pathways through the system.

A purely analytical approach to determining the effective parameters of a system is effective medium theory. Effective medium theory (EMT) typically relies on idealizing the structure of a mixture such that analytical solutions are possible then applies known solutions of Laplace’s equation or a Green’s function approach to solving the system [92]. It can be applied to a system which contains a conductive and non-conductive element or it can be applied to
systems which contain any number of conductive elements. Due to its analytical nature it is useful not just as a modeling tool for comparison against existing data but it can be used to make predictions about mixture conductivities. Section 1.3.2 provides a brief overview of some of the classic EMTs which are commonly used in the literature.

1.3.2 Effective Medium Theory

When considering effective medium theory, one of the earliest works on the subject was performed by Maxwell in the mid-1800s [93]. Maxwell estimated the effective electrical conductivity for a collection of spherical inclusion particles contained within a continuous matrix material. This was accomplished by considering the analytical Laplace solution for the external potential of a single spherical inclusion in a continuous and infinite matrix. The potentials of each individual inclusion particle were then added up at some field point far away from the mixture being considered and the resulting far field potential was compared to a pseudo homogeneous material which represented the effective conductivity. Maxwell-Garnett later arrived at the same solution by considering the average E-field contained within the mixture for the same geometry [94]. Both of these theories and all theories derived directly from their architecture are subject to the assumption known as the dilute limit approximation. This approximation limits the theories to very dilute suspensions because of the use of the Laplace solution for each particle in an infinite surrounding matrix. Any interference between particles is ignored. Fricke was the first to extend the results to non-spherical inclusions [95]. Using Maxwell-Garnett’s approach the problem was recast with spheroidal shaped inclusions that were randomly oriented to preserve the isotropic nature of the matrix.
To extend the dilute limit approximations of the above theories Bruggeman applied the unsymmetrical theory (BUT) [96]. This theory recursively operates in the dilute limit to build up the volume fraction of the inclusion material. Alternatively, Bruggeman also developed the symmetrical theory (BST) [96]. This theory does not utilize the dilute limit approximations but instead examines a mixture which is composed of randomly distributed spherical particles of different types. The material is symmetric in this case in that it does not consist of a clearly defined matrix and inclusion. The effective conductivity was derived by placing a heterogeneous mixture adjacent to a pseudo-homogeneous material with the same effective conductivity and examining the interface between the two regions. Bruggeman’s BUT result for spherical inclusions was then extended to spheroids by Meredith [97].

The above is not a comprehensive list of classical EMTs such as those given by Landauer, Reynolds and Hough, or Tobias [98-101] but it does represent some very commonly used approximations in fuel cell modeling: Maxwell’s dilute approximation [102,103], BUT [88-91,104], and BST [104,105]. BUT is probably the most widely used EMT in the fuel cell literature however, and it is fairly common to see it mixed with eq. 1.1 when considering a material which exhibits percolation. While BUT is developed for the general case where the two components have any conductivity, it does take a similar form to eq. 1.1 when the inclusion is considered as an insulator with $f_p = 0$ and $n = 1.5$. Usually, the so called Bruggeman exponent ($n = 1.5$) is used in conjunction with an experimentally measured percolation limit. BUT does not predict a percolation limit which is often cited as a weakness and adding one is a potential improvement but it is important to note that the analytical theory itself does not account for it.
1.4 Goals and Objectives

The next four chapters of this thesis focus on modeling transport in polymer electrolyte membranes, both PEM and AEM, for fuel cell applications. These studies range in complexity beginning with the calculation of water diffusion coefficients in chapter 2. This type of study is critical for predicting the water balance in the MEA of the fuel cell since diffusion is one of the major contributors to water transport in the membrane. The importance of membrane hydration and its implications in transport phenomena is a theme that carries throughout the studies.

Chapter 3 addresses carbon dioxide gas permeation in the PEM Nafion and the deconstruction of the permeability of membrane, as a function of temperature and hydration, into the diffusivity and solubility. A classical model for this which is commonly applied to such systems is used. To accurately interpret the results of the classic, homogeneous model, a new bicontinuous model is introduced. As mentioned earlier, understanding gas permeation through polymer electrolytes is necessary to accurately evaluate losses related to fuel cross over. In the case of carbon dioxide, as will be discussed in chapter 3, it is necessary to properly predict methanol cross over losses in a direct methanol fuel cell (DMFC) configuration.

Making use of the some of the lessons learned in the gas permeation studies, an ion exchange model is developed in chapter 4 which is used to examine the interaction of AEMs with carbon dioxide. This theoretical development captures the transient formation of carbonate and bicarbonate in an AEM, originally in a hydroxide form, exposed to air. This fundamental knowledge of the exchange process can be helpful for developing mitigation strategies in the future.
Finally, chapter 5 studies the membrane performance of a high pressure oxygen generating electrolyzer developed by Hamilton Sundstrand for use in the International Space Station. In this final study on polymer electrolyte membranes the performance of a membrane under operation is simulated through the use of a DFM development. The DFM is a diffusive hydraulic model which attempts to account for the effects of both diffusion and hydraulic flow in the membrane during operation. This work applies the DFM to an operating high pressure electrolyzer system which has many similarities to the PEMFC but also several key differences which have yet to be explored from a theoretical standpoint.

As mentioned in section 1.3.2, a common tool in the fuel cell community is BUT. The effective medium theory is also applied in several of the aforementioned studies in this thesis as a means of correcting diffusion coefficients. The final portion of the thesis, chapter 6, examines these theories and also expands them to account for more complex structures. Case studies are then performed to test the validity of the theories. The first links back to the gas permeation studies and provides credibility to the use of the original BUT on polymer membrane structures. The second applies the newly developed theories to a more complex structure where the original BUT is clearly not applicable; the highly anisotropic gas diffusion layer materials used on many low temperature fuel cell systems.
Chapter 2*: Calculation of Water Diffusion Coefficients

* Adapted from [106]

2.1 Overview

As mentioned in chapter 1 the water balance of the polymer electrolyte membrane is critical for proper fuel cell operation. If the membrane is too dry it will not conduct ions. One important mechanism for water transport in polymer electrolyte membranes is diffusion. Water diffusion in these membranes can be described with Fick’s law where the water diffusion coefficient itself, like many membrane properties, is a function of the local water content. The exact nature of this function has been the subject of debate but a prevailing theory is it is the product of the Darken factor, a function of the water uptake behavior of the membrane which accounts for the non-ideal nature of the membrane, and the self-diffusion coefficient of water in the membrane environment [107-110].

Many attempts have been made to predict or measure the water diffusion coefficient of Nafion. Some of the more established methods include nuclear magnetic resonance (NMR) [107,110-112], sorption [113,114], and permeation [108,109,115,116]. The NMR technique can be used to directly measure the self-diffusion coefficient as a function of water content in the membrane. This is achieved through the use of an NMR spectrometer which imposes a magnetic field gradient on a membrane sample, equilibrated in different relative humidity environments, and measures the response. To convert from the self-diffusion coefficient to the chemical diffusion coefficient the Darken factor is multiplied by the result of the NMR experiment. This technique offers the advantage of directly measuring the self-diffusion coefficient but is also quite experimentally involved.
Sorption is another common technique applied to measuring water diffusion coefficients. This technique involves placing the membrane in a certain relative humidity and recording the weight change over time as the membrane actively absorbs or desorbs water. If the process is assumed to be controlled by diffusion then a calculated time lag can be used to determine the water diffusion coefficient. The advantage here is the experiment is relatively simple and offers a fairly direct calculation of the diffusion coefficient. However, the influence of the transient swelling of the membrane is not entirely clear. It is possible that the transient water sorption is not controlled entirely by Fickian diffusion since the membrane must actively swell during the process. In this study, a steady state approach is desired so as to try and isolate the diffusion aspect.

The last technique listed here is the permeation technique which measures the steady state flux of water across the membrane in the presence of a concentration gradient. In this scenario the membrane is generally exposed to a humidified flow on one side and a dry flow on the other to create a gradient to drive diffusion. By measuring water contents of each of the streams before and after entering the test cell and performing a mass balance the steady state flux through the membrane can be calculated. This flux is then related to the diffusion coefficient through Fick’s law. The advantage here is the experiment is not complicated and the operation is steady state. The membrane is also in an environment most akin to a fuel cell during steady state operation. The drawback is the permeation technique requires a model with carefully defined physics to accurately calculate the diffusion coefficient.

Hallinan et al. noted that the range of reported diffusivities for Nafion in the literature span several orders of magnitude [117]. Even within a given technique agreement can span by more than an order of magnitude with NMR seeming to possess the tightest span. This chapter
presents the use of a permeation approach to measuring the water diffusion coefficient since the need for an accurate model is attainable. The developed numerics are combined with the results of an experimental apparatus to calculate water diffusion coefficients as a function of membrane water content. The method is first applied to Dupont’s Nafion 117 as a means of validation then extended to the AEM SnowPure Excellion I-200. As part of the validation process the values for the diffusion coefficient obtained for Nafion are compared with a different technique, NMR, in order to strengthen the validity of both measurements.

2.2 Experimental Apparatus:

In order to measure the steady state flux of water across a given membrane for varying volumetric flow rates, a permeation type cell was designed as shown in figure 2.1.
Figure 2.1 [106]: a) Cross section of the experimental cell involving a membrane contained between two serpentine flow plates. b) Schematic of the experimental rig. Humidified nitrogen is passed on one side of the cell and initially dry nitrogen is passed on the other facilitating diffusion through the membrane. Flagged T and P denote areas where temperature and pressure readings are taken. The * denotes standard conditions.

As shown in figure 2.1, the cell consisted of a membrane placed between two graphite flow plates. It is emphasized that there were neither gas diffusion layers used nor a catalyst layer in the experiment. This was done to focus on the water transport through the membrane itself. Stainless steel plates which contained heater cartridges for temperature control held the entire assembly together. The graphite flow plates were machined with serpentine paths as indicated in figure 2.1a. Diffusion was measured by flowing initially dry nitrogen on one side of the membrane while humidified nitrogen was flowed on the other. The nitrogen was humidified to a set level through the use of a humidity bottle upstream of the cell. Flow rates on either side of the
cell were set so as to attain equal pressure across the membrane to remove any influence of hydrodynamic permeability (this amounted to often negligible differences in flow rates in either channel). In order to ensure uniform heating of the cell it was well insulated during operation. The exiting gas streams on either side of the cell were passed through desiccant chambers to remove all water vapor. These chambers were weighed before and after each experiment to determine the total flux of the water through the membrane and to ensure the correct mole balance on the water. Experiments were performed using Nafion 117, a proton exchange membrane, and SnowPure Excellion I-200, an anion exchange membrane. Operating temperatures were selected to be 50 and 60 °C. These elevated temperatures were chosen for several reasons. First, there were concerns that fluctuations in temperature at lower absolute temperatures would lead to water condensation in the cell. Since 95% was the target humidity, fluctuations of less than 1 °C at 30 °C would lead to condensation in the channel which would complicate the physics of the system. Testing at elevated temperatures is also more representative of operating fuel cell systems. Finally, the elevated temperatures allowed for greater volumes of water to be picked up by the desiccant tubes due to the higher saturation pressures. This improved the accuracy of the measurement and increased collection rates allowing for shorter run times of the experiments. This was especially important in the case of the SnowPure Excellion membrane which had a much lower overall flux of water than Nafion. Each experiment was run for at least 30 minutes to allow for an appreciable amount of water to collect in the desiccant tubes (at least 0.2 grams). Before each experiment, when new conditions were set the cell was allowed 12 hours to equilibrate. Table 2.1 gives an outline of the experimental parameters run.
Table 2.1 [106]: Experimental Parameters.

<table>
<thead>
<tr>
<th></th>
<th>Nafion® 117 PEM</th>
<th>SnowPure Excellion™ I-200 AEM</th>
</tr>
</thead>
<tbody>
<tr>
<td>Functional group</td>
<td>sulfonic acid</td>
<td>benzyl-trimethylammonium</td>
</tr>
<tr>
<td>Cell temperature</td>
<td>50 °C, 60 °C</td>
<td>50 °C, 60 °C</td>
</tr>
<tr>
<td>Initial RH in dry channel</td>
<td>0%</td>
<td>0%</td>
</tr>
<tr>
<td>Initial RH in wet channel</td>
<td>95%</td>
<td>95%</td>
</tr>
<tr>
<td>Channel length</td>
<td>3 m</td>
<td>3 m</td>
</tr>
<tr>
<td>Channel depth</td>
<td>1 mm</td>
<td>1 mm</td>
</tr>
<tr>
<td>Channel width</td>
<td>0.75 mm</td>
<td>0.75 mm</td>
</tr>
<tr>
<td>Membrane thickness</td>
<td>0.178 mm</td>
<td>0.447 mm</td>
</tr>
</tbody>
</table>

2.3 Computational Approach:

2.3.1 Steady State Water Flux Model:

The development of the steady state water flux model begins with several key assumptions justified below.

1. The steady state diffusion of water through the membrane is one dimensional.
2. The dominant mode of transport is diffusion
3. The serpentine channel can be assumed to be one long straight channel for modeling purposes
4. The cell is isothermal.
5. The membrane thickness is constant.
Assumption 1 can only be justified if the water flux in the x and z directions, as shown in figure 2.1a, are shown to be negligible compared with the y direction flux. The length of the channel in the x direction is orders of magnitude greater than the y direction and the concentration gradient is less. This indicates diffusion in the x direction is negligible to the y direction. Water flux can occur in the z direction and influence the results by creating a crossover between adjacent channel segments. The distance between adjacent channel segments is more comparable to the membrane thickness at 0.9mm but the concentration gradients are much smaller leading to the argument that the flux in the z direction is much less than in the y direction.

The second assumption is difficult to justify up front and as such will be taken as valid for the remainder of the development and analysis. Its validity is discussed in relation to the results presented in section 2.4. If this assumption is invalid due to improperly accounted physics, the calculated diffusion coefficient for Nafion 117, which serves as a means of validation for the study, would likely be skewed and fail to match any literature values.

Assumption 3 has validity due to the long, straight sections of the serpentine channel making up 98% of the total length. The convective mass transport was shown to be negligible compared to diffusion in [118] which adds credence to the assumption that corner effects are negligible.

An isothermal cell is assumed for several reasons. The cell itself is well insulated to avoid any convective losses of the generated heat. The material the cell is comprised of has a high thermal conductivity (graphite and stainless steel) to help distribute heat. Finally, the thermal
couples placed in the cell monitor the temperature over time and insure it stays within ±0.5 °C of the target temperature.

Finally, there is the assumption of membrane thickness being invariant. In performing in-house thickness variation tests on both Nafion 117 and SnowPure Excellion a thickness increase of 11% and 9% were found, respectively, when equilibrated with liquid water at 30 °C. Due to average water content value during steady state experiments being much lower than the liquid water equilibrated value, and the fact that the membrane was no free to swell while confined in the cell, it was assumed that the membrane’s nominal thickness given in table 2.1 was appropriate for the calculations.

Using these assumptions the physics of the system can be represented using a 1-D marching scheme down the length of the flow channel where the membrane/channel assembly is divided into multiple computational cells. Figure 2.2 shows this in detail.
Figure 2.2 [106]: A visual representation of the computational cells in the numeric model. The steady state water flux through the membrane is evaluated in each cell and simple mass balances are performed to determine the boundary conditions of the next cell.

In order to solve the steady state water flux for each cell in figure 2.2, the water vapor activity, $a$, in the channels, which serves as the boundary conditions for water flux across the membrane, must be converted to an equivalent water content, $\lambda$, in the membrane. The water content of the membrane is defined as the moles of water per mole of functional group. The conversion is done using a least squares fit of uptake data taken from the literature [20,108] as shown in eq. 2.1.
Here the cubic function fits have been purposely anchored so a water activity of zero gives a water content of zero. Many cubic fits given in the literature show a slight hydration at an activity of zero and physical meaning has been given to this result. However, it is difficult to determine what influence experimental error has over those reported values and anchoring the curve at zero is not expected to influence the results of this study. Also, a useful analytical form of the Darken factor in terms of activity can be written when anchoring the curve at a water content of zero for zero water activity. With the boundary conditions determined the flux through the membrane, $J_m$, can be determined using an integral form of Fick’s law as shown in eq. 2.2.

$$ J_m = -\frac{c_f}{\delta} \int_{\lambda_0}^{\lambda} D_w d\lambda $$

(2.2)

Once the water flux through the membrane is calculated via eq. 2.2 it is a simple matter of performing a mass balance of the cell to update the boundary conditions for the adjacent computational cell.

$$ c_{h,2} = \frac{c_{h,1} v_{h,1}}{v_{h,2}} - \frac{J_m A_m}{v_{h,2} A_c} \tag{2.3} $$

$$ c_{d,2} = \frac{c_{d,1} v_{d,1}}{v_{d,2}} + \frac{J_m A_m}{v_{d,2} A_c} \tag{2.4} $$

A complication for the current experimental cell arises when considering the velocity terms in eq. 2.3 and 2.4 ($v_{h,1}$, $v_{h,2}$, $v_{d,1}$, and $v_{d,2}$). These represent the entrance and exit velocities of the stream passing through the computational cell. Pressure drops down the length of the flow channel of up to 48 kPa are observed experimentally at the highest standard nitrogen flow rates.
run. This pressure drop implies the velocities in the channels cannot be considered as constant. There are two possible contributors to a variation in velocity and pressure in the channels. One is the effect of wall friction acting on the flow while the other is due to a changing composition from water flux leaving or entering the channel. Since the length to hydraulic diameter ratio of the flow channel is around 3500 the friction and compressibility effects of the flow gas is likely the major contributor here [119]. The changing composition is not likely to be a major contributor due to the mixture being primarily composed of nitrogen but the effects are included in the following analysis for completeness. To derive the variation of the mixture velocity as a function of channel position a few more assumptions regarding the system are first made.

1. The mixture flow is steady and one-dimensional in the channel.
2. Changes in the mixture properties are continuous.
3. The mixture composes a semi-perfect gas.

With these assumptions, a control volume of the channel can be constructed as depicted in figure 2.3.
Figure 2.3 [106]: Control volume for the channel configuration. The bottom wall is the impermeable graphite flow channel while the top wall is the membrane. This particular control volume shows water being added since it depicts the dry stream. In the humid stream water is lost from the stream into the membrane.

The momentum equation for the control volume can be written as given by eq. 2.5.

\[-AdP - \tau_w dA_w = wdv + vdw + dvdw\]  

(2.5)

The shear stress term, \( \tau_w \), is defined as

\[ \tau_w = \frac{f \rho v^2}{2} \]  

(2.6)
The term $dA_w$ represents the differential wall area. It can be rewritten for the specific geometry as

$$dA_w = \frac{4A}{D_h} dx$$ (2.7)

Upon substitution of eq. 2.6 and 2.7 into 2.5 the governing equation becomes

$$-A_c dP - \frac{2 f \rho v^2 A_c}{D_h} dx = w dv + v dw + dvdw$$ (2.8)

It should be noted that the change in mass flow rate is equal to the cross over flux of water due to membrane diffusion, $dw = J_m W_c dx$. The continuity equation for the mixture in the flow channel is given by eq. 2.9.

$$w = \rho A_c v$$ (2.9)

This equation can be differentiated to obtain

$$\frac{dw}{w} = \frac{d\rho}{\rho} + \frac{dv}{v}$$ (2.10)

Where the differential cross sectional area term drops out for a constant cross section channel. The state equation for the mixture is given by eq. 2.11.

$$P = \rho RT$$ (2.11)

This can also be differentiated to obtain

$$\frac{dP}{P} = \frac{d\rho}{\rho}$$ (2.12)
Eq. 2.12 assumes the change in the individual gas constant, $R$, for the mixture is negligible as the stream either hydrates or dehydrates. The final forms of the momentum, continuity, and state equations can be solved in the numerical scheme set forth previously for the three unknowns; change in velocity, $\Delta v$, change in pressure, $\Delta P$, and change in mixture density, $\Delta \rho$. This will allow for the velocities in eq. 2.3 and 2.4 to be updated in each computational cell giving an accurate concentration variation down the length of the channel in consideration of the pressure drops observed.

Once the numerical system has been evaluated, the net flux is computed by averaging the steady state water fluxes for all the equally sized cells. This provides a direct comparison to the experimentally measured net water flux through the membrane.

2.3.2 Back out Algorithm:

In order to match the experimental data obtained for a given membrane to a diffusion coefficient a back out algorithm was developed. This algorithm attempts to match the water flux model developed in section 2.3.1 with experimental data from the rig outlined in figure 2.1. The water diffusion coefficient is assumed to be the product of the self-diffusion coefficient, $D_{\text{self}}$, and the Darken factor as indicated by eq. 2.13.

$$D_w = D_{\text{self}} \left[ \frac{\partial \ln(a)}{\partial \ln(\lambda)} \right]_{\text{Darken}}$$

(2.13)

Using eq. 2.1, the Darken factor can be written analytically as
\[
\left[ \frac{\partial \ln (a)}{\partial \ln (\lambda)} \right]_{Darken} = \frac{\alpha a^2 + \phi \alpha + \varepsilon}{3\theta a^2 + 2\phi a + \varepsilon}
\] (2.14)

With the Darken factor defined based on the water uptake characteristics of the membrane, the only remaining unknown is the self-diffusion coefficient. The self-diffusion coefficient is assumed to be dependent on local water content within the membrane and is fitted with a quadratic where the coefficients, \( \alpha \) and \( \beta \), are unknown and determined through a best fit algorithm.

\[
D_{\text{self}} = \alpha a^2 + \beta a
\] (2.15)

To determine the best values for \( \alpha \) and \( \beta \), the water flux model and the experimental data are compared for a range of \( \alpha \) and \( \beta \) values. This is a similar approach taken by Ge et al. [108]. As shown in the flowchart in figure 2.4, a set of possible fitting parameters is chosen and the associated water diffusion coefficients are set. This leads to an array of possible net water flux curves with varying standard volumetric flow rates in the channels. The error, \( Err \), between the experimental data and the computations are then minimized to determine the best pair of \( \alpha \) and \( \beta \).

\[
Err = \sqrt{(J_{\text{exp}} - J_{\text{num}})^2}
\] (2.16)
Numerical algorithm used to determine $\alpha$ and $\beta$ in Eq. 2.15. An array of possible values is chosen and the best fit pair is determined by comparing to experimental data as indicated above.
2.4 Results and Discussion:

The methodology described in section 2.3.2 was first applied to Nafion as a validation exercise. Once the approach was validated it was then extended to SnowPure Excellion. Figure 2.5 gives the calculated diffusion coefficients for Nafion 117 at 50 and 60 °C with operating conditions given in table 2.1.

![Graph showing calculated diffusion coefficients](image)

Figure 2.5 [106]: Calculated diffusion coefficients for Nafion at 50 and 60 °C. The results were compared to data taken from the literature [110]. Literature data was converted to a water diffusion coefficient from a self-diffusion coefficient and adjusted for temperature.

The calculated values of the diffusion coefficients obtained in this study for Nafion 117 were compared to experimental NMR data from Zawodzinski et al. [110]. Since the data from the
literature was measured at 30 °C an adjustment needed to made in order to make it comparable to
the 50 and 60 °C diffusion coefficients obtained in this study. To accomplish this, the self-
diffusion coefficient was adjusted via an Arrhenius relationship given by eq. 2.17.

\[
D_{\text{self}}(T) = D_{\text{self},0} \exp \left[ \frac{E}{R} \left( \frac{1}{T_0} - \frac{1}{T} \right) \right]
\] (2.17)

The activation energy, \( E \), in eq. 2.17 can be calculated from the current study giving a value of
17.13 kJ mol\(^{-1}\) K\(^{-1}\) which compares well with an available literature value of 20.25 kJ mol\(^{-1}\) K\(^{-1}\) [120]. One of the most striking features of the water diffusion coefficient in figure 2.5 is the
spike that occurs at a water content of about 3. This spike stems from the Darken factor in eq.
2.14. The Darken factor is derived from the derivative behavior of the water uptake curve and the
water uptake curve has a “knee” around a water content of about 3. This knee has a near zero
derivative associated with it that causes the sudden spike in the Darken factor which, in turn,
causes a large jump in the calculated water diffusion coefficient. The region just after the knee
where the uptake changes little with increasing water vapor activity is described as being a
region in which the ionic clusters in the membrane are forming. The sharper uptake behavior at
very high activities is associated with the swelling of the interconnected channels between the
clusters [121]. The diffusion coefficients measured by Zawodzinski et al. and the current study
are in close agreement. This is encouraging considering the completely different methods used.
In the case of Zawodzinski et al., the self-diffusion coefficient was measured using NMR while
here a water permeation cell was utilized. This result confirms the earlier assumption that
diffusion is the dominant mode to mass transport with regards to water in the current system
being studied. There have been a number of discussions recently which attribute major mass
transport resistance of water across the membrane to an interfacial resistance [108,122]. This
interfacial resistance is said to exist primarily between the humidified channel and the membrane. The results of this study do not support these claims however. The NMR study performed in the literature involved measuring the self-diffusion coefficient of Nafion in a vapor equilibrated environment. Based on the accounting of the experiment one could argue that there was no net mass transport occurring through the membrane or across the interface. The permeation experiment measures the diffusivity by imposing a concentration gradient across the membrane and across the vapor/membrane interface, thus any interfacial resistance would surely be buried in the result. Since comparison between the two techniques is close, this implies that the interfacial mass transport resistance is minimal. In more recent work performed by Caulk et al. [123], the importance of what is deemed device resistance is stressed for permeation type experiments. The scientists in that work demonstrated that after properly accounting for device resistance in their experimental rig, they were able to observe the expected behavior in the diffusion coefficient without accounting for interfacial mass transport as membrane thickness varied.

With the approach validated for Nafion 117 an extension was made to the AEM SnowPure Excellion. Figure 2.6 shows the result of performing the experiment and subsequent calculations for SnowPure Excellion.
The SnowPure Excellion™ AEM is constructed with a polypropylene backbone and benzyltrimethylammonium side chain group.

Figure 2.6 shows that SnowPure Excellion exhibits a diffusivity almost an order of magnitude lower than Nafion on average. The calculated activation energy based on the two temperatures measured is 27.43 kJ mol\(^{-1}\) K\(^{-1}\), somewhat higher than what was calculated for Nafion 117. In terms of published diffusivity values for AEM materials, SnowPure is on the low end of the spectrum. Values reported in the literature for various membranes have a wide range from \(10^{-11}\) to \(10^{-10}\) m\(^2\)/s [121,124]. Large variations in the measured diffusivity for different AEM materials are not unexpected since there is no generally accepted standard at the moment. Volkov et al. [124] demonstrated that lower self-diffusivities similar to the one measured here are obtained for
AEMs with higher DVB contents which act as cross linking agents for reducing membrane swelling. As reported by Vega et al. [29] there are many different backbone materials being used to synthesize different AEM materials including polyethylene, polypropylene, and polystyrene which may account for some of the variation in the water diffusion coefficients. It is noted here that the SnowPure Excellion membrane uses a polypropylene backbone material.

Figure 2.7 shows the raw experimental data used in the current study for determining the water diffusion coefficients of SnowPure Excellion.

Figure 2.7 [106]: Net flux through SnowPure Excellion as a function of the standard flow rate of nitrogen through the dry channel. The error bars for the experimental points are the collective results of both statistical as well as instrumental uncertainty. The dotted lines represent the maximum possible net flux allowable through the membrane which occurs when the channels equilibrate.
When examining the data it is important to ensure that the measured flux trends diverge from the maximum theoretical water flux through the membrane. The maximum theoretical flux curves are represented by the dotted lines in figure 2.7. These lines are the derived by assuming that equilibrium occurs between the two channels at some point in the cell. Assuming the exit humidities are equal on both sides of the membrane eq. 2.18 can be derived.

\[
J_{\text{max}} = \frac{c_{h,i} v_{h,i} - c_{d,i} v_{d,i}}{v_{h,f} - v_{d,f}} \frac{A_m}{A_c} \left( \frac{1}{v_{d,f}} + \frac{1}{v_{h,f}} \right)
\]  

(2.18)

Eq. 2.18 is completely independent of any membrane properties. In the case that the two channels reach equal concentrations, regardless of where that equilibrium point occurs along the flow path, the net flux will be the same maximum value. This situation creates problems for the back out algorithm since the solution for the diffusion coefficient will not be unique. If the measured flux coincides with the maximum flux line it cannot be used to obtain a solution in the back out algorithm. In figure 2.7 there is a single data point for the 60 °C case that falls on the maximum flux line so it was not used in the calculations of the water diffusion coefficient. All other data points were used. Coincidence of the measured water flux and the maximum flux line generally occurs at low flow rates, as seen in figure 2.7, or low entrance relative humidities of the humidified channel. Having a thin membrane or one that happens to possess a very large diffusivity will cause the water flux to be close to the maximum flux. Increasing the range of flow rates run or the relative humidity of the humidified stream at the entrance would then be needed to obtain useful data for the back out algorithm.
The reason increasing the range of flow rates can alleviate the issues of coincidence with the maximum flux line has to do with the typical behavior of the experimental curves in figure 2.7. As the flow rate increases the curves eventually reach a maximum flux and then begin to decay slightly. The maximum flux lines, however, continue to increase fairly monotonically causing a divergence of the two sets of curves. The reason for the experimental flux exhibiting such a behavior can be elucidated by again considering figure 2.3 as well as eq. 2.3 and 2.4. Clearly, as velocity becomes very large, the second term on the right hand side of both equations becomes negligible. This means so much water is being supplied so quickly in the humidified channel that the amount lost to diffusion through the membrane becomes insignificant and the concentration of water vapor in the humidified channel tends to stay constant at the entrance value. Vice versa, in the dry channel, the water entering by diffusing through the membrane is swept away so rapidly that there is no appreciable buildup of water vapor in the downstream portions of the dry channel. In this situation, the maximum water flux through the membrane (not to be confused with the concept related to eq. 2.18) is obtained because the maximum concentration gradient through the membrane is maintained throughout the flow field. However, compressibility effects complicate matters. If there were no compressibility effects the flux would achieve a maximum value and remain constant for any increase in flow rate. Due to the compressibility effects the flux curve starts to turn over. This effect can be explained by the \( v_{h,1}/v_{h,2} \) ratio in eq. 2.3 and 2.4 which is expected to decrease as the pressure drop down the channel length increases (which increases as flow rate increases). This causes the water vapor concentration down the length of the channel to start decreasing leading to the observed decrease in the net flux behavior with increasing flow rate of figure 2.7 after the maximum net flux through the membrane is attained. While the turn over shown in figure 2.7 is somewhat slight
there have been other works which show similar behavior in water flux vs. flow rate curves [122,125]. A very important note to make here is that this pressure drop behavior does not have to occur through the cell to affect the results. If there is a significant pressure drop occurring anywhere between the humidifier and the cell similar behavior should be expected. This is because, even at elevated absolute pressures, the saturation pressure of water is relatively constant. So if the gas stream is pressurized when it passes through the humidifier, and then depressurized before or through the cell, the water concentration in the stream exposed to the membrane will decrease via the type of affect captured by eq. 2.3 and 2.4. If these pressure drops are present but ignored, potentially erroneous conclusions can result. In fact, the theoretical maximum flux of water through the membrane discussed previously may never actually be obtained if the pressure drop behavior is severe enough.

2.5 Conclusions

Due to the delicate nature of the water balance in polymer electrolyte fuel cells, water transport has been a focus of research in polymer electrolyte membranes. Increasing water content in the membrane increases ionic conductivity but too much water floods catalyst sites and prevents fuel from reacting. To best design fuel cell systems, accurate measurements of the fundamental mechanisms which contribute to the overall water balance are necessary. One such mechanism, water diffusion, was the subject of this chapter where the identifying characteristic is the water diffusion coefficient. Using a permeation technique, which involves the measuring of the steady state water flux across the membrane coupled with a model for the experimental cell used, a water diffusion coefficient was calculated for Nafion 117 as a function of local water
content. It was found that the resulting curve compared very well with published literature. Such close agreement between differing techniques in the literature was largely absent before. Some discussion was also given to the concept of interfacial transport resistance and its effect on the results which were argued to be minimal in this study. With the technique validated against Nafion 117 it was then extended to an anion exchange membrane, SnowPure Excellion I-200. It was found that the diffusivity of the AEM was roughly an order of magnitude smaller on average than that of Nafion. There was also discrepancy between the measured SnowPure Excellion AEM diffusion coefficient and other data existing in the literature for other AEMs. However, due to wide variations in the current AEM construction it was not deemed to be unreasonable.
Chapter 3: Transport of Carbon Dioxide through Nafion

3.1 Overview:

Over the past couple decades direct methanol fuel cells (DMFCs) have gained interest for their use in portable power applications [6,7,126-130]. A major reason for this interest is due to their ability to directly oxidize the high energy density liquid methanol fuel, which makes them attractive for small and portable applications for which hydrogen storage is a challenge.

One of the major issues with DMFCs is methanol crossover, which leads to increased performance losses [6,7,126-128,131-135]. A common practice for measuring this crossover rate involves analyzing the effluent of the cathode for carbon dioxide since methanol crossing the membrane electrolyte will be directly oxidized at the cathode. The carbon dioxide present in the stream will actually be a product of both the oxidation product from the crossover methanol, as well as the carbon dioxide permeating through the membrane (i.e., from the anode). A need for a correction to account for this extra CO\(_2\) presence in the cathode effluent has been noted in the literature over the past decade [127,128,133,136,137].

Dohle et al. investigated methanol permeation in DMFCs using Nafion 117 and 112 membranes [133]. By using half-cell operation the authors were able to separately evaluate the contributions of measured carbon dioxide from the anode and cathode oxidation reactions. N\(_2\) was present on the cathode side of the cell to prevent methanol oxidation during carbon dioxide flux measurements. The authors found that in scenarios where methanol concentration was less than 1 M, the carbon dioxide crossover exceeded the methanol crossover in the membrane. It
was also noted that the presence of methanol in the membrane enhanced the carbon dioxide transport.

Jiang and Chu also took up measuring the carbon dioxide permeation in Nafion membranes, which was calculated relative to the methanol permeation [127]. Their study utilized a Nafion 117 based MEA and several cell types. An inactive cell with no catalyst material and a single cell with a methanol tolerant catalyst at the cathode were used to measure the carbon dioxide crossover in the presence of various methanol concentrations. This study also observed an increase in carbon dioxide permeability in the presence of methanol which was attributed to the increased swelling of the membrane. After examining the carbon dioxide permeation rates through Nafion 117 a normal single cell was run. It was found that crossover currents were reduced by upwards of 50% when the carbon dioxide crossover was accounted for. The work was later continued with carbon dioxide being monitored on both sides of a single DMFC [128]. This was done by utilizing a Ba(OH)$_2$ solution and observing the precipitation of BaCO$_3$ as the effluent streams were passed through it. The BaCO$_3$ was weighed with a high accuracy, five decimal balance to calculate the amount of carbon dioxide collected.

Ma et al. commented on the need for a comprehensive study of carbon dioxide transport through Nafion membranes; two articles published by the group addressed this concern [136,137]. In their later work they noted that, despite the fact that the presence of methanol enhanced the crossover of carbon dioxide, most DMFC systems would operate with a methanol concentration less than 1 M, making the enhancement negligible. The group measured the steady state permeation of carbon dioxide through Nafion 117 as a function of hydration and temperature using a permeation cell with a mass spectrometer. They determined there was a
strong effect of hydration on the transport and that the hydrophilic domain of the membrane was the primary pathway for carbon dioxide transport.

The focus of the present study in this chapter is to expand upon the sentiment contained in work done by Ma et al. By utilizing a permeation cell and taking transient measurements of the carbon dioxide content of effluent gases, as carbon dioxide is exposed to one side of the membrane, the permeability of Nafion 117 is resolved into the diffusivity and solubility according to a classic homogeneous diffusion model. These measurements are done over a range of hydration states and temperatures in order to obtain empirical expressions for the permeability, diffusivity, and solubility of Nafion 117 to carbon dioxide. After applying the commonly used homogeneous model, the results are reinterpreted using a separately derived bicontinuous model. The major difference between the two is the bicontinuous model allows for simultaneous transport through the hydrophilic and hydrophobic domains of the membrane whereas the homogeneous model does not.

3.2 Experimental Setup

3.2.1 Membrane Preparation

The membrane used in this study was Nafion 117. The samples were prepared by first boiling them in 3% hydrogen peroxide for one hour then thoroughly rinsing with deionized water. After this initial treatment they were boiled in 1M sulfuric acid at 135 °C for 2 hours then boiled in deionized water for another two hours. The final, conditioned, samples were then stored in a closed beaker of deionized water until they were used in the cell. In the event of a dry membrane test the entire test cell, with the membrane installed, was placed in a vacuum oven at 100-115 °C
with a vacuum of -96 kPa for at least two hours. The vacuum oven was located in a dry room with a dew point of < -80 °C. Once the cell was removed from the oven it was capped to prevent moisture from entering while it was transported to the test rig.

3.2.2 Test Cell:

The test cell used in this application was a Fuel Cell Technologies single cell with a 5 cm$^2$ active area. It was determined that the post holes in the graphite flow plates, which are intended to be used for alignment of the cell, caused a significant cross leak of carbon dioxide. A new set of Teflon gaskets were designed to deal with this problem. This design made use of the bolts in the steel bipolar plates for alignment. The Nafion membrane was placed in the cell fully hydrated and without any gas diffusion layers or electrodes. Due to the presence of the Teflon gaskets there was a spacing of about 10 μm between the flow channels and the membrane meaning the entire 5 cm$^2$ area of the membrane was exposed to pure carbon dioxide or nitrogen.

3.2.3 Experimental Rig:

The basic design of the experimental procedure used to investigate carbon dioxide cross over is described in the schematic shown in figure 3.1. Here nitrogen (Airgas Ultra High Purity Nitrogen) is flowed on one side of the test cell and carbon dioxide (Air Products UN-1013) is flowed on the other.
The partial pressure difference of carbon dioxide results in a net transport through the membrane. The carbon dioxide which enters the nitrogen stream is then detected by an IR based detector (Horiba VIA-510) which outputs the transient response to a computer through a serial connection to LabView (National Instruments). The test gas is first dried before sending it to the analyzer by passing it through a copper coil submerged in ice water. This is done to prevent any inaccuracies caused by water vapor being present in the analyzer. Various operational parameters can be controlled through the use of the Fuel Cell Technologies Test Station utilized in the experiments such as the relative humidity and flow rate of the feed gases, the cell temperature, and the pressure of the carbon dioxide stream. For the purpose of this study, the flow rates were kept constant at 200 sccm for CO₂ and 400 sccm for nitrogen. The nitrogen was kept at a higher flow rate for the purpose of purging between tests. The pressure was also kept fixed at atmospheric pressure. Valve #1 and Valve #2 shown in the Figure 1 were used to control the carbon dioxide exposure of the cell. Before a test was performed Valve #2 would be closed and Valve #1 would
be open to pass nitrogen through both sides of the cell and keep it purged of any carbon dioxide. At the start of each test Valve #1 would be closed then Valve #2 was immediately opened.

3.3 Analysis

3.3.1 Homogeneous Model

In order to calculate transport parameters a popular model applied to polymer membrane gas transport was used. This model involves the use of Fick’s first and second laws subject to a few key assumptions [138].

1. The diffusivity is constant.
2. The concentration of the diffusing species is zero on the downstream surface of the membrane.
3. The absorption of the diffusing species is instantaneous relative to the diffusion process and can be represented with Henry’s law.
4. There is only one pathway for diffusion and thus only one characteristic diffusion coefficient.

The assumption regarding constant diffusivity is valid since the diffusivity is expected to depend on the hydration of the membrane which is kept uniform for a given test. The concentration of carbon dioxide on the downstream surface can be assumed as constantly zero since the measured concentration levels of carbon dioxide on the downstream side of the membrane are on the order of single to hundreds of ppm. This is always negligible compared to the pure carbon dioxide concentration on the upstream side of the membrane. The final two assumptions listed above are
not easily validated upfront. As such their validity, as well as the gravity of the assumptions themselves, is discussed in the results and discussion section. As will be seen later, the validity of assumption 4 leads to the development of the bicontinuous model mentioned in section 3.1.

With these assumptions, the permeability of carbon dioxide through the membrane can be obtained using the steady state flux. The steady state flux is given by eq. 3.1 assuming constant diffusivity and solubility.

\[ J_{SS} = P_h \frac{\Delta p}{l} \]  \hspace{1cm} (3.1)

It is clear that the equation above is based on Fick’s first law indicating that the permeability \( P_h \) is the product of the solubility and diffusivity as indicated by eq. 3.2.

\[ P_h = D_h \times S_h \]  \hspace{1cm} (3.2)

The steady state flux of eq. 3.1 can be calculated from the steady state concentration of carbon dioxide detected in the nitrogen stream using eq. 3.3.

\[ J_{SS} = \frac{Q_{ch} c_{CO_2}}{A_{mem}} \]  \hspace{1cm} (3.3)

By combining eq. 3.1 and eq. 3.3, the permeability can be determined. However, it is impossible to resolve the permeability into the diffusivity and solubility without the use of the transient data. To determine the diffusivity, Fick’s second law is used with the boundary conditions described in eq. 3.4.
\[
\frac{\partial c_{CO_2}}{\partial t} = D_h \frac{\partial^2 c_{CO_2}}{\partial x^2}
\]

\[c_{CO_2}(0,x) = 0 \]

\[c_{CO_2}(t,0) = C_1 \]

\[c_{CO_2}(t,l) = 0 \]  

(3.4)

The solution to eq. 3.4 is given by 3.5.

\[
J(t) = \frac{DC_1}{l} \left[ 1 + 2 \sum_{n=1}^{\infty} (-1)^n \exp \left( -\frac{n^2 \pi^2 D_h t}{l^2} \right) \right]
\]

(3.5)

The diffusivity can be determined by taking the integral of eq. 3.5 and considering large t resulting in eq. 3.6.

\[
Q_t = \frac{D_h C_1}{l} \left( t - \frac{l^2}{6D_h} \right)
\]

(3.6)

Eq. 3.6 is a linear relationship and the diffusion coefficient can be calculated by considering the t-intercept (t_{lag}) which is determined experimentally.

\[
D_h = \frac{l^2}{6t_{lag}}
\]

(3.7)

Once the diffusion coefficient has been calculated it is a simple task to calculate the solubility using eq. 3.2. It is noted that the permeability and diffusivity are related to the membrane dimensions, which are expected to change with hydration due to the free standing scenario described in the experimental section. To account for this swelling data was used from the work of Morris and Sun [139].
3.3.2 Post Processing Analysis

In many applications it is necessary to correct transient data to account for the machine’s inability to respond instantly to an input signal. The VIA-510 gas analyzer has a delay in its response which is of the same order of magnitude as the transient phenomena it was being used to measure. Figure 3.2a shows the gas analyzer’s normalized response to a step input of carbon dioxide.

Figure 3.2: a) Normalized response to step input from the VIA-510 gas analyzer. The region labeled machine aspiration is the initial delay caused by the gas needing to travel through the plumbing of the experiment. b) A sample signal response which is first calibrated then corrected for time delay.

There are two distinct features in this response. The first feature, labeled machine aspiration, is the time it takes the gas to travel through the external plumbing to the measuring device and it can simply be subtracted out. The second feature is the response of the machine to the actual step
input. To correct this response and recover the step input in figure 3.2a a discrete time correction algorithm was adopted. This algorithm works by taking the machine response data to a step input after the aspiration has been subtracted and keeping track of the time differences, Δt, between the desired step function and the actual output. The Δt values are then subtracted from the discrete time values in the data set as a correction. Obviously, a cutoff has to be established to preserve the steady state “shelf” otherwise the entire steady state range would be collapsed into a vertical line at t = 0. A cutoff of 99% was selected in this case meaning any time after the 99% rise time has the 99% rise time Δt subtracted from it. This process is represented by eq. 3.8.

\[
\begin{align*}
t_{corr} = \\
t - \Delta t_{m\%} & \quad \text{if } m < 99\% \\
t - \Delta t_{99\%} & \quad \text{if } m > 99\%
\end{align*}
\]

(3.8)

Once the Δt values are computed for the machine response to a step input they can then be applied to any arbitrary output signal to obtain the true input signal as indicated in figure 3.2b.

As the characteristic time lag of the measurement grows smaller any errors associated with the machine response and aspiration time are enhanced. For reasons discussed in the next section the characteristic time lag of the transient response decreases with increasing hydration and temperature. The worst case scenario studied here for error associated with machine response and aspiration time was for the 80 °C fully hydrated case. In this scenario if the machine response and aspiration are unaccounted for the calculated diffusivity is reduced to 25% of the calculated value with the corrections applied. If only machine response is unaccounted for then the diffusivity is reduced to 50% of the corrected value. This results in an associated error in the calculated solubility as determined by eq. 3.2.
3.4 Results and Discussion

Results for carbon dioxide transport through Nafion 117 were obtained for temperatures ranging between 30 and 80 °C and at varying vapor equilibrated conditions from fully dry up to 100% RH. In order to help explain the nature of the transport in these different conditions it is useful to characterize the structure and put forth some definitions up front. As Nafion uptakes water it undergoes a phase separation between the hydrophilic and hydrophobic regions [30,120]. The hydrophilic regions are characterized by hydrated sulfonic acid clusters which are amorphous in nature. The hydrophobic region is composed of the semi-crystalline Teflon backbone. In the remainder of this discussion these two regions will be considered as separate pathways for transport where the goal will be to differentiate between the contributions in transport stemming from both.

3.4.1 Permeability

To help validate the results obtained in this study the permeability measurements obtained from the steady state response are compared with the available literature data for the 100% RH equilibrated, dry, and intermediate hydrations in figure 3.3.
Figure 3.3: a) Permeability results obtained for the 100% RH and dry condition at varying temperature. b) Permeability values calculated for varying hydrations and temperatures. Error bars indicate max/min values for given test conditions where appropriate.

As shown in figure 3.3a the fully hydrated permeability agrees well with the results obtained by Ma and Skou as well as by Jiang and Chu [127,137]. It should be noted that the results taken from Ma and Skou work were altered to account for a growing partial pressure of water vapor. Ma and Skou state that a partial pressure of 1 atm for CO$_2$ was assumed through all tests. At low temperatures the saturation pressure of water can be assumed to be insignificant compared to atmospheric pressure but at a temperature of 80 °C the saturation pressure of water is approximately 47 kPa which is almost half that of atmospheric pressure. This indicates that if the experiment is run at atmospheric pressure the CO$_2$ partial pressure exposed to the membrane will decrease with increasing temperature for the hydrated cases. Adjusting the numbers obtained by that group to account for this yields the comparison shown in figure 3.3a where it appears that the permeability is invariant with temperature when the membrane is equilibrated in a 100% RH
environment. A constant permeability at this condition does not indicate an invariant nature to the transport behavior, as will soon be evident with the investigation of the diffusivity and solubility behavior.

Figure 3.3a also gives the measured dry membrane permeability values obtained through this work as well as by others. Generally speaking, the permeability values for the dry case are at least almost one order of magnitude lower for the dry case indicating a strong dependence on hydration as noted by others [136,137,140]. Also, the dry permeability increases with increasing temperature which at this point should be considered little more than the result of a balancing act between the diffusivity and solubility whose product is the permeability. It is evident in the comparison between all the data sets that none exactly agree and the values reported here for the dry permeability are greatest. This variation in the reported values may be due to the difficulty in establishing completely dry conditions. Ma and Skou dried their membrane samples by placing them in a vacuum oven operating at 40 °C with a vacuum pump pressure of $1 \times 10^{-2}$ kPa. The samples were dried for 48 hours in that work [137]. Chiou and Paul dried their samples in an unspecified vacuum pressure for 5 days prior to installation in their test cell. After installation the samples were dried further in the cell under vacuum at 35 °C for 1 week [140]. As stated above the membrane studied in this work was subject to extensive drying methods and great care was taken to not to introduce any unwanted humidity to the system when dry experiments were being conducted. The test rig was also flushed with dry nitrogen overnight to remove any unwanted humidity. When all the drying methods are compared this work had the highest drying temperature and perhaps the greatest vacuum pressure. However, Chiou and Paul had the longest drying time totaling almost two weeks prior to testing while this work had the shortest time at 2 hours. Since Chiou and Paul have the lowest permeability it may be that drying time is the most
important parameter in establishing a completely dry membrane. Alternatively, it should be noted that the equilibration time when taking time varying permeability measurements of carbon dioxide through dry Nafion is substantially longer than for the hydrated case. At 30 °C the rate of carbon dioxide crossover didn’t reach steady state for over 1.5 hours in this study. This being the case it is possible the other mentioned works terminated testing prematurely. However, no transient data sets are presented in those works so this remains only one possible explanation. It is also possible the drying method used here was too harsh for the membrane. After removing the membranes from the cell they had yellowed which may indicate degradation after being dried in high vacuum and temperature. For the reasons listed above only the permeability was calculated for the fully dry condition and the extremely low permeability in the dry condition is noted.

Figure 3.3b shows the comparison between the permeability for varying hydration obtained in this study and that obtained by Ma et al. [136]. Good agreement is obtained between the values given by Ma et al. for 25 °C and those obtained in this study for 30 °C. The small temperature difference when comparing the studies is not a great concern due to the weak temperature influence on the permeability which is observed in this work. Again, this weak temperature dependence of the permeability for varying hydration does not necessarily indicate that temperature has little effect on the transport mechanisms. To evaluate the detailed effect of temperature the permeability will need to be resolved into the diffusivity and solubility which is handled in the proceeding discussion.
3.4.2 Applicability of the Homogeneous Model

Before proceeding with the results of the diffusivity and the solubility it is useful to first interrogate how well the homogeneous model presented in section 3.3.1 represents the data. It is important to stress that the model utilized here, and elsewhere, to describe the gas transport through polymer electrolyte membranes hinges on single pathway transport. In other words, the model does not account for multiple pathways through the medium of interest. As was stated above the belief is that the membrane is still permeable to carbon dioxide even in the dry condition implying transport occurs through the hydrophobic region although this transport is believed to be quite small. There is no reason to believe this hydrophobic region transport does not occur simultaneously with the hydrophilic region transport when the membrane is hydrated to varying degrees. That being the case the calculated diffusion coefficient for varying hydration will really be some sort of weighted average of the diffusivity for the dry case and the hydrated case. In this particular scenario however, the time lag associated with the dry diffusivity is so much greater than even the lowest measured hydrated case that the influence of the hydrophobic region transport on the calculated diffusivity is insignificant. Due to this sharp contrast between the respective time lags the measured diffusivity for all the intermediate hydration conditions can be assumed to be completely associated with the transport through hydrophilic region. Another important assumption of the model used to describe the transport is that the absorption of the gas at the gas-membrane interface is instantaneous compared to the diffusion. The validity of this assumption is best explored by investigating the quality of the fit between the experimental data and the model. Figure 3.4 shows this comparison for a typical case with a cell temperature of 60 °C and a humidity of 50%. To quantify the error between the model curve and the experimental data the normalized root-mean-square deviation (NRMSD) was calculated over a time interval of
3t_{lag}. In figure 8 the NRMSD is 0.044. Over all the cases studied the average NRMSD was 0.041 with a variance of $8.4 \times 10^{-4}$. It is stressed that no curve fitting method was imposed here. The model curve in figure 3.4 is obtained by taking the diffusivity as determined from time lag and plugging it into eq. 3.5 where the flux is converted to concentration of carbon dioxide.

The excellent agreement between the model and the data suggests, but does not prove, that the assumptions of the model are appropriate. The presence of other limiting mechanisms influencing transport would most likely alter the shape of the response curve. Also, returning to the topic of multiple pathways, if two pathways for diffusion were being utilized with comparable time lag behavior one would expect to see a “knee” shape in the transient portion of the curve as the transport through one of the pathways reached steady state but the other

Figure 3.4: Comparison between the model output and the experimental data (Cell temperature: 30 °C, Humidity: 60%, NRMD: 0.044).
remained in the transient phase. It is important to note that the convenient characteristics which lend themselves to the use of the described model will not necessarily remain consistent as different gases are tested through different membranes. This may prompt the need for an investigation into both co-limiting and multiple pathway modeling efforts which will be the subject of section 3.4.5.

3.4.3 Diffusivity

Figure 3.5 shows the behavior of the calculated diffusion coefficient at varying temperature for the 100% RH equilibrated case.

![Figure 3.5: Diffusivity for the membrane equilibrated with 100% RH as a function of temperature.](image)
Fitting the 100% RH equilibrated data with an Arrhenius type relation yields an activation energy of 24.8 kJ mol\(^{-1}\). It has been put forth already that carbon dioxide transport is dominated by transport through the hydrophilic regions present in the membrane when it is hydrated [136,137]. This theory is supported by the obtained activation energy of 24.8 kJ mol\(^{-1}\) which compares well with an activation energy of 19.5 kJ mol\(^{-1}\) for carbon dioxide diffusing in pure water [141]. As discussed by Chiou and Paul, the transport for the dry case is likely to occur through the hydrophobic region of the polymer, which consists of both ionic groups and the fluorocarbon [140]. For this sort of transport one would expect a different activation energy to describe the temperature variation in the diffusivity. One question of interest at this point is whether the activation energy calculated is a strong function of hydration. Using an Arrhenius type fit once again at the 50% RH and 75% RH equilibrated conditions yields activation energies of 21.2 kJ mol\(^{-1}\) and 20.8 kJ mol\(^{-1}\). The similarity between the activation energies at these varying humidities implies consistent transport behavior which is primarily through the hydrophilic regions of the membrane.

Figure 3.6 shows the behavior of the calculated diffusivity as a function of relative humidity.
As shown in figure 3.6 the carbon dioxide diffusivity has a strong dependence on the membranes hydration. This dependence fits with the assertion that the carbon dioxide utilizes the hydrophilic regions in the membrane as a means of transport. As the pores swell and interconnection between them becomes strong the carbon dioxide should have an easier time traversing the membrane structure if the hydrophilic region is the primary transport pathway. Eq. 3.9 fits the diffusivity trends versus activity with a simple linear expression.

\[
2.53 \times 10^{-6} \ a \exp \left[ \frac{2.23 \times 10^{-4}}{R} \left( \frac{1}{303} - \frac{1}{T} \right) \right] \quad \text{for } RH \geq 20\% \quad (3.9)
\]
3.4.4 Solubility

With the diffusivity of carbon dioxide through Nafion calculated it is a simple matter of applying eq. 3.2 to obtain the solubility. In this instance it is useful first to look at the solubility as a function of hydration due to the interesting nature of the results. Figure 3.7 shows the solubility of CO$_2$ in Nafion 117 as a function of relative humidity and temperature.

![Figure 3.7](image)

Figure 3.7: a) Solubility of CO$_2$ in Nafion 117 as a function of relative humidity for different temperatures. b) Calculated solubility of CO$_2$ for hydrated Nafion 117 plotted against temperature. The dotted line is the solubility of CO$_2$ in pure water.

As seen in figure 3.7a there is a weak dependence of the solubility on relative humidity compared with the diffusivity. As shown in figure 3.7b these values actually correspond closely with the solubility of carbon dioxide in pure liquid water. The calculated enthalpy of mixing in the fit is -18.6 kJ/mol which is close to -16.6 kJ/mol, the enthalpy of mixing of CO$_2$ in pure water [141]. Taking these fitting results, along with the observation that the solubility of CO$_2$ in the
membrane is approximately constant at the intermediate hydration conditions, the following empirical formula is derived.

\[ S^H = 3.21 \times 10^{-10} \exp \left( -\frac{1.86 \times 10^4}{R} \left( \frac{1}{303} - \frac{1}{T} \right) \right) \quad \text{for } RH \geq 20\% \quad (3.10) \]

The solubility results of figure 3.7 are actually quite perplexing due to the nature of the homogeneous model. If a simple parallel pore model is applied for the single phase transport described by the homogeneous model a counter-intuitive outcome occurs. The correction factor between the homogeneous diffusivity of eq. 3.2 and the diffusivity of carbon dioxide in liquid water ends up being the inverse of the tortuosity squared \( \tau^2 \). The implication after comparing this with the correction factor for the permeability is that the homogeneous solubility relates to the liquid water solubility as \( S_h = \varepsilon S_\alpha \) where \( S_\alpha \) is the pure water solubility and \( \varepsilon \) is the wet porosity. This is clearly not the case looking at figure 3.7 as it was just indicated how similar the calculated solubility was to carbon dioxide in liquid water. The inconsistency here implies the homogeneous model is oversimplified. The next section introduces the concept of the bicontinuous model which helps interpret the homogeneous model results as well as generalizing the governing equations for other systems.

### 3.4.5 The Bicontinuous Model

In the bicontinuous model, the Nafion membrane material is assumed to consist of two distinct phases, \( \alpha \) and \( \beta \), which represent the hydrophilic water filled phase and the dry membrane phases respectively. Initially, the governing equations are derived with no assumptions being made about one phase being the primary transport phase over the other. For
the specific case studied here it will be assumed that the \( \beta \) phase actively absorbs carbon dioxide during the transient diffusion process but it possesses negligible diffusivity. In other words, the hydrophobic region of the membrane will act as a carbon dioxide sink. It is only in this scenario that the transient behavior of the permeation would still have the same shape as depicted in figure 3.4. These results will be analogous to the theory presented by Goodknight et al. [142,143] which accounts for the effect of dead end pores on transient time lag measurements.

Figure 3.8 shows a traditional parallel pore visualization of the membrane. For simplicity, only one pore is shown.

![Parallel pore model](image)

Figure 3.8: Parallel pore model

A mass balance is performed on the two phases which is given generically by eq. 3.11 and 3.12.
\[
\dot{M}_\text{in}^\alpha + \dot{M}_g^\alpha - \dot{M}_\text{out}^\alpha = \dot{M}_\text{st}^\alpha 
\]  
(3.11)

\[
\dot{M}_\text{in}^\beta + \dot{M}_g^\beta - \dot{M}_\text{out}^\beta = \dot{M}_\text{st}^\beta 
\]  
(3.12)

In this scenario the dissolved gases in the \(\alpha\) and \(\beta\) phases can be thought of as two different species. The transfer from one phase to the other can then be described as a generation term in eq. 3.11 and 3.12. This is akin to the approach originally used by Goodknight et al. [142,143]. To describe the diffusive transport we make use of Fick’s law. Beginning with the \(\alpha\) phase;

\[
\dot{M}_\text{in}^\alpha = n_{\text{bulk}}^\alpha A 
\]  
(3.13)

Where;

\[
n_{\text{bulk}}^\alpha = \frac{A_{\alpha}}{A} n_{\text{pore}}^\alpha = -\frac{\varepsilon}{\tau_{\alpha}^2} D_{\alpha} \frac{\partial C_{\alpha}}{\partial x} 
\]  
(3.14)

The outflow of species \(\alpha\) can then be represented by;

\[
\dot{M}_\text{out}^\alpha = -\frac{\varepsilon}{\tau_{\alpha}^2} D_{\alpha} \frac{\partial C_{\alpha}}{\partial x} A - \frac{\varepsilon}{\tau_{\alpha}^2} D_{\alpha} \frac{\partial^2 C_{\alpha}}{\partial x^2} A dx 
\]  
(3.15)

The storage term is described by;

\[
\dot{M}_\text{st}^\alpha = \frac{\partial C_{\alpha}}{\partial t} dV_{\alpha} = \varepsilon A \frac{\partial C_{\alpha}}{\partial t} dx 
\]  
(3.16)

At this point the generation term needs to be defined. Continuing with the theme of representing the carbon dioxide in each phase as different species, the generation term can be written as an elementary reaction as given by eq. 3.17.
\begin{equation}
\dot{M}_g^\alpha = -\dot{M}_g^\beta = -(k_1 C_\alpha - k_2 C_\beta) dA_{\alpha-\beta} = -k_1 \left( C_\alpha - \frac{1}{K_{eq}} C_\beta \right) dA_{\alpha-\beta}
\end{equation}

(3.17)

The forward rate constant in eq. 3.17 has the units of a convective mass transport coefficient \([\text{m} \cdot \text{s}^{-1}]\). The equilibrium constant in eq. 3.17 represents the ratio of the \(\beta\) phase concentration to the \(\alpha\) phase concentration at equilibrium at a given location, \(x\). For now it will be left as an equilibrium constant but one assumption that can be made is this constant is equal to the solubility ratio, \(K_{eq} = \frac{S_\beta}{S_\alpha}\). Setting this definition assumes that one can define a pseudo partial pressure, \(p_i\), at any location within the membrane and \(p_i\) is defined by the ratio of the concentration, at that point, and the solubility of the phase. It also assumes that, at equilibrium, the value of \(p_i\) in each phase will be equal at a given \(x\). This implies there is a partition coefficient between the two phases equal to the ratio of the solubilities. The mass balance of eq. 3.11 can now be written as;

\begin{equation}
\frac{\partial C_\alpha}{\partial t} = \frac{D_\alpha}{\tau_\alpha^2} \frac{\partial^2 C_\alpha}{\partial x^2} - k_1 dA_{\alpha-\beta} \left( C_\alpha - \frac{1}{K_{eq}} C_\beta \right)
\end{equation}

(3.18)

All the concentrations are given in terms of pore volume in eq. 3.18. A similar approach can be taken to obtaining the \(\beta\) equation. However, it is recognized here that the \(\beta\) phase does not have the cylindrical pore structure. It is the matrix that the \(\alpha\) phase pores are contained in. The diffusive flux through this phase can still be described with an equation analogous to eq. 3.14 though.

\begin{equation}
\begin{aligned}
\eta^\beta_{\text{bulk}} &= \frac{A_{\beta}}{A} \eta^\beta_{\text{matrix}} = -\left(1 - \varepsilon \right) D_\beta \frac{\partial C_\beta}{\partial x} \\
\end{aligned}
\end{equation}

(3.19)

The nature of the \(\beta\) phase tortuosity is left ambiguous for now but it is likely relatable to the \(\alpha\) phase tortuosity. Using a similar approach as before the \(\beta\) “species” equation becomes;
\[
\frac{\partial C_\beta}{\partial t} = \frac{D_\beta}{\tau_\beta^2} \frac{\partial^2 C_\beta}{\partial x^2} + \frac{k_1 dA_{\alpha-\beta}}{(1-\varepsilon)A} \left( C_\alpha - \frac{1}{K_{eq}} C_\beta \right)
\]  
(3.20)

For a simple cylindrical pore the \(dA_{\alpha-\beta}\) term can be derived using geometric relations.

\[
dA_{\alpha-\beta} = 2\sqrt{\pi NA\varepsilon_{\alpha}} \, dx
\]  
(3.21)

Where \(N\) in eq. 3.21 is the number of pores. This simplifies eq. 3.17 and 3.20 as shown below.

\[
\frac{\partial C_\alpha}{\partial t} = \frac{D_\alpha}{\tau_\alpha^2} \frac{\partial^2 C_\alpha}{\partial x^2} - \frac{2k_1 \sqrt{\pi NA\varepsilon_{\alpha}}}{\varepsilon A} \left( C_\alpha - \frac{1}{K_{eq}} C_\beta \right)
\]  
(3.22)

\[
\frac{\partial C_\beta}{\partial t} = \frac{D_\beta}{\tau_\beta^2} \frac{\partial^2 C_\beta}{\partial x^2} + \frac{2k_1 \sqrt{\pi NA\varepsilon_{\alpha}}}{(1-\varepsilon)A} \left( C_\alpha - \frac{1}{K_{eq}} C_\beta \right)
\]  
(3.23)

The boundary conditions are then given by:

\[
C_\alpha(0, x) = C_\beta(0, x) = 0 \\
C_\alpha(t, 0) = C_\alpha^u, \quad C_\beta(t, 0) = C_\beta^u \\
C_\alpha(t, L) = C_\beta(t, L) = 0
\]  
(3.24)

For the case where the \(\beta\) phase has negligible diffusion the expressions can be rewritten in a form similar to that presented by Goodknight et al.

\[
\frac{\partial C_\alpha}{\partial t} = \frac{D_\alpha}{\tau_\alpha^2} \frac{\partial^2 C_\alpha}{\partial x^2} - \frac{(1-\varepsilon)}{\varepsilon} \frac{\partial C_\beta}{\partial t}
\]  
(3.25)

\[
\frac{\partial C_\beta}{\partial t} = \frac{2k_1 \sqrt{\pi NA\varepsilon_{\alpha}}}{(1-\varepsilon)A} \left( C_\alpha - \frac{1}{K_{eq}} C_\beta \right) = k_1^u \left( C_\alpha - \frac{1}{K_{eq}} C_\beta \right)
\]  
(3.26)
Where;

$$k_1^* = \frac{2k_1 \sqrt{\pi N A \epsilon \tau}}{(1 - \epsilon) A}$$  \hspace{1cm} (3.27)

This shows that, for sufficiently large $k_1$, the specific geometry of the interface between the two phases becomes irrelevant. However, at lower $k_1$ values it should be expected that hydration would play a role in the interphase transport term due to the presence of the volume fraction. The exact nature of this dependency would be related to the specific geometry.

If the analysis is taken a step further one can cast eq. 3.25 and 3.26 into a form exactly analogous to Goodknight et al. and take advantage of the analytical solution. We accomplish this by defining a new variable $C_\beta^*$ such that;

$$C_\beta^* = \frac{1}{K_{eq}} C_\beta$$  \hspace{1cm} (3.28)

Then eq. 3.25 and 3.26 can be rewritten;

$$\frac{\partial C_\alpha}{\partial t} = \frac{D_\alpha}{\tau_\alpha^2} \frac{\partial^2 C_\alpha}{\partial x^2} - \frac{K_{eq}(1 - \epsilon)}{\epsilon} \frac{\partial C_\beta^*}{\partial t}$$  \hspace{1cm} (3.29)

$$\frac{\partial C_\beta^*}{\partial t} = \frac{k_1^*}{K_{eq}} (C_\alpha - C_\beta^*)$$  \hspace{1cm} (3.30)

Eq. 3.29 and 3.30 are exactly analogous to the Goodknight et al. equations where $Y = k_1^*/K_{eq}$ and $V_2/V_1 = K_{eq}(1 - \epsilon)/\epsilon$. This implies that the time lag is given by;

$$t_{lag} = \frac{\tau_\alpha^2 L^2}{6D_\alpha} \left(1 + \frac{(1 - \epsilon)}{\epsilon} K_{eq}\right)$$  \hspace{1cm} (3.31)
In the event that this model accurately captures the behavior of the experiments we have run the
time lag will be equal to the homogeneous time lag to provide a relationship between the
calculated diffusion coefficient and the water phase diffusion coefficient.

\[
\frac{\tau_{\alpha}^2 L^2}{6D_{\alpha}} \left( 1 + \frac{(1-\varepsilon)}{\varepsilon} K_{eq} \right) = \frac{L^2}{6D_h} \tag{3.32}
\]

If the prior assumption that the equilibrium constant is equal to the solubility ratio is made then
the homogeneous diffusivity is equal to;

\[
D_h = \frac{D_{\alpha}}{\tau_{\alpha}^2 \left( 1 + \frac{(1-\varepsilon)}{\varepsilon} \frac{S_{\beta}}{S_{\alpha}} \right)} \tag{3.33}
\]

Through simple geometry arguments we can argue that the measured permeability is related to
the permeability of the \( \alpha \) as follows;

\[
P_h = \frac{\varepsilon}{\tau^2} P_{\alpha} \tag{3.34}
\]

Since the permeability is the product of the solubility and diffusivity the measured solubility can
be related to the two phase solubilities as simply;

\[
S_h = \varepsilon S_{\alpha} + (1-\varepsilon)S_{\beta} \tag{3.35}
\]

There are some interesting limiting scenarios when looking at eq. 3.33 and 3.35. If the solubility
of the \( \beta \) phase is zero the homogeneous analysis we have done before is recovered, i.e. \( D_h = D_{\alpha}/\tau_{\alpha}^2 \) and \( S_h = \varepsilon S_{\alpha} \). If the phase solubilities are equal then \( D_h = \varepsilon D_{\alpha}/\tau_{\alpha}^2 \) and \( S_h = S_{\alpha} \). This second
scenario is what is observed in section 3.4. The question is whether the solubility of the
hydrophobic and hydrophilic phases are equal. Solubilities of carbon dioxide in the dry membrane are not reported for all the conditions considered in this study but the value reported by Chiou and Paul [140] for dry Nafion at 35 °C and the value given by Pasternak et al. [144] for PTFE is very similar to the liquid water solubility implying \( D_h = \varepsilon D_a/\tau_a^2 \) and \( S_h = S_a \) which is consistent with the results of this study.

In terms of the general trends that the above model would predict there are several possibilities. If the diffusivity of one of the phases is negligible and the solubility of the other is either zero or \( k_1 \) is large, one would expect to see a transient response curve much like the one in figure 3.4. If \( k_1 \) is intermediate then a slow rise in what would normally be the steady state region of the exponential curve should be expected. If the diffusivities of both phases are comparable then there are two possible characteristic curves. In the first, if the interaction between the two phases is slow (\( k_1 \) is small) then one would expect to see a knee develop in the overall transient response curve since it would be the summation of two exponential curves with distinct time constants. However, if the interaction between the phases is fast (\( k_1 \) is small) then a typical exponential response curve like the one in figure 3.4 should be expected. The results of the bicontinuous model are important because they imply that, generally speaking, in a membrane material where both phases significantly contribute to the transport, application of the homogeneous model can produce misleading results. Only in the case that one of the phases is totally inactive in the transport is the homogeneous model truly applicable. This also has important implications in the application of effective medium theory. Generally speaking the Bruggeman correction is analogous to the \( \varepsilon/\tau^2 \) ratio so it should be applicable to the measured \( P_h \) assuming the partition coefficient is equal to the solubility ratio but generally it is not applicable.
to the measured D_h or S_h except for the diffusivity when the phase solubilities are equal. Further discussion of this topic is given in chapter 6.

3.5 Conclusions

The transport of carbon dioxide in Nafion 117 was measured as a function of temperature and hydration. Through the use of the time lag method and associated transient measurements, the permeability, a commonly reported parameter, was resolved into the diffusivity and solubility. The diffusivity and solubility behavior was fit using empirical formulas to account for changing hydration and temperature. It was found that over the range of conditions studied the transport through the membrane was primarily through the hydrophilic region with negligible contribution stemming from the hydrophobic region. This conclusion is supported by the permeability and diffusivity trending towards minute values at low relative humidity. The activation energy for the diffusivity also remained relatively constant for intermediate hydrations with the value being close to the activation energy of carbon dioxide diffusion in pure liquid water. However, inconsistencies were found in the interpretation of the calculated diffusivities and solubilities using the homogeneous model which inspired the introduction of a more general bicontinuous model. In the limit of negligible hydrophobic phase diffusivity, it was found that the bicontinuous model was able to provide a satisfactory interpretation of the results.
Chapter 4: Transient Ionic Conversion of an Anion Exchange Membrane Exposed to Carbon Dioxide

4.1 Overview

As discussed in chapter 1, a major issue with AEMs currently is the carbon dioxide interaction issue. Exposure of the AEM to carbon dioxide causes an ion exchange process. The counter-ions in the membrane convert from a hydroxide to a carbonate/bicarbonate composition [22,23,25,26]. These bulkier anions have lower mobility in the membrane than the hydroxide, leading to the lower conductivities. There are also thermodynamic losses associated with pH imbalances which can occur if the AEMFC is operated in the presence of carbon dioxide [18]. It has been shown in the literature that the hydroxide anions can be completely displaced even in the presence of air which contains roughly 385 ppm carbon dioxide. The focus of the present chapter is on the carbon dioxide interaction issue. This issue is directly linked to two commonly reported shortcomings of AEMs: ionic conductivity and stability. Carbon dioxide contamination lowers ionic conductivity which cannot be recovered by increasing the ionic membranes ionic content (IEC) without having a negative impact on the mechanical stability. However, it has been noted that the carbonate/bicarbonate form of the membrane is markedly more stable than the hydroxide form [28,29] giving incentive to investigate operating the fuel cell with a carbonate/bicarbonate form membrane. Whichever route is chosen, understanding the fundamental interaction between AEMs and carbon dioxide is important for fuel cell design. This research will seek to employ modeling techniques to understand the ion exchange process.
between the hydroxide anions and the carbonate/bicarbonate anions. In developing the model, comparisons will be made to titration data available in the literature as a means of validation [23,145]. Dimensional analysis on the governing equations is performed with calculated Thiele modules used to help explain the prevalent physics in the system. Finally, an extension to calculate membrane conductivity is made.

4.2 Theory

Transient measurements of anion concentrations in an AEM exposed to carbon dioxide have been made by Varcoe and associates [145] on their ETFE membranes as well as the Tokuyama Corporation on their A201 membranes [23]. These membranes started in a hydroxide form at t = 0 then were exposed to atmospheric levels of carbon dioxide under open circuit conditions with no electrodes. Warder’s titration method was used to measure the concentration of hydroxide, bicarbonate, and carbonate at various time steps during the ion conversion process that occurred. The theoretical development outlined here attempts to mimic the aforementioned conditions. Figure 4.1 shows a sketch of the hypothesized physical process. In this picture the membrane is imagined as a two phase material consisting of the polymer phase and a hydrated pore. The hydrated pores are lined with the membrane’s functional groups, benzyltrimethylammonium. A certain percentage of the various anionic species dissociate from these functional groups giving the membrane its ionic conductivity.
After the membrane is initially exposed to atmospheric air, which contains carbon dioxide, the carbon dioxide dissolves into the liquid water in the hydrated pore. After being absorbed, the carbon dioxide diffuses into the membrane due to the concentration gradient that exists. Upon coming into contact with the hydroxide species in the membrane, reactions may occur forming carbonate and bicarbonate. Each of the dissociated ionic species will also be subject to diffusion as concentration gradients form due to the reactions. As dissociated hydroxide is consumed via the reactions, more will dissociate and as carbonate and bicarbonate are produced they may re-associate with the fixed cation groups.

For the purpose of modeling the ion exchange process it is assumed that the reactions occurring within the bulk ionic solution mimic the formation of carbonate and bicarbonate in
pure liquid water. This assumption was previously used by Grew et al. for steady state calculations of the ionic conductivity of Tokuyama’s A201 membranes [22]. Due to the high pH environment, the following reactions are believed to take precedence [146]:

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

The kinetic rate constants and equilibrium constants for eq. 4.1-4.3 are available in the literature [146,147]. In addition to the reactions occurring in the bulk solution there are also dissociation reactions between the anions and the functional groups to be accounted for.

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

The kinetic rate constants for reactions 4.4-4.6 are unknown. They can be treated as fitting parameters or assumptions can be made. One possibility is the reactions are fast compared to the kinetics occurring in the bulk solution or compared to the diffusion in the membrane. The latter was discussed by Helfferich [148] and based on primarily on the works of Schulze [149] and Boyd [150] but also observed by many others for ordinary ion exchange processes [151-155]. This assumption will be shown to give the best results. It should be noted here that in order for the ions to react as indicated in eq. 4.4-4.6 they must move from the bulk solution in the center of the hydrophilic pores to the wall of the pores where bound water and the fixed cation groups exist. Some sort of absorption mechanism should be expected to take place here which, as of
now, is not explicitly written into the governing equations. Separating the effect of this absorption mechanism from the dissociation reactions would be difficult. Also, since this absorption type behavior would likely occur in series with eq. 4.4-4.6, if it turns out that those reactions must be fast when considered without the absorption mechanism to compare well with the experimental data then it would imply that the absorption itself would also be fast. Either way, it is pointed out here that this mechanism is not currently bookkept and should be acknowledged for future reference. Equilibrium constants for eq. 4.4-4.6 were fit in the study by Grew et al. and will be used here [22]. In that study the anions were assumed to dissociate with equal affinity. Additionally, it is assumed here that the equilibrium constants, originally derived for the A201 membrane, are applicable to the ETFE membrane.

In the absence of advection, the scenario in figure 4.1 can be described through the use of a diffusion reaction equation.

\[
\frac{\partial C_i}{\partial t} = \frac{\partial}{\partial x} \left( D_i^{\text{eff}} \frac{\partial C_i}{\partial x} \right) + \dot{R}_i
\]  

(4.7)

Boundary conditions are given by eq. 4.8 where the air-membrane interface has a flux boundary condition for carbon dioxide and a zero flux boundary condition for all other species. The flux boundary condition for carbon dioxide is set using an absorption coefficient \( k_{\text{abs}} \) and the equilibrium concentration according to Henry’s law (the first term in the brackets). At the centerline of the membrane the flux of all species is set to zero due to symmetry as both faces of the membrane are exposed to atmospheric carbon dioxide.
\[ J_{CO_2(aq)}(0,t) = k_{abs} \left( \frac{P^\text{gas}_{CO_2}}{M_{H_2O(l)}} \frac{\rho_{H_2O(l)}}{k_H - C_{CO_2(aq)}} \right) \]

\[ J_i(0,t) = 0; \quad i \neq CO_2(aq) \]

\[ J_i(L/2,t) = 0 \]  

(4.8)

If the absorption coefficient is sufficiently large the flux boundary condition for carbon dioxide at the air-membrane interface will mimic a Henry’s law concentration boundary condition. It will be shown later on that this gives the best comparisons to experimental data. The zero flux boundary condition at the air-membrane interface is applied to preserve electroneutrality in the case of the charged species while for water it is assumed that the membrane is in an equilibrated hydration state. Initial conditions are given by eq. 4.9.

\[ C_{OH^-}(x,0) = \alpha C_0 \]

\[ C_{(TMA)OH}(x,0) = (1 - \alpha) C_0 \]

\[ C_{H_2O(l)}(x,0) = \frac{\rho_{H_2O(l)}}{M_{H_2O(l)}} \]

\[ C_i(x,0) = 0 \]  

(4.9)

The fixed charge concentration, \( C_0 \), and the degree of dissociation, \( \alpha \), can be calculated with eq. 4.10 and 4.11 respectively.

\[ C_0 = \frac{\rho_{H_2O(l)}}{\lambda M_{H_2O(l)}} \]  

(4.10)

\[ \alpha = \frac{1}{2} \left[ -\frac{K_4}{C_0} + \left( \frac{K_4}{C_0} \right)^2 + 4 \frac{K_4}{C_0} \right] \]  

(4.11)

The initial conditions have the membrane in a completely hydroxide form where the dissociated hydroxide anion concentration is equal to the product of the fixed charge concentration and the degree of dissociation. The associated hydroxide anion concentration is then the remaining
proportion of the fixed charge concentration. The initial water concentration is taken as that of pure water. It is allowed to fluctuate due to eq. 4.2 and 4.3 but the changes are negligible as expected.

To correct the species diffusion coefficients for the tortuous membrane pathways, a Bruggeman model is adopted.

\[
D_i^{eff} = \varepsilon^q D_i,H_2O
\]

(4.12)

The wet porosity, \( \varepsilon \), is given by eq. 4.13.

\[
\varepsilon = \frac{\lambda}{\lambda + \frac{\rho_{H_2O(l)}}{M_{H_2O(l)}\rho_{mIEC}}}
\]

(4.13)

For the system under consideration it is assumed that the diffusivities of any associated anions or the fixed functional groups are equal to zero. Surface site hopping of the associated anions between the fixed cation sites may be occurring but it is assumed to have a negligible impact.

In order to fully solve the ion exchange process occurring in the membrane as hypothesized in figure 4.1 there are 10 species which must be solved for. These are: \( \text{CO}_2(aq) \), \( \text{H}_2\text{O}(l) \), \( \text{H}^+ \), \( \text{(TMA)}^+ \), \( \text{OH}^- \), \( \text{HCO}_3^- \), \( \text{CO}_3^{2-} \), \( \text{(TMA)}\text{OH} \), \( \text{(TMA)}\text{HCO}_3 \), and \( \text{(TMA)}_2\text{CO}_3 \). To solve this system the partial differential equation (PDE) in eq. 4.7 is specified for \( \text{CO}_2 \), \( \text{H}_2\text{O} \), \( \text{OH}^- \), \( \text{HCO}_3^- \), \( \text{CO}_3^{2-} \), \( \text{(TMA)}\text{OH} \), and \( \text{(TMA)}\text{HCO}_3 \). The remaining species are accounted for through the use of other restrictions. For \( \text{H}^+ \) it is assumed that eq. 4.3 equilibrates instantaneously so that the concentration at any given point is determined by the equilibrium constant.

\[
C_{H^+} = K_w \frac{C_{H_2O}}{C_{OH^-}}
\]

(4.14)

Using the simplification given by eq. 4.14 the kinetic source term in eq. 4.7 can be written for each species using eq. 4.1-4.6. Table 4.1 summarizes the kinetic source terms for each species.
Table 4.1: Kinetic source terms (eq. 4.7)

<table>
<thead>
<tr>
<th>Species</th>
<th>( \hat{R}_i )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( CO_{2(aq)} )</td>
<td>(-k_1^+C_{CO_{2(aq)}}C_{OH^-} + k_1^-C_{HCO_3} )</td>
</tr>
<tr>
<td>( H_2O(l) )</td>
<td>( k_2^+C_{HCO_3}C_{OH^-} - k_2^-C_{CO_3^{2-}}C_{H_2O(l)} )</td>
</tr>
<tr>
<td>( OH^- )</td>
<td>(-k_1^+C_{CO_{2(aq)}}C_{OH^-} + k_1^-C_{HCO_3} - k_2^+C_{HCO_3}C_{OH^-} + k_2^-C_{CO_3^{2-}}C_{H_2O(l)} + k_4^+C_{(TMA)OH} - k_4^-C_{(TMA)^+}C_{OH^-} )</td>
</tr>
</tbody>
</table>
| \( HCO_3^- \)   | \( k_1^+C_{CO_{2(aq)}}C_{OH^-} - k_1^-C_{HCO_3} - k_2^+C_{HCO_3}C_{OH^-} + k_2^-C_{CO_3^{2-}}C_{H_2O(l)} \)
|                | \( + k_5^+C_{(TMA)HCO_3} - k_5^-C_{(TMA)^+}C_{HCO_3} \)                      |
| \( CO_3^{2-} \) | \( k_2^+C_{HCO_3}C_{OH^-} - k_2^-C_{CO_3^{2-}}C_{H_2O(l)} \)
|                | \( + k_6^+C_{(TMA)_2CO_3} - k_6^-C_{(TMA)^2}C_{CO_3^{2-}} \)                  |
| \( (TMA)OH \)   | \(-k_4^+C_{(TMA)OH} + k_4^-C_{(TMA)^+}C_{OH^-} \)                           |
| \( (TMA)HCO_3 \)| \(-k_5^+C_{(TMA)HCO_3} + k_5^-C_{(TMA)^+}C_{HCO_3} \)                       |

Two species remain unaccounted for at this point; \((TMA)^+\) and \((TMA)_2CO_3\). The \((TMA)^+\) species can be accounted for using the electroneutrality condition while the \((TMA)_2CO_3\) concentration can be specified through a mole balance on the fixed charge species.

\[
C_{(TMA)^+} = C_{OH^-} + C_{HCO_3} + 2C_{CO_3^{2-}} - C_{H^+} \quad (4.15)
\]

\[
C_{(TMA)_2CO_3} = \frac{1}{2} \left\{ \frac{C_0 - C_{(TMA)^+} - C_{(TMA)OH} - C_{(TMA)HCO_3}}{C_{(TMA)HCO_3}} \right\} \quad (4.16)
\]

In order to solve the system of equations a numeric parabolic PDE solver was used. The conditions are assumed to be room temperature with the membrane in a fully hydrated state for both membrane types. The physical parameters used are contained in table 4.2.
Table 4.2: Physical parameters of the system

<table>
<thead>
<tr>
<th>Parameter</th>
<th>A201</th>
<th>Radiation Grafted ETFE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kinetics</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$k_1^+$ (cm$^3$ mol$^{-1}$ s$^{-1}$)$^{[146]}$</td>
<td></td>
<td>$2.0 \times 10^{18} \exp\left[-\frac{7698}{T}\right]$</td>
</tr>
<tr>
<td>$k_1^-$ (s$^{-1}$)$^{[146]}$</td>
<td></td>
<td>$3.0 \times 10^{19} \exp\left[-\frac{13712}{T}\right]$</td>
</tr>
<tr>
<td>$k_2^+$ (cm$^3$ mol$^{-1}$ s$^{-1}$)$^{[147]}$</td>
<td></td>
<td>$6.0 \times 10^{12}$</td>
</tr>
<tr>
<td>$k_2^-$ (cm$^3$ mol$^{-1}$ s$^{-1}$)</td>
<td></td>
<td>$k_2^+$</td>
</tr>
<tr>
<td>$k_4^+, k_5^+, k_6^+$ (s$^{-1}$)</td>
<td></td>
<td>$K_i$</td>
</tr>
<tr>
<td>$k_4^-, k_5^-, k_6^-$ (cm$^3$ mol$^{-1}$ s$^{-1}$, cm$^3$ mol$^{-1}$ s$^{-1}$, cm$^6$ mol$^{-2}$ s$^{-1}$)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$K_2^{[156]}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$K_4, K_5, K_6$ (mol cm$^{-3}$, mol cm$^{-3}$, mol$^2$ cm$^{-6}$)$^{[22]}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$K_w$ (mol cm$^{-3}$)$^{[156]}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>General Properties</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$D_{CO_2,H_2O}$ (cm$^2$ s$^{-1}$)$^{[141]}$</td>
<td></td>
<td>$2.17 \times 10^{-5} \exp\left[-2345\left(\frac{1}{T} - \frac{1}{303}\right)\right]$</td>
</tr>
<tr>
<td>$D_{OH^-,H_2O}$ (cm$^2$ s$^{-1}$)$^{[157]}$</td>
<td></td>
<td>$2.89 \times 10^{-5} \exp\left[-1750\left(\frac{1}{T} - \frac{1}{273.15}\right)\right]$</td>
</tr>
<tr>
<td>$D_{HCO_3,H_2O}$ (cm$^2$ s$^{-1}$)$^{[158]}$</td>
<td></td>
<td>$7.016 \times 10^{-5}\left(\frac{T}{204.0282}-1\right)^{2.3942}$</td>
</tr>
<tr>
<td>$D_{CO_3^{2-},H_2O}$ (cm$^2$ s$^{-1}$)$^{[158]}$</td>
<td></td>
<td>$5.447 \times 10^{-5}\left(\frac{T}{210.2646}-1\right)^{2.1929}$</td>
</tr>
<tr>
<td>$D_{H_2O,H_2O}$ (cm$^2$ s$^{-1}$)$^{[159]}$</td>
<td></td>
<td>$2.025 \times 10^{-5}$</td>
</tr>
<tr>
<td>$k_H$ (cm$^2$ N$^{-1}$)$^{[160]}$</td>
<td></td>
<td>$6.129 \times 10^{-5} \exp\left[2400\left(\frac{1}{T} - \frac{1}{298.15}\right)\right]$</td>
</tr>
<tr>
<td>$M_{H_2O(l)}$ (g mol$^{-1}$)</td>
<td></td>
<td>$18$</td>
</tr>
<tr>
<td>$P_{CO_2}^{gas}$ (N cm$^{-2}$)</td>
<td></td>
<td>$0.0038$</td>
</tr>
<tr>
<td>$T$ (K)</td>
<td></td>
<td>$293$</td>
</tr>
</tbody>
</table>
To further investigate the behavior of the kinetics and transport in the membrane, the governing equations can be put in a dimensionless form given by eq. 4.17 and 4.18.

\[
\frac{\partial \overline{C}_i}{\partial \overline{t}} = \frac{\partial^2 \overline{C}_i}{\partial \overline{x}^2} + \overline{R}_i
\]  
(4.17)

Where;

\[
\overline{C}_i = \frac{C_i}{C_i^{ref}}
\]

\[
\overline{x} = \frac{x}{L}
\]

\[
\overline{t} = \frac{D_i^{eff} t}{L^2}
\]  
(4.18)

The reference concentration appearing in eq. 4.18 is the maximum concentration of the species. The dimensionless reaction rate term in eq. 4.17 depends on the species being considered but the coefficients which multiple each of the terms in table 4.1 resemble the square of a Thiele modulus, \( \phi^2 \). The calculated Thiele modules are contained in section 4.3.2.

<table>
<thead>
<tr>
<th>( \rho_{H_2O(l)} ) (g cm(^{-3}))</th>
<th>Membrane Properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>IEC (mol g(^{-1})) [^{[23,145]}]^*</td>
</tr>
<tr>
<td>1.58</td>
<td>select such that Bi ( \geq 1 \times 10^4 )</td>
</tr>
<tr>
<td>1.53</td>
<td></td>
</tr>
<tr>
<td>0.0028</td>
<td>0.0080</td>
</tr>
<tr>
<td>0.0080</td>
<td></td>
</tr>
<tr>
<td>17</td>
<td>21</td>
</tr>
<tr>
<td>1.00</td>
<td>1.52</td>
</tr>
<tr>
<td>1.52</td>
<td>* IEC values taken to be the average of the total equivalent of experimental titration data</td>
</tr>
</tbody>
</table>
4.3 Results and Discussion

4.3.1 General Discussion

Figure 4.2 shows the comparison between the numeric simulation and the available experimental data from the literature for the radiation grafted ETFE membranes [145] and the Tokuyama A201 membranes [23]. Figure 4.2 plots the contributions of each anionic species to the overall IEC. As mentioned in section 4.2 the membranes are not in a fuel cell configuration. They are exposed to atmospheric levels of carbon dioxide (385 ppm) at room temperature for fully hydrated conditions. A brief sensitivity study to these conditions is performed in section 4.3.3. The solid lines in figure 4.2 represent the total anion concentration present in the membrane, both associated and dissociated. The dotted lines represent just the dissociated level of the respective anions. It is assumed that the nature of the experimental practices represent the combined contribution of the associated and dissociated anions. Siroma et al. describe that an excess amount of NaCl was used to induce desorption of the ionic species in the membrane prior to titration using Warder’s method [25]. This approach should replace all ionic species in the membrane with Cl\(^-\) making the measurement a reflection of both the dissociated and non-dissociated anions.

Before continuing to discuss the results it is necessary to justify the two assumptions made in section 4.2. These assumptions involve the magnitude of the kinetic rate constants for eq. 4.4-4.6 and the absorption coefficient in eq. 4.8. The validity of these assumptions can be tested by varying the kinetic rate constants and the absorption coefficient and comparing to the experimental data.
Figure 4.2: Comparison between titration data available in the literature (A201 data from [23] and ETFE data from [145]) to the developed equations in this work. a) A201, b) ETFE. The dotted vertical line running through both figures separates what is referred to as the hydroxide depletion region and the bicarbonate accumulation region referred to in the text.

If the absorption coefficient, $k_{abs}$, is increased the numeric predictions in figure 4.2 will shift to the left. Eventually, as the magnitude of the absorption coefficient becomes sufficiently large, the
flux boundary condition will mimic a concentration boundary condition described by Henry’s law.

\[ C_{CO_2}^{aq}(0,t) = P_{CO_2}^{gas} \frac{\rho_{H_2O(l)}}{M_{H_2O(l)}} k_H \]  

(4.19)

This transition occurs for a mass Biot number \( Bi = \frac{k_{abs} L}{2 D_{CO_2}} \) of approximately \( 1 \times 10^4 \). At this point, there is no longer any rate limiting contribution of the carbon dioxide absorption through the air-membrane interface so the curve will no longer shift to the left as the absorption coefficient is increased. If the absorption coefficient in eq. 4.8 is set to a value which correspond to \( Bi < 1 \times 10^4 \) then the result is a slower overall ion exchange process. It is clear from figure 4.2, which represents the limit in which eq. 4.19 is applicable, that a large absorption coefficient is appropriate since it provides the best comparison to the experimental data. It is worth mentioning here that this result is consistent with the behavior observed for Nafion in chapter 3.

A similar study of the kinetic rate constants for eq. 4.4-4.6 can be done as with the absorption coefficient. Here, the effect of varying the kinetic rate constants can be summarized with two extremes. These extremes are the case in which the kinetic rate constants are very fast compared to other processes occurring and thus do not affect the speed of the conversion process and the case when they are very slow or near zero in magnitude. Figure 4.2 shows the result for the former extreme. To understand why this extreme best matches the data, consider the hydroxide species in the limit that the kinetic rate constants for the dissociation reactions are approximately zero or extremely sluggish compared to the other reactions occurring. If the hydroxide ions must dissociate before reacting with carbon dioxide to form carbonate and bicarbonate via eq. 4.1-4.3 then after the initially dissociated hydroxide has been consumed there will still be a large amount of associated hydroxide in the membrane. If the kinetic rate constant
for the dissociation reaction is near zero then the hydroxide anions are effectively stuck and a large concentration of hydroxide would be expected to be observed in the experimental results at large time. Obviously this is not the observed behavior implying eq. 4.4-4.6 are not slow. It could be argued that an intermediate to the two extremes would be best however similar behavior to the absorption coefficient is observed. As the kinetic rate constants are decreased, the curves in figure 4.2 shift to the right leading to a poorer fit to experimental data. It is only when the kinetic rate constants are very large, such that they are not rate limiting, that the best fit is obtained. This implies, as stated in section 4.2, that the absorption of the ionic species to the pore wall from the bulk solution, which has not been bookkept here, would also be fast for the present cases studied. The dimensional analysis in section 4.3.2 was used to determine a suitable limit for the rate constants in eq. 4.4-4.6.

With the previous two assumptions justified the results can be interrogated. Examining figure 4.2 reveals that both membranes exhibit the same basic behavior where the hydroxide concentration drops off sharply and is initially replaced solely with carbonate. This is referred to as the hydroxide depletion region (see label in figure 4.2). Once the hydroxide is fully depleted, some bicarbonate begins to form at the expense of the carbonate until equilibrium is attained. This second characteristic region is referred to as the bicarbonate accumulation region (see label in figure 4.2). The calculated equilibrium state is given by table 4.3.

Table 4.3: Calculated anion contributions to the overall IEC at equilibrium (mmol g$^{-1}$)

<table>
<thead>
<tr>
<th>Species</th>
<th>A201</th>
<th>ETFE</th>
</tr>
</thead>
<tbody>
<tr>
<td>OH</td>
<td>0.000446</td>
<td>0.000471</td>
</tr>
<tr>
<td>HCO$_3$</td>
<td>0.365</td>
<td>0.385</td>
</tr>
<tr>
<td>CO$_3$</td>
<td>0.610</td>
<td>0.572</td>
</tr>
</tbody>
</table>
The transient behavior captured by the two aforementioned regions can be explained by examining the kinetics of the system during the conversion process. The kinetics for the production of carbonate and bicarbonate have equilibrium constants defined by eq. 4.20 and 4.21.

\[
K_1 = \frac{C_{HCO_3^-}}{C_{CO_2^{(aq)}} C_{OH^-}} \quad (4.20)
\]

\[
K_2 = \frac{C_{CO_3^{2-}} C_{H_2O}}{C_{HCO_3^-} C_{OH^-}} \quad (4.21)
\]

The values of \( K_1 \) and \( K_2 \) can be computed from table 4.2 and the result is \( K_1 >> K_2 >> 1 \). This indicates that the reactions given by eq. 4.1 and 4.2 will proceed in the forward direction when there is an abundance of hydroxide and carbon dioxide is introduced. Figure 4.3a gives the proposed dominate reaction scheme in the hydroxide depletion region.
In this region the dissociated hydroxide reacts with the carbon dioxide entering the system to produce bicarbonate which immediately reacts with more hydroxide to produce carbonate and water. The forward reactions for eq. 4.1 and 4.2 completely dominate in the hydroxide depletion region with eq. 4.1 being the rate limiting step as indicated in figure 4.3a. eq. 4.1 being rate limiting is documented in the literature [146,147] and supported by the dimensional analysis in
section 4.3.2. As the dissociated hydroxide is consumed by eq. 4.1 and 4.2 the dissociation reaction given by eq. 4.4 will begin to proceed in the forward direction to replenish the hydroxide in solution. Conversely, as the carbonate anions are produced in solution eq. 4.6 will begin to proceed in the reverse direction and some of the dissociated carbonate anions will become associated with the fixed charge cations.

When the hydroxide has been essentially fully depleted, and the carbonate reaches a maximum concentration, the transition into the bicarbonate accumulation region takes place. This is because, even though $K_2$ is large, there is no significant amount of hydroxide left in the system and bicarbonate has not yet developed. Figure 4.3b shows the dominating reaction scheme within the bicarbonate accumulation region. In this region eq. 4.2 proceeds primarily in the reverse direction which produces bicarbonate and hydroxide at the expense of carbonate. As hydroxide is produced by the reverse reaction of eq. 4.2 it is continually consumed by the forward reaction of eq. 4.1 as evidenced by the lack of any accumulation of hydroxide after it has been depleted in the system. Eq. 4.1 continues to proceed in the forward direction due to the extremely large equilibrium constant, $K_1$, given by eq. 4.18. The forward reaction for eq. 4.1 is still the rate limiting reaction as the transition is made to the bicarbonate accumulation region. As carbonate anions are consumed by the reverse reaction of eq. 4.2, eq. 4.6 proceeds primarily in the forward direction to maintain equilibrium between the associated and dissociated anions. Likewise, as bicarbonate anions are produced eq. 4.5 proceeds primarily in the reverse direction to maintain the dissociation equilibrium.

Figure 4.2 reveals a discrepancy between the conversion times of the two membranes where the A201 membrane takes about 30 minutes for the hydroxide to be depleted and the ETFE membrane takes about 60 minutes. The difference can be primarily explained by the
diffusive transport mechanism for carbon dioxide. Figure 4.4 shows the accumulation of carbon dioxide over time in the membranes.

Figure 4.4: Carbon dioxide accumulation in the membrane over time. The solid lines represent the spatial average while the dotted lines represent the minimum and maximum concentrations in the membrane at each time step (note that both membranes share the same maximum which is the Henry’s law concentration at the air/membrane interface and the minimum value represents \(x = L/2\).) The inset figure plots the normalized results.

As shown in figure 4.4, the accumulation of carbon dioxide in either membrane is a relatively slow process. This is caused by a combination of the continued consumption of carbon dioxide by eq. 4.1 and the inward diffusion. Since the ETFE membrane is much thicker than the A201, as indicated in table 4.2, the conversion time is longer due to the diffusion process. The inset figure in figure 4.4 shows the normalized concentration \(\bar{C}_{CO_2} = \frac{C_{CO_2}}{C_{CO_2}^{ref}}\) versus normalized time.
\( \tilde{\mathbf{t}} = t \frac{D_{\text{eff}}^{\text{CO}_2}}{L^2} \) for each membrane. If this was a pure diffusion process, the curves would be expected to collapse. The large variation in the normalized curves points to the importance of the kinetics in the accumulation of carbon dioxide in the membrane. Given the transient nature of the ion exchange process, the effect of the hydrophobic phase actively absorbing carbon dioxide as discussed in section 3.4.5 should be considered. If similar characteristics for the carbon dioxide transport in Nafion are shared with these AEMs then the hydrophobic phase absorbs but does not diffuse carbon dioxide. The immediate question is what effect does this have on the results? As it turns out, due to the immense amount of carbon dioxide flooding the membrane to facilitate the ion exchange reactions, accounting for this absorption into the backbone has no detectable effect on the results whatsoever. The flux of carbon dioxide into the membrane is so great compared to the amount that would be absorbed by the hydrophobic backbone (assuming a solubility of the backbone which is within a few orders of magnitude of Nafion) that adding the extra sink term does not register in the results.

It is important to point out that the model curves in figure 4.2 represent spatial averages for each of anion species. While the detailed calculation accounts for spatial variation of the species concentrations in the membrane, the experimental measurements being compared to represent bulk values meaning the numeric output has to be averaged for comparison. As it turns out, the spatial variations in the anionic concentrations at any given point in time according to the simulations is negligible compared to their average magnitudes. This outcome is supported by the dimensional analysis in section 4.3.2. The observed behavior is due to the average concentration of the anionic species being far greater than carbon dioxide, which initializes the whole process, as well as the anions having sufficiently large diffusivities. Henry’s law dictates the carbon dioxide concentration in the membrane pore will reach a concentration of \( 1.49 \times 10^{-8} \)
mol cm\(^{-3}\) at equilibrium while the anionic species have concentrations on the order of \(10^{-3}\) mol cm\(^{-3}\) depending on the membrane and species under consideration. In order to investigate the relative concentration gradients and transport behavior, figure 4.5 plots the difference of the spatial concentrations of each species and their minimums \((C_i - C_{\text{min}})\) at given time steps as well as the local fluxes at those time steps for the Tokuyama A201 membrane. Times \(t = 15, 30,\) and 120 minutes are chosen since they represent the hydroxide depletion region, the transition between the two characteristic regions, and the bicarbonate accumulation region respectively. The ETFE membrane simulations display similar behavior when comparable times are selected.
Figure 4.5: Spatial variations ($x = 0$ to $L/2$) of species concentration and flux for $\text{CO}_2$, $\text{OH}^-$, $\text{HCO}_3^-$, and $\text{CO}_3^{2-}$ at 15, 30, and 120 minutes of carbon dioxide exposure in the Tokuyama A201 membrane. Inset figures are blow ups of the trends shown for 30 and 120 minutes. Concentration
values are the difference between the local concentration and the minimum concentration at that time step. Similar trends exist for the ETFE membrane for similar conversion times.

At the 15 minute mark shown in figure 4.5 there is a sharp variation in carbon dioxide concentration from the air-membrane interface ($x = 0$) to the membrane centerline ($x = L/2$). This is due to the abundance of hydroxide available for reaction which prevents carbon dioxide from accumulating in the interior of the membrane. Since there is a higher concentration of carbon dioxide towards the air-membrane interface there is a lower concentration of hydroxide there and a higher concentration of carbonate. Due to these concentration gradients there is a flux induced for hydroxide towards the air-membrane interface while a flux of carbonate develops in the opposite direction towards the centerline of the membrane.

In the transition between the hydroxide depletion region and the bicarbonate accumulation region at 30 minutes a similar behavior endures for hydroxide with a now accumulating level of bicarbonate. Since bicarbonate is produced at the expense of carbonate, the concentration profile for carbonate has inverted causing a slight flux of carbonate towards the air-membrane interface. At this time carbon dioxide has penetrated further into the membrane as one might expect since diffusion continues to take place and the reaction consuming it has slowed down. The overall fluxes and concentration variations are significantly lower at this point due to diffusion constantly working to equalize spatial concentrations. As bicarbonate accumulates near the air-membrane interface due to the reactions, a positive flux develops driving diffusion towards the centerline of the membrane.

Well into the bicarbonate accumulation region at 120 minutes the hydroxide has been almost completely consumed by the kinetics and bicarbonate and carbonate are the only anions
present within the membrane in significant quantities. At this time carbon dioxide is still diffusing into the membrane but is now accumulating at the centerline. The overall variation in concentration and the fluxes of the anionic species are negligible compared to earlier times due to constant diffusion and the slowing down of the kinetics.

An extension can be made to transient ionic conductivity using the model results. Eq. 4.22 gives the ionic conductivity of the membrane as detailed by Grew et al. [22].

$$\sigma = \frac{F}{RT} \sum \frac{z_i^2 D_i^{eff} (1 + \lambda)}{\lambda(1 + \delta_i)} C_i \quad (4.22)$$

Where;

$$\delta_i = \frac{1}{\lambda} \left( \frac{\rho_{H_2O(i)}}{M_{H_2O(i)} \rho_{IEC}} \right)^{2/3} \left( \frac{M_{i,M}^*}{M_{i,H_2O}^*} \right)^{1/2} \quad (4.23)$$

Using eq. 4.22 and 4.23 along with the transient anionic concentrations the conductivity of the membrane can be plotted as a function of time as shown in figure 4.6. Plotted with the transient conductivity is the transient carbon species absorption which mirrors the conductivity behavior.
Figure 4.6: Transient ionic conductivity (left axis) and transient volumetric absorption of carbon species (right axis) for the Tokuyama A201 membrane (a) and ETFE membrane (b). The red dotted lines represent the range of experimental data taken from the literature for equilibrium conditions (data from [22] for the A201, data from [21] for the ETFE).

The trend in the transient conductivity can be understood by considering the relative contributions of each anion to the overall ionic conductivity. This would be the dissociated hydroxide, bicarbonate, and carbonate. The conductivity of each of these species can be ranked according to the critical parameters in eq. 4.22. Doing this sort of exercise, it is clear that hydroxide has the highest conductivity due to its high diffusivity ($D_{i,H_2O}$) and its low molecular...
mass \( (M_i) \). When comparing carbonate and bicarbonate the diffusivities and molecular masses are similar but carbonate has a valance of -2 giving it the higher conductivity according to the assumptions made here. Using these arguments the transient behavior in figure 4.6 can be explained where the initial sharp drop off in conductivity right after \( t = 0 \) is due to the rapid loss of hydroxide in the presence of carbon dioxide. The secondary, slow decay in ionic conductivity occurs at the transition from the hydroxide depletion region to the bicarbonate accumulation region. This secondary decay develops as some of the carbonate, which eq. 4.22 predicts has a higher ionic conductivity than bicarbonate, is replaced with bicarbonate. Unfortunately, as far as the author is aware, there is no transient ionic conductivity data available for comparison in the literature. Steady state values for various forms have been done. The comparison was already made by Grew et al. for the Tokuyama A201 membrane as shown in figure 4.6a [22]. To the author’s knowledge, the radiation grafted ETFE has no air equilibrated data available but measurements in the hydroxide form have been done as indicated in figure 4.6b [21]. The ETFE data has a rather wide spread with the prediction falling in the upper tier but this may be due to the difficulty in keeping the membrane in a purely hydroxide form. If even small amounts of carbon dioxide were to contaminant the membrane the exchange process could cause the conductivity to plummet in which case one would expect the prediction to be within the upper tier of the measurements. The agreement of the available steady state values gives credibility to the model but transient data would be preferable in the future should it become available.

4.3.2 Dimensional Analysis

This section contains dimensional calculations based on eq. 4.17 and 4.18 along with discussion of implications to the system being analyzed. Table 4.4 contains values for the Thiele
modules which are born from the kinetic source terms appearing in table 4.1. Each module is a resulting dimensionless grouping that appeared in the kinetic source term for a given species when the dimensionless definitions of eq. 4.18 were invoked. For example, $\phi_1$ and $\phi_2$ represent dimensionless groupings for the two components of the kinetic source term for carbon dioxide in table 4.1. Subsequent numberings of the modules in table 4.2 are assigned based on the order of individual components of the kinetic source terms for each of the species in table 4.1. The dimensionless kinetic source term, $\tilde{R}_i$, of eq. 4.17 is then a combination of the Thiele modules appearing in table 4.4 for the species $i$. As mentioned in section 4.2, reference values for concentration are taken as the maximum concentration observed during the transient ion exchange process.

Table 4.4: Thiele Modules based on eq. 17

<table>
<thead>
<tr>
<th>Species Equation</th>
<th>Thiele Modulus Form</th>
<th>A201</th>
<th>ETFE</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO$_2$</td>
<td>$\phi_1 = \sqrt{k_1^+ \left( \frac{L^2 C_{\text{ref}}^{\text{OH}^-}}{D_{\text{CO}_2^{(aq)}}} \right)}$</td>
<td>144</td>
<td>294</td>
</tr>
<tr>
<td></td>
<td>$\phi_2 = \sqrt{k_1^- \left( \frac{L^2 C_{\text{ref}}^{\text{HCO}<em>3^-}}{D</em>{\text{CO}<em>2^{(aq)}} C</em>{\text{CO}_2^{(aq)}}^{\text{ref}}} \right)}$</td>
<td>2.42</td>
<td>5.13</td>
</tr>
<tr>
<td>OH$^-$</td>
<td>$\phi_3 = \sqrt{k_1^+ \left( \frac{L^2 C_{\text{ref}}^{\text{CO}<em>2^{(aq)}}}{D</em>{\text{OH}^-}} \right)}$</td>
<td>0.331</td>
<td>0.722</td>
</tr>
</tbody>
</table>
\[ \phi_4 = \sqrt{k_1^{-} \left( \frac{L^2 C_{\text{ref}}^{\text{HCO}_3}}{D_{\text{OH}^-} C_{\text{OH}^-}^{\text{ref}}} \right)} \]

\[ \phi_5 = \sqrt{k_2^+ \left( \frac{L^2 C_{\text{ref}}^{\text{HCO}_3}}{D_{\text{OH}^-} C_{\text{OH}^-}^{\text{ref}}} \right)} \]

\[ \phi_6 = \sqrt{k_2^+ \left( \frac{L^2 C_{\text{ref}}^{\text{CO}_2^{\text{aq}}}}{D_{\text{OH}^-} C_{\text{OH}^-}^{\text{ref}}} \right)} \]

\[ \phi_7 = \sqrt{k_4^+ \left( \frac{L^2 C_{(\text{TMA})\text{OH}}^{\text{ref}}}{D_{\text{OH}^-} C_{\text{OH}^-}^{\text{ref}}} \right)} \]

\[ \phi_8 = \sqrt{k_4^+ \left( \frac{L^2 C_{(\text{TMA})^+}^{\text{ref}}}{D_{\text{OH}^-}} \right)} \]

\[ \phi_9 = \sqrt{k_1^{-} \left( \frac{L^2}{D_{\text{HCO}_3}} \right)} \]

\[ \phi_{10} = \sqrt{k_1^{-} \left( \frac{L^2}{D_{\text{HCO}_3}} \right)} \]

\[ \phi_{11} = \sqrt{k_2^+ \left( \frac{L^2 C_{\text{OH}^-}^{\text{ref}}}{D_{\text{HCO}_3}} \right)} \]

\[ \phi_{12} = \sqrt{k_2^+ \left( \frac{L^2 C_{\text{CO}_2^{\text{aq}}}^{\text{ref}}}{D_{\text{HCO}_3} C_{\text{HCO}_3}^{\text{ref}}} \right)} \]

<table>
<thead>
<tr>
<th>( \phi_4 )</th>
<th>( \phi_5 )</th>
<th>( \phi_6 )</th>
<th>( \phi_7 )</th>
<th>( \phi_8 )</th>
<th>( \phi_9 )</th>
<th>( \phi_{10} )</th>
<th>( \phi_{11} )</th>
<th>( \phi_{12} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00560</td>
<td>0.0126</td>
<td>3.71x10^4</td>
<td>7.87x10^4</td>
<td>712</td>
<td>1.55x10^3</td>
<td>&gt;33.1</td>
<td>&gt;72.2</td>
<td>&gt;33.1</td>
</tr>
<tr>
<td>1.48</td>
<td>3.12</td>
<td>0.0249</td>
<td>0.0544</td>
<td>1.66x10^5</td>
<td>3.40x10^5</td>
<td>3.18x10^3</td>
<td>6.70x10^3</td>
<td></td>
</tr>
</tbody>
</table>

**HCO_3^-**
It is important to explain that the \( \phi_{15} \) and \( \phi_{16} \) in table 4.4 were not derived from eq. 4.20 directly. Had eq. 4.20 been used the resulting modules would have contained the rate constant for the limiting reaction (eq. 4.1). In reality, the rate of formation and consumption of carbonate is controlled by eq. 4.1. This is supported by the fact that the Thiele modules involving the kinetic rate constants of eq. 4.1 are consistently the smallest in magnitude in table 4.4. Therefore, the diffusive rate of transport should not be compared to the kinetic rate of eq. 4.2 when trying to

<table>
<thead>
<tr>
<th>( \phi_3 )</th>
<th>( \phi_4 )</th>
<th>( \phi_5 )</th>
<th>( \phi_6 )</th>
<th>( \phi_7 )</th>
<th>( \phi_8 )</th>
<th>( \phi_{13} )</th>
<th>( \phi_{14} )</th>
<th>( \phi_{15} )</th>
<th>( \phi_{16} )</th>
<th>( \phi_{17} )</th>
<th>( \phi_{18} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \phi_{13} = \sqrt{k_3^+ \left( \frac{L^2 C_{(TMA)HCO_3}^{ref}}{D_{HCO_5} C_{HCO_5}^{ref}} \right)} )</td>
<td>( \phi_{14} = \sqrt{k_4^- \left( \frac{L^2 C_{(TMA)^+}^{ref}}{D_{HCO_5}} \right)} )</td>
<td>( \phi_5^+ = \sqrt{k_5^+ \left( \frac{L^2 C_{CO_2}^{ref} C_{OH}^{ref}}{D_{CO_3^-} C_{CO_3^2-}^{ref}} \right)} )</td>
<td>( \phi_6^- = \sqrt{k_6^- \left( \frac{L^2 C_{HCO_5}^{ref}}{D_{CO_3^-} C_{CO_3^2-}^{ref}} \right)} )</td>
<td>( \phi_7^+ = \sqrt{k_7^+ \left( \frac{L^2 C_{(TMA)HCO_3}^{ref}}{D_{CO_3^-} C_{CO_3^2-}^{ref}} \right)} )</td>
<td>( \phi_8^- = \sqrt{k_8^- \left( \frac{L^2 C_{(TMA)^+}^{ref}}{D_{CO_3^-}} \right)} )</td>
<td>&gt;148</td>
<td>&gt;312</td>
<td>&gt;148</td>
<td>&gt;312</td>
<td>1.18</td>
<td>2.57</td>
</tr>
</tbody>
</table>
ascertain the relative speed of transport to kinetics. As mentioned in section 4.3.1, the kinetic rate constants for eq. 4.4–4.6 are set based on the present analysis. Their values are set such that the resulting Thiele modules are at least two orders of magnitude greater than the Thiele modules involving the kinetic rate constants for eq. 4.1 for each species as indicated in table 4.4 (i.e. $100\phi_3 < \phi_{7,8}, 100\phi_9 < \phi_{13,14}$, and $100\phi_{15} < \phi_{17,18}$). This ensures the dissociation reactions are not rate limiting in the ion conversion process.

In surveying the modules in table 4.4 it is reasoned that the important modules are $\phi_1, \phi_3, \phi_9,$ and $\phi_{15}$ for this study. This is due to the initial state of the membrane being a purely hydroxide form causing the forward reactions for eq. 4.1 and 4.2 to dominate with eq. 4.1 being rate limiting. Since $\phi_1$ is much greater than the other three it indicates a much stronger effect of diffusion for carbon dioxide versus the charged species. This is reflected in the simulation results since carbon dioxide maintains a large concentration gradient relative to its maximum concentration level for an extended period of time during the conversion process. Carbon dioxide diffusion is also largely responsible for the discrepancy between conversion times for the A201 and ETFE membranes due to thickness differences (see figure 4.2). Conversely, the anionic species maintained a relatively uniform concentration profile through the membrane thickness throughout the conversion process.

4.3.3 Sensitivity Study

The final section of this chapter presents a sensitivity study on the experimentally controlled parameters from the literature data [23,145]. Figure 4.7 shows the variation in the numerical results for both membranes when the hydration of the membrane (a), the temperature
(b), and the concentration of atmospheric carbon dioxide of 385 ppm (c) are varied +/-20% from the values reported in table 4.2.
Figure 4.7: ±20% variation in select conditions. a) Membrane hydration, $\lambda$ (A201: 13.6 to 20.4, ETFE: 16.8 to 25.2). b) Operating temperature, $T$ (16 to 24 °C). c) Atmospheric carbon dioxide concentration (308 to 462 ppm). The solid lines and points represent the model output from the previous sections and the experimental data taken from the literature respectively. Dotted lines represent the variation caused by adjusting the individual parameters.

The dotted lines in figure 4.7 represent the variation in the results due to adjusting the previously listed parameters. Decreasing hydration, temperature, or atmospheric carbon dioxide levels tends to slow the ionic conversion process down. The right most dotted lines represent the degree to which the process slows down as the parameters are decreased by 20% while the leftmost dotted lines represent how fast the process speeds up when the same parameters are increased by 20%. Table 4.5 gives the equilibrium results for each case.

Table 4.5: Calculated anion contributions to the overall IEC at equilibrium for ±20% of selected parameters (mmol g⁻¹)

<table>
<thead>
<tr>
<th>Species</th>
<th>A201</th>
<th>ETFE</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Membrane Hydration (-20%, +20%)</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>OH</td>
<td>(0.000405, 0.000482)</td>
<td>(0.000429, 0.000507)</td>
</tr>
<tr>
<td>HCO₃</td>
<td>(0.331, 0.394)</td>
<td>(0.350, 0.415)</td>
</tr>
<tr>
<td>CO₃</td>
<td>(0.626, 0.595)</td>
<td>(0.590, 0.558)</td>
</tr>
<tr>
<td><strong>Temperature (-20%, +20%)</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>OH</td>
<td>(0.000319, 0.000621)</td>
<td>(0.000337, 0.000656)</td>
</tr>
<tr>
<td>HCO₃</td>
<td>(0.388, 0.342)</td>
<td>(0.409, 0.361)</td>
</tr>
<tr>
<td>CO₃</td>
<td>(0.598, 0.621)</td>
<td>(0.560, 0.584)</td>
</tr>
<tr>
<td><strong>Atmospheric Carbon Dioxide Concentration (-20%, +20%)</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>OH</td>
<td>(0.000506, 0.000402)</td>
<td>(0.000535, 0.000424)</td>
</tr>
<tr>
<td>HCO₃</td>
<td>(0.331, 0.394)</td>
<td>(0.349, 0.416)</td>
</tr>
<tr>
<td>CO₃</td>
<td>(0.626, 0.595)</td>
<td>(0.590, 0.557)</td>
</tr>
</tbody>
</table>
As indicated in table 4.5, increasing the hydration tends to increase the concentration of hydroxide and bicarbonate slightly at the expense of carbonate. This is due to eq. 4.21 where, as increased hydration dilutes the anionic species, the equilibrium constant favors higher concentrations of hydroxide and bicarbonate over carbonate. The opposite is then true as hydration is reduced. Temperature increases cause increases in hydroxide and carbonate concentrations and decreases in bicarbonate concentrations due to the Arrhenius behavior of the equilibrium constants in eq. 4.20 and 4.21. Finally, as atmospheric levels of carbon dioxide increase the membrane tends to favor a bicarbonate state over a carbonate state. This is again due to the equilibrium constants given by eq. 4.20 and 4.21. It is interesting to note that the Tokuyama experimental data from [23] displays higher concentrations of bicarbonate vs. carbonate. It is possible that part of the reason for the discrepancy in figure 4.2 between the experimental A201 data and the simulated predictions has to do with the elevated carbon dioxide levels during the experiment although the discrepancy between the value used in this study and the experimental conditions would have to be much greater than 20%. The number used in this study (385 ppm) is a standard for outdoor conditions but it can vary due to location and time of year. A confined laboratory space may also have elevated carbon dioxide levels compared to the outdoors. Better comparisons can be made to the Tokuyama A201 data by increasing the carbon dioxide levels in the simulation but an excess of 1000 ppm is required to capture the trends of the data. Figure 4.8 shows the result when 1000 ppm levels of carbon dioxide are exposed to the membrane.
While these levels are not highly unlikely in closed spaces, there is no direct information available on the laboratory conditions in which the experiment was performed so a standard value of 385 ppm was used in this study. It is also worth mentioning that there are inherent errors in the experimental methods reported in the literature and unfortunately no confidence values were reported for the Tokuyama data. The fact that the trends were successfully captured by the numeric of the present study points to its validity.

### 4.4 Conclusions:

The work presented in this chapter models the transient ion exchange of an anion exchange membrane initially in a hydroxide form exposed to air. The developed theory makes use of well-established kinetics involving the formation of bicarbonate and carbonate in water when water is exposed to carbon dioxide where it is assumed that the fully hydrated membrane will mimic this behavior. The predicted numeric trends were compared to two membranes with
transient data available in the literature; the Tokuyama corporations A201 membrane and the radiation grafted ETFE membrane developed by Varcoe and associates. It was found that the general trends matched and several conclusions could be drawn from the model.

1. It was argued that the absorption of the carbon dioxide through the membrane/air interface is fast compared to the internal transport and kinetics. This implies Henry’s law is appropriate in this case to specify the concentration boundary condition for carbon dioxide.

2. The kinetic rate constants for the ion dissociation reactions are fast such that they do not influence the rate of conversion in the system. This conclusion is also drawn based on the fact that it gives the best comparison to experimental measurements.

3. The primary reason for different conversion rates between the A201 membrane and the ETFE membrane is due to the diffusion process for the carbon dioxide. Also, the concentration variations of the different anions within the membrane are on the same scale or greater than the carbon dioxide but are negligible compared to the average magnitude of those species. Dimensional analysis was performed in an effort to illuminate the reasons for the observed behavior and it was found that the calculated Thiele modulus for the carbon dioxide was much larger than for the anionic species supporting the observations.

It is stressed once more that the above results are, strictly speaking, only applicable to the case of a membrane in open air and not representative of an operating fuel cell since current and electrode reactions were not considered.
Chapter 5*: Membrane Transport in a High Pressure Oxygen Generating Electrolyzer

*Adapted from [162]

5.1 Overview

High-pressure oxygen-generating PEM water electrolyzers have garnered interest as a method of producing breathable oxygen for use in applications where oxygen is scarce or unavailable. An attractive feature of these particular electrolyzers is the lack of external compressors taking up extra space, adding weight, decreasing reliability, and drawing excess power due to various inefficiencies. It has been demonstrated that the electrolyzer itself can produce product gases at high pressure with the added cost being an increase in the cell potential. Of course, the electrolyzer must be designed to accommodate the high-pressure operation. This necessity of design has been demonstrated in industry. One example is the Hydrogen/oxygen generator (HOGEN) developed by Proton Energy Systems which is designed to deliver hydrogen at pressures of 1.4 MPa [163]. Another example is Mitsubishi’s High-pressure hydrogen energy generator (HHEG) which delivers hydrogen at upwards of 35 MPa for future use in the automotive industry [164]. Yet another example is Hamilton Sundstrand’s High-pressure oxygen generating assembly (HPOGA), developed for space applications, which generates oxygen at pressures over 20 MPa [165].

In high-pressure PEM electrolyzers it is convenient in some applications to supply liquid water to the electrode opposite to where the evolution of the desired product gas occurs. This ensures that the gas of interest is easily separated for storage [165-167]. The literature is
somewhat sparse regarding high-pressure electrolyzers with the majority of these works focusing on high-pressure hydrogen generation [168-171]. However, in high-pressure hydrogen generating electrolyzers liquid water is typically supplied to the anode, which is the same electrode where the electrolysis reaction occurs, generating oxygen, protons, and electrons. The protons transport across the membrane and recombine with the electrons to form hydrogen gas at the cathode. Alternatively, a high-pressure oxygen-generating PEM electrolyzer differs in that water may be supplied to the cathode at ambient pressure where it will first have to traverse the membrane before reacting at the anode to generate oxygen. Figure 5.1 shows a schematic of Hamilton Sundstrand’s HPOGA which is a cathode-fed high-pressure oxygen-generating PEM electrolyzer.
Figure 5.1 [162]: Schematic representation of a Hamilton Sundstrand’s high-pressure oxygen-generating PEM electrolyzer. Liquid water is supplied to the cathode of the cell at ambient pressure where it crosses the membrane to react at the anode producing protons, electrons and oxygen gas. The protons then form the charge carrier molecules, hydronium, and travel back through the membrane. They then combine with the electrons, which traveled through the external circuit, to form hydrogen.

In this type of system water transport within the membrane becomes significant and is a limiting factor in the performance of the cell. The importance of the water transport is actually twofold. The water must physically cross the membrane to react leading to mass-limiting behavior at high current densities. Also, it has been shown that the conductivity of PEMs is directly related to the hydration state [107,172]. So as the membrane dries out with increasing operating current density the conductivity will decrease leading to higher ohmic performance losses in the membrane. Therefore, it is important to consider the coupled water and charge carrier transport within the membrane to determine the performance characteristics and capture dry-out behavior.

The description of species transport within the membrane of a high-pressure hydrogen or oxygen water electrolyzer in the literature is sparse. The existing literature makes use of simulation techniques used to describe water transport within PEM fuel cells. Medina and Santarelli [170] studied water transport within a high-pressure hydrogen-generating electrolyzer where hydrogen pressures reach upwards of roughly 7 MPa. Their work focused on coupling modeling and experimental work to determine electro-osmotic drag coefficients within the electrolyzer environment. Marangio et al. [169] analyzed the performance of a high-pressure hydrogen-producing electrolyzer produced by Giner Inc. They calculated the theoretical
polarization curves for the cell and compared them to experimental data for varying pressure and temperature. Water transport was calculated as a means of determining the membrane hydration state which led to membrane polarization calculations using conductivity data. Gorgun [168] predicted the performance of a hydrogen producing electrolyzer including the filling of a hydrogen storage device. Water transport was also bookkept in this scenario as a means of determining membrane overpotential. Staser and Weidner [173] investigated the effect of water transport properties on the production of hydrogen and sulfuric acid in a PEM electrolyzer.

All of the work described above uses the same method of describing water transport within the PEM. This simulation method is described by Weber and Newman [35] to be a combined computational approach involving the superposition of hydraulic and diffusive water transport components via linear combination. This is a typical method of calculating water transport in a fuel cell which usually involves the addition of Fickian diffusion, Darcy permeation and electro-osmotic drag components. Indeed, all of the pre-described analyses make use of these three transport mechanisms with the exception of Gorgun [168] which accounts for only diffusion and electro-osmotic drag. Commonly, once water transport has been determined, a bridge is then made to membrane overpotential via an empirical correlation between conductivity and membrane hydration as was done in all the works noted above with the exception of Medina and Santarelli [171] who exclusively simulated water transport. An alternative method for this sort of computational analysis is given by the DFM [81,82,174] which couples water and charge-carrier transport within the membrane. The DFM also allows for the direct calculation of the membrane overpotential without the need for conductivity measurements. The DFM has been extensively studied by Thampan et al. [82] for Nafion membranes and by Grew and Chiu [40] for various alkaline anion exchange membranes. As mentioned all but one of the works noted
above involves the use of permeation flow to account for the pressure drop across the cell since, in high-pressure electrolyzer operation, only one side of the MEA is typically pressurized. However, it has been proposed in other works that a meniscus exists at the MEA gas interface [175]. This implies that some or all of the gas pressure is taken up by the meniscus depending on the morphology of the pore structure within the membrane.

The goal of this research is to describe species transport across the membrane of a high-pressure oxygen-generating PEM electrolyzer with a cathode water feed configuration and to characterize the dehydration of the cell. To accomplish this task a DFM is developed which builds on the generalized Stefan-Maxwell equations for multicomponent diffusion. In principle, the DFM simply treats the membrane and the solute species within the membrane as a mixture with the membrane being one of the species in the governing equations. This membrane species can be visualized as extremely large “dust” particles in comparison to the other molecules with these “dust” particles remaining immobile in the fixed reference frame. The remaining two species of interest in the PEM are water and the charge carrier. Given the high-differential gas pressure across the cell, the concept of a meniscus existing at the liquid-vapor boundary, as well as the possibility of Darcy permeation, are considered. The developed DFM is capable of describing either.

The developed DFM for species transport in a high-pressure oxygen-generating PEM electrolyzer with a cathode water feed is calibrated against polarization data, in the linear loss region extending to the onset of dry-out, from Hamilton Sundstrand’s HPOGA [165]. This HPOGA makes use of Nafion 1110 as the proton-exchange membrane and operates at a temperature of 38 °C. Anode pressures are upwards of just over 20 MPa (3000 psi) with the cathode at ambient pressure. To support the MEA under these high-differential pressure
conditions porous metal plates are placed on either side. In order to calibrate the membrane model against the polarization data a simplified governing equation for the overall cell voltage, including the external cell resistance, is developed. The membrane diffusion coefficient and the external resistance of the cell are adjusted as a function of differential oxygen pressure to match the experimental data. The resulting governing equations are then cast in a dimensionless form in order to investigate the dehydration of the cell and how it is affected by operational current density, differential oxygen pressure, as well as electro-osmotic drag.

5.2 Theoretical Development

5.2.1 Membrane Species Transport:

The development begins with the major assumptions that will be made:

1. Transport through the membrane is 1-D.
2. The membrane diffusion coefficients for water and hydronium, the two species of interest, ($D^e_{1M}$ and $D^e_{2M}$) are equal. The water-hydronium and hydronium-water diffusion coefficients are equal ($D^{e_{12}}$ and $D^{e_{21}}$).
3. Hydronium is the charge carrier within the membrane structure.
4. Species flux is driven solely by gradients created by the reactions occurring at the anode.
5. The mixture activity coefficients are constant or have negligible variation.
6. Only the transport of hydronium and water is considered.
7. The cell is assumed to operate at isothermal conditions.
Beginning with assumption 1, the membrane is exposed to liquid water which is evenly dispersed over the active area of a thin membrane material. This implies 1-D transport is a reasonable assumption. Assuming equal membrane diffusivities for water and hydronium stems from the similarities of the structures of these molecules. By Onsager reciprocal relations water-hydronium and hydronium-water diffusion coefficients are equal ($D_{12}^c = D_{21}^c$). Assumption 3 is based on the belief that a strong contributor to proton transport through liquid water is the Grottouss mechanism which involves the protonation of water molecules [40,82]. Species flux being driven solely by gradients caused by the reactions at the anode is assumed because while there is, in fact, some water vapor accumulation occurring in the oxygen chamber due to interfacial mass transport, this additional water flux is negligible compared to the flux driven by the reactions. Unity activity coefficients as mentioned in assumption 5 is a common assumption also made by Fimrite et al. [176] In fact, the activity coefficients do not have to be equal to one but just have negligible variations. In considering the species transport in the membrane only hydronium and water were considered. In reality, there will also be oxygen and hydrogen present due to cross over effects. However, based on performance evaluations from [165] these fluxes were assumed to be small up front and cross over effects were neglected. Finally, the isothermal cell condition was adopted because the temperature of the cell was controlled by heating the inlet liquid water at the cathode. This water makes direct contact with the MEA. The liquid feed stream varies from inlet to outlet by less than 1 °C over the range of operation. The cell is also well insulated to ensure uniform heating. Taking assumption 7 neglects any thermal osmotic drag.

To model the species transport within the membrane of the HPOGA a DFM development was used along the same lines as developed by Thampan et al. [82] and based on the work of
Mason and Malinauskas [81]. The major difference between the work by Thampan et al. and this study is the application of the DFM to an operational cell which increases the complexity. The formulation begins with the generalized Stefan-Maxwell equations.

\[
-\frac{c_i}{RT} \nabla T \mu_i^c = \sum_{j \neq i}^n \frac{c_i c_j}{c D_{ij}} \left( v_i^D - v_j^D \right)
\]  

(5.1)

The existence of three species in the membrane is considered: water (subscript of 1), hydronium (subscript of 2), and the membrane structure itself (subscript of M). The diffusive velocity, \( v_i^D \), can be related to the species velocity through the addition of a bulk convective velocity which is defined by Schlögl’s equation [40,81,82].

\[
v = -\frac{B_0}{\eta} \left[ \nabla P + \left( \sum_{j=1}^n c_j z_j \right) F \nabla \phi \right]
\]

(5.2)

The variable \( B_0 \) in eq. 5.2 is the Darcy permeability and it is taken to be equal to the electro-kinetic permeability, i.e. it is used as the multiplier for both the pressure gradient term and the potential gradient term in eq. 5.2. This common simplification is related to the assumption of radial uniformity of the charged species within the pore [40,82]. The semi-empirical Carman-Kozeny relationship can be used to calculate the Darcy permeability of the membrane structure [177,178].

\[
B_0 = \frac{\varepsilon^3 r_0^2}{45(1-\varepsilon)^2}
\]

(5.3)

The porosity term, \( \varepsilon \), in eq. 5.3 is the volume fraction of the hydrated phase of the membrane and is given by eq. 5.4.
The water content, \( \lambda \), of the membrane is defined as the ratio of the bulk water concentration and the fixed charge concentration \( c_1/c_f \). Even though eq. 5.3 and 5.4 show a variation of permeability with hydration, an average value is computed and used in all subsequent calculations based on the operational parameters of the HPOGA. This is done for simplicity and because the Carman-Kozeny equation is developed for packed soil beds rather than membrane structures. Also, the pore radius, \( r_0 \), will also vary within the membrane structure and with hydration state. The calculated value of \( 1.2 \times 10^{-20} \text{ m}^2 \) agrees reasonably well with the experimental value of \( 2.18 \times 10^{-20} \text{ m}^2 \) obtained by Evans et al. [179] for a fully hydrated, heat-treated, H\(^+\) form of Nafion membrane. Obtaining a slightly lower value here makes sense given that the membrane is not fully hydrated throughout the thickness during operation and lower hydration indicates a lower hydraulic permeability.

At this stage it is possible to modify eq. 5.1 by isolating the membrane species from the summation term on the right hand side of the equation and realizing that the velocity of the membrane species is zero. The diffusive velocity terms can be replaced with the species velocity terms as described above, which introduces Schlögl’s equation, and the species flux can be introduced as the product of the velocity and the concentration of the species. Making these adjustments gives eq. 5.5 where the \( n \) now represents the number of remaining species in the summation, in this case \( n = 2 \).

\[
-\frac{c_i}{RT} \nabla T \mu_i^e = \sum_{j=1}^{n} \frac{1}{c_i c_j C_{ij}} (c_j N_i - c_i N_j) + \frac{N_i}{D_{ik}^e} + \frac{C_i B_0}{\eta D_{ik}^e} \left[ \nabla P + \left( \sum_{j=1}^{n} c_j z_j \right) F \nabla \phi \right] \tag{5.5}
\]
The diffusion coefficients appearing in eq. 5.5 represent the effective diffusivities in the presence of the membrane structure. Eq. 5.6 defines the electrochemical potential gradient term in eq. 5.5.

\[
\nabla_i \mu_i^e = RT \ln c_i + RT \ln \gamma_i + \nabla_i \nabla P + z_i F \nabla \phi
\]

(5.6)

The electrochemical potential gradient term can be simplified according to assumption 5.5. Taking this simplification and applying eq. 5.5 to the water and hydronium species gives the governing equations for the system being considered.

\[
-\left( c_1 \nabla \ln c_1 + \frac{c_1 V}{RT} \nabla P \right) = \frac{1}{cD_{12}^e} \left( c_2 N_1 - c_1 N_2 \right) + \frac{N_1}{D_{1M}^e} + \frac{c_1 B_0}{\eta D_{1M}^e} \left[ \nabla P + c_2 z_2 F \nabla \phi \right]
\]

(5.7)

\[
-\left( c_2 \nabla \ln c_2 + \frac{c_2 V}{RT} \nabla P + \frac{c_2 z_2 F}{RT} \nabla \phi \right) = \frac{1}{cD_{21}^e} \left( c_1 N_2 - c_2 N_1 \right) + \frac{N_2}{D_{2M}^e} + \frac{c_2 B_0}{\eta D_{2M}^e} \left[ \nabla P + c_2 z_2 F \nabla \phi \right]
\]

(5.8)

The potential gradient term of the electrochemical potential for eq. 5.7 drops out since the water is not a charged species however the potential gradient still influences the water transport directly through the electro-kinetic permeability term on the right hand side of the equation. Using assumption 4, the water flux and the hydronium fluxes can be directly calculated based on the cell operating conditions.

\[
N_1 = \left( 0.5 + c_{od} \right) \frac{i}{F} = \chi \frac{i}{F}
\]

(5.9)

\[
N_2 = -\frac{i}{F}
\]

(5.10)

The hydronium flux is set as a one to one ratio with the flux of electrons moving through the external circuit while the flux of water is equal to stoichiometric amount required by the anode reaction plus an offset due to the effect of electro-osmotic drag. The electro-osmotic drag coefficient, \( c_{od} \), is taken to be 1 [180]. The actual value of the electro-osmotic drag coefficient
varies in the literature with some claiming it to be functionally dependent on the water content of the membrane [181,182]. It has also been demonstrated that the coefficient is greatest when the membrane is equilibrated with liquid water [180]. This work focuses on the HPOGA which operates with liquid water in contact with one side of the membrane and gas on the other making the choice for the electro-osmotic drag coefficient not an obvious one. However, focus is on the dehydration behavior of the cell at the anode and since the electro-osmotic drag initiates in this drier region a constant value of 1 was used. The coefficient was not allowed to vary spatially within the membrane due to effect on water flux spatially. If the water flux in eq. 5.9 were to vary spatially in the membrane there would be violations of mass continuity of the water species.

The water hydronium diffusion coefficient in eq. 5.7 and 5.8 is calculated via the Bruggeman relationship.

\[ D_{12}^c = D_{21}^c = D_{12}(\varepsilon - \varepsilon_p)^{1.5} \] (5.11)

The constant \( D_{12} \) in eq. (5.11) is the infinite dilution diffusivity of hydronium in water. This value is taken to be \( 12.76 \times 10^{-9} \) m\(^2\)/s for the operating temperature of Hamilton Sundstrand’s HPOGA [183]. The scaling behavior is eq. 5.11 is meant to take into account the tortuous pathways for diffusion as well as the reduction of open volume. The constant, \( \varepsilon_p \), is the percolation limit for the transport of the species. Below this limit transport is not expected to proceed. A water content of 1.9 is adopted to calculate the percolation limit porosity [139]. The water hydronium diffusion coefficient is thought to represent two primary modes of transport through the membrane. These two mechanisms are lumped into the diffusivity and include mutual diffusion as well as the Grotthuss mechanism, proton diffusion through the water-hydrogen bond network [107]. Other mechanisms, such as surface site hopping along the fixed
charge groups, are said to exist in the membrane as a means of charge transport but these are not expected to be major contributors [1,82,184]. In this study the membrane diffusion coefficient, $D_{mb}$, in eq. 5.7 and 5.8 is treated as a fitting parameter as is common in the literature [40,82,185,186].

Currently in the derivation, the system has three unknowns: the water concentration, the hydronium concentration, and the electrical potential. Since only two governing equations have been developed at this point there is a need to relate the gradient of the hydronium concentration to the gradient of the water concentration. The hydronium concentration is the product of the fixed-charge concentration of the side chain groups within the membrane and the degree of dissociation, $\kappa$.

$$c_2 = \kappa c_f$$  \hspace{1cm} (5.12)

This degree of dissociation is related to the local water concentration as given by eq. 5.13 [82].

$$\kappa = \frac{\left(\lambda + 1\right)^{-1}}{2 \left(1 - \frac{1}{K_{A,C}}\right)} \left(1 + \frac{1}{K_{A,C}}\right) - 4 \lambda \left(1 - \frac{1}{K_{A,C}}\right)$$ \hspace{1cm} (5.13)

The equilibrium constant for proton solvation ($K_{A,C}$) in eq. 5.13 is a parameter calculated at varying temperature based on an Arrhenius behavior as shown in eq. 5.14 [82].

$$K_{A,C} = 6.2\exp\left[-\frac{\Delta H^0}{R} \left(\frac{1}{T} - \frac{1}{298}\right)\right]$$ \hspace{1cm} (5.14)

The enthalpy change for proton solvation ($\Delta H^0$) in eq. 5.14 is taken to be $-52.3$ kJ mol$^{-1}$ [187]. Using eq. 5.12-5.14 the 1-D gradient of the hydronium concentration is related to the 1-D gradient of the water concentration.
\[
\frac{dc_2}{dy} = \frac{dc_1}{d\lambda} \frac{dc_1}{dy} \quad (5.15)
\]

The derivative of the degree of dissociation with respect to the water content can be determined by differentiating eq. 5.13. It will be referred to as \( \Gamma \) from now on. By introducing eq. 5.15 into eq. 5.8 and simplifying to 1-D, as specified by assumption 1, the governing equations can be rewritten as shown below.

\[
-\Gamma \frac{dc_1}{dy} = A_2 + B_2 \frac{d\phi}{dy} \quad (5.16)
\]

\[
-\frac{dc_1}{dy} = A_1 + B_1 \frac{d\phi}{dy} \quad (5.17)
\]

Where;

\[
A_1 = \frac{1}{cD_{12}^s} (c_2 N_1 - c_1 N_2) + \frac{N_1}{D_{1M}^c} + c_1 \nabla p \left( \frac{B_0}{\eta D_{1M}^e} + \frac{\bar{V}_1}{RT} \right) \quad (5.18)
\]

\[
B_1 = \frac{c_1 c_2 B_0 z_2 F}{\eta D_{1M}^e} \quad (5.19)
\]

\[
A_2 = \frac{1}{cD_{21}^s} (c_1 N_2 - c_2 N_1) + \frac{N_2}{D_{2M}^c} + c_2 \nabla p \left( \frac{B_0}{\eta D_{2M}^e} + \frac{\bar{V}_2}{RT} \right) \quad (5.20)
\]

\[
B_2 = c_2 z_2 F \left( \frac{c_2 B_0}{\eta D_{2M}^e} + \frac{1}{RT} \right) \quad (5.21)
\]

Finally, the unknown gradient for the water concentration and potential can be solved.

\[
\frac{dc_1}{dy} = \frac{A_1 B_2 - B_1 A_2}{\Gamma B_1 - B_2} \quad (5.22)
\]

\[
\frac{d\phi}{dy} = \frac{A_2 - \Gamma A_1}{\Gamma B_1 - B_2} \quad (5.23)
\]
Eq. 5.15, 5.22 and 5.23 represent three equations for the three unknowns \( c_1, c_2 \) and \( \phi \) that can be solved numerically. These governing equations are solved using a 4\(^{th}\) order Runge-Kutta marching scheme.

5.2.2 Oxygen MEA Interface Meniscus Model:

Due to the high differential pressure of the operating electrolyzer being studied, the nature of this pressure drop across the cell is of interest. In many traditional PEM systems hydraulic permeation can be a major contributor to water transport in the membrane due to the application of hydrophobic gas diffusion layers. While the system being considered does not make use of traditional gas diffusion layers, the up to 20 MPa pressure existing in the gas at the anode side of the cell could certainly be expected to impact the water transport. However, it is generally believed that the water exists within Nafion in the condensed state which means a meniscus should form within the pore-space between the oxygen gas and the liquid water in the catalyst layer \[175\]. Given the extremely small pore sizes present in Nafion (nanometer scale) it is conceivable that the meniscus could take up much of the pressure drop. This implies there could be a proportion of the pressure drop occurring across the meniscus with the remainder occurring across the membrane itself. Numerous works have proposed capillary pore models for Nafion to represent the structure of the material \[188-191\]. In the case of parallel cylindrical pores the pressure change across the meniscus is given by eq. 5.24.

\[
P_c = \frac{2\sigma}{r_0} \cos(\theta)
\]  

(5.24)
The picture of perfectly cylindrical capillary pores is oversimplified in the case of studying the meniscus effects on pressure drops. Experimental evidence collected by Divisek et al. [192] shows an array of pore sizes existing within the membrane. More complex pore structures have also been proposed such as the cluster network model [30,31]. The cluster network model envisions the membrane to hydrate in a way that the sulfonic acid groups cluster together and tube-like pores connect them.

This work attempts to represent the pore structure with a wavy-wall concept. This wavy-wall picture attempts to combine the experimental observations of Divisek et al. [192] with the physical picture presented by the cluster network model while maintaining a geometry that is easy to work with analytically. As the name implies, the wavy-wall approach defines the walls of the pores as a series of sinusoidal waves of varying size and shape. This concept is depicted in figure 5.2
Figure 5.2 [162]: (A) diagram of a randomized wavy wall pore. The pore structure is represented as a series of sinusoidal waves in which the parameters, defined in (B), are randomized within a range of values. The variable of interest is the expected value of the meniscus penetration depth.

Eq. 5.25 and 5.26 show the modified relationship for the capillary pressure when visualizing the pores in this way.

\[ P_c = \frac{2\sigma}{r_0} \cos(\theta + \Phi) \]  

(5.25)

\[ \Phi = \tan^{-1}\left(2\pi \frac{\psi}{\delta} \cos\left(\frac{2\pi x}{\delta}\right)\right) \]  

(5.26)

Parameters which define the pore structure are the mean radius, \( r_0 \), the sine wavelength, \( \delta \), and the sine wave amplitude, \( \psi \). These parameters are randomized according to table 5.1

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Distribution</th>
</tr>
</thead>
<tbody>
<tr>
<td>( r_0 )</td>
<td>mean pore radius</td>
<td>2 nm (log normal, 2nm variance) [128]</td>
</tr>
<tr>
<td>( \delta )</td>
<td>pore wavelength</td>
<td>uniform 2.5 – 7.5 nm (average wavelength taken from [174])</td>
</tr>
<tr>
<td>( \psi / r_0 )</td>
<td>ratio of pore sine wave amplitude to mean radius</td>
<td>uniform 0.01 – 0.95</td>
</tr>
</tbody>
</table>

Eq. 5.25 allows for a changing capillary pressure based on position within the membrane due to the varying pore radius and the angle of the wall. The implication of this is, as the gas pressure changes in the oxygen stream, the meniscus can adapt by moving to a suitable location within the pore. Using statistics it is possible to calculate an expected position of the meniscus relative to the oxygen interface with the membrane as defined in figure 5.2.
5.2.3 Cell Voltage Model:

Experimental polarization data of the HPOGA, primarily in the linear loss region, was taken previously for oxygen pressures ranging from 0 to over 20 MPa [165]. The current scans were started after the activation polarization leveled off and terminated just as mas transport limiting effects were observed. The polarization behavior measured by these experiments can be represented with eq. 5.27.

\[
V = E_0 + \phi + iAR_{\text{ext}}
\]  

(5.27)

The constant \( E_0 \) in eq. 5.27 represents a y-intercept for the linear polarization region and can be calculated by linear extrapolation of the data. It accounts for any initial jump from the equilibrium cell voltage due to activation overpotential as well as the Nernst potential. The last two terms in eq. 5.27 represent the membrane overpotential and the external resistive losses. Since the DFM can only account for the membrane losses the resistive losses is treated as a fitting parameter. Cross over losses were also considered since current efficiency data provided in [165] indicated a change in the oxygen cross over rate with current density due to membrane hydration changes. However, the Butler-Volmer kinetics predicted negligible effects.

5.3 Results and Discussion

5.3.1 Oxygen MEA Interface Meniscus Model

Before proceeding with the implementation of the DFM derived in section 5.2.1 it is necessary to first determine what the nature of the pressure drop across the meniscus is. Figure 5.3 plots the expected meniscus penetration depth vs. the oxygen pressure of the cell.
Figure 5.3 [162]: The expected meniscus penetration depth is shown at various differential oxygen pressures across the membrane. Contact angles are varied to accommodate the upper range of expected values within the pore. Local variations in the curves are attributed to the randomized parameters in the calculations.

Small, local variations in the curves shown in figure 5.3 represent the randomized construction of the membrane pore via the parameters in table 5.1. The general trend of the curves is unchanged by these small variations. The contact angles shown in figure 5.3 are an upper limit of those that might be expected [193,194]. In the hydrophilic sections of the membrane these contact angles would be lower. Even with the large contact angles, the calculated penetration depth in only on the order of single nanometers within the range of pressures studied. This is negligible compared to the overall membrane thickness and shows the meniscus at the liquid-gas interface is easily capable of supporting the high oxygen pressures. This means the pressure gradient terms in eq. 5.18 and 5.20 are set to zero.
5.3.2 Membrane Species Transport

After the nature of the pressure drop across the MEA was ascertained, the model was calibrated to the experimental polarization data available in [165] for the HPOGA. To calibrate the model the membrane diffusion coefficient and the external resistance were both fitted. When adjusting the membrane diffusion coefficient the slope of the linear loss region is affected as well as the dry out behavior. Adjusting the external resistance solely affects the slope of the linear loss region of the polarization curve. For each polarization curve at a given oxygen pressure, the membrane diffusion coefficient and the external resistance were chosen to minimize the error between the experimental data and the output of eq. 5.27. The methodology was as follows; a guess of the membrane diffusion coefficient was made leaving the external resistance the only unknown parameter in the system. Using eq. 5.27 and the experimental data from [165] the external resistance was calculated at each datum point over the range of current densities measured. More guesses of the membrane diffusion coefficient were made within a range of reasonable values and the process was repeated through all of them. Finally, the best fitting pair of membrane diffusion coefficient and external resistance was chosen based on a least squares error analysis. Ultimately, one constant external resistance, and membrane diffusion coefficient was chosen for each polarization curve, at a given pressure, for the range of current densities examined which based matched the data overall. Figure 5.4 shows the comparison between the predictions and the experimental data as well as the resulting fits for the membrane diffusion coefficient and the external resistance.
Figure 5.4 [162] a): Comparison of data from [165] to computational output after calibration.

Nonlinearities seen in predicted polarization curves at the highest current densities as mentioned in [165] are attributed to low water content causing a significant decrease in membrane conductivity; b): Membrane diffusion coefficient as a function of oxygen pressure. The diffusion
coefficient decreases linearly with increasing pressure; c): External cell resistance as a function of oxygen pressure. The linear increase in external cell resistance with increasing pressure can be attributed to increasing contact resistance as the oxygen pressure relaxes the preload in the cell.

The plotted predictions shown in figure 5.4a are based on the linear trends plotted in figure 5.4b and 5.4c as opposed to the individual best fit pairs (symbols plotted in figure 5.4b and 5.4c) of diffusion coefficients and external resistances for each pressure. The nonlinear increase in the polarization occurring at high current densities in the predictions of figure 5.4a is caused by low ionic conductivity of the membrane due to dehydration.

The pressure dependency of the membrane diffusion coefficient in figure 5.4b, which decreases with increasing differential pressure, is given by eq. 5.28 (units of $D_M^e$ : m$^2$ s$^{-1}$, Units of P: MPa gauge).

$$D_M^e = 1.12 \times 10^{-9} - 2.26 \times 10^{-11} P$$ (5.28)

With the assumptions made it is appropriate to compare eq. 5.28 directly to the Fickian diffusion coefficient of section 2.4 or any other measured value in the literature. Hallinan et al. [117] notes the range of Fickian diffusion coefficients for water in Nafion, reported by various authors using a wide variety of techniques, ranges in magnitude from as low as $10^{-13}$ to $10^{-9}$ m$^2$ s$^{-1}$. The membrane diffusion coefficient given by eq. 5.28 falls in the upper limit of that range. In comparing to the previously derived Fickian diffusion coefficient from section 2.4 the result is well within an order of magnitude. While closer agreement with the results from section 2.4 would be ideal, the fact that the fitted diffusivity of this study fell within an order of magnitude of the results of section 2.4 is encouraging given the number of simplifications taken and the overall complexity of the system being studied in this case. Previously, the concern was
measuring the water flux across an inactive (no current) membrane. In the development of the DFM presented in this chapter, the membrane is subject to much more complex transport behavior due to the current flow.

Despite the magnitude of the membrane diffusion coefficient being reasonable, the decreasing value with increasing pressure is unintuitive. Such a change would seem to indicate a structural change of the membrane as oxygen pressure increases. It is doubtful that this is the case however, due to the characteristics of the HPOGA assembly. The thickness of the membrane is not expected to change significantly due to oxygen pressure increasing and the proposed meniscus is theorized to take up the pressure drop across the MEA. It would seem that it is possible that the membrane diffusion coefficient has some unaccounted for physics lumped into it. The nature of these physics would cause the mass transport losses of the polarization curve to dominate at lower current densities as oxygen pressure increases. One possible mechanism is the presence of the oxygen in the membrane environment. Apart from the traditional cross-over losses occurring, the oxygen present in the membrane would be expected to increase as oxygen pressure at the anode increased. It is possible that this oxygen could provide a building resistance to the water transport through the membrane and partly contribute to the observed pressure dependence of the membrane diffusion coefficient. To account for this behavior, another species equation would need to be added to the DFM development for oxygen. Another possible mechanism is the nature of the oxygen transport at the catalyst site. If the transport of the oxygen from the catalyst site within the MEA to the bulk oxygen stream is heavily impeded with increasing oxygen pressure, it could create mass transport limiting behavior at the catalyst sites and cause a dry out affect.

Figure 5.4c shows the pressure dependency of the external resistance. This resistance
increases with increasing pressure. It is rationalized that this increase is related to increasing contact resistance due to the preload on the cell assembly being relaxed. A linear trend is desirable as it indicates that, while the preload is relaxing, it has not been overcome and the seals remain intact. Since the numeric data indicate this behavior and it is known to be the case in the actual test cells studied, it provides merit to the modeling. The pressure dependency is given by eq. 5.29 for the external resistance (units of $R_{ext}$: mΩ, Units of P: MPa gauge).

$$R_{ext} = 4.58 + 0.262P$$

Additional tests conducted by Hamilton Sundstrand indicate that the cross-cell resistance measured by a HP 4338A millohmeter ranges between about 4.1 mΩ at ambient pressure to 4.8 mΩ at the highest differential oxygen pressure operation [195]. The results in Figure 5.4c agree relatively well with these findings at low operating pressures then begin to deviate at the higher pressures. It should be noted that pressurized cross-cell resistance tests are run in an inoperable cell using nitrogen which may account for some of the discrepancy. The nitrogen gas used has been boiled off from a cryo farm and is in an almost completely dry state causing the membrane to dry out during the cross-cell resistance test.

5.3.3 Dimensional Analysis

As a means of further probing the physics of the system being studied a dimensional analysis was performed. Table 5.2 outlines the dimensionless parameters utilized.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Definition</th>
<th>Reference (term appearing in the denominator)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$y^*$</td>
<td>$y/\delta$</td>
<td>Membrane thickness ($\delta$)</td>
</tr>
</tbody>
</table>
\[ c_1^* \frac{c_1}{c_0} \] Membrane water concentration when saturated with liquid water (\( c_0 \))

\[ c_2^* \frac{c_2}{c_0} \] Membrane water concentration when saturated with liquid water (\( c_0 \))

\[ \phi^* \frac{\phi}{E_0} \] Reference cell voltage (\( E_0 \))

\[ V^* \frac{V}{E_0} \] Reference cell voltage (\( E_0 \))

\[ \kappa^* \frac{\kappa}{\kappa_0} \] Acid dissociation constant for a liquid equilibrated membrane (\( \kappa_0 \))

\[ D_{12}^e \frac{D_{12}^e}{D_{12}^0} \] Maximum species diffusion coefficient (\( D_{12}^0 \))

\[ D_{1M}^e \frac{D_{1M}^e}{D_{1M}^0} \] Average membrane diffusion coefficient for a given \( O_2 \) pressure (\( D_{1M}^0 \))

It is noted that \( D_{1M}^e \) in Table 5.2 is simply equal to 1 due to the membrane diffusion coefficient being a constant during the modeling process and thus drops out of the dimensionless form of the governing equations. Applying the definitions in Table 5.2 to eq. 5.7 and 5.8, after simplifying by setting the pressure term to zero, results in eq. 5.30 and 5.31 respectively.

\[
\frac{dc_1^*}{dy^*} = \frac{i\delta}{c_0 FD_{1M}^0} \frac{D_{1M}^0}{D_{12}^0} \frac{1}{D_{12}^e} (\chi x_2 + x_1) + \frac{i\delta}{c_0 FD_{1M}^0} \chi + c_1^* c_2^* \frac{D_{12}^0}{D_{1M}^0} \frac{c_0 B_0 z FE_0}{nD_{12}^0} \frac{d\phi^*}{dy^*} \tag{5.30}
\]

\[
\frac{dc_2^*}{dy^*} = -\frac{D a}{D_{12}^e} \frac{D_{1M}^0}{D_{12}^0} (x_1 + \chi x_2) - Da + \left( c_2^* c_2^* \frac{D_{12}^0}{D_{1M}^0} Pe - c_2^* \frac{z FE_0}{RT} \right) \frac{d\phi^*}{dy^*} \tag{5.31}
\]

Eq. 5.15 can also be cast in dimensionless form:

\[
\frac{dc_2^*}{dy^*} = \frac{c_f \kappa_0}{c_0} \frac{dk^*}{dc_1^*} \tag{5.32}
\]

Finally, using eq. 5.30, 5.31, and 5.32 it is possible to write dimensionless versions of eq. 5.22 and 5.23.

\[
\frac{dc_1^*}{dy^*} = \frac{\bar{A}_2 B_2 - \bar{A}_1 B_1}{c_f \kappa_0 \frac{dk^*}{dc_1^*} \bar{B}_1 - \bar{B}_2} \tag{5.33}
\]
\[
\frac{d\phi^*}{dy^*} = \frac{\bar{A}_2 - \frac{c_f \kappa_0}{c_0} \frac{d\kappa^*}{dc_1^*} \bar{A}_1}{\frac{c_f \kappa_0}{c_0} \frac{d\kappa^*}{dc_1^*} \bar{B}_1 - \bar{B}_2} 
\]  
(5.34)

Where;

\[
\bar{A}_1 = \frac{\text{Da}}{D_{12}^c \times D_{12}^0} \left( x_1 + \chi x_2 \right) + \chi \text{Da} 
\]  
(5.35)

\[
\bar{B}_1 = c_1 \times c_2 \times \frac{D_{12}^0}{D_{1M}^0} \text{Pe} 
\]  
(5.36)

\[
\bar{A}_2 = \left[ \frac{\text{Da}}{D_{12}^c \times D_{12}^0} \left( x_1 + \chi x_2 \right) + \text{Da} \right] 
\]  
(5.37)

\[
\bar{B}_2 = c_2^2 \frac{D_{12}^0}{D_{1M}^0} \text{Pe} - c_2 \times \frac{z_2 \text{FE}_0}{\text{RT}} 
\]  
(5.38)

Inspecting the dimensionless equations reveals a set of dimensionless groupings identified in eq. 5.39, 5.40, and 5.41.

\[
c_1^*_* = f\left(y^*; \text{Da}, \frac{D_{1M}^0}{D_{12}^0}, \chi, \text{Pe}, \frac{c_f \kappa_0}{c_0} \right) 
\]  
(5.39)

\[
c_2^*_* = f\left(y^*; \text{Da}, \frac{D_{1M}^0}{D_{12}^0}, \chi, \text{Pe}, \frac{z \text{FE}_0}{\text{RT}}, \frac{c_f \kappa_0}{c_0} \right) 
\]  
(5.40)

\[
\phi^*_* = f\left(y^*; \text{Da}, \frac{D_{1M}^0}{D_{12}^0}, \chi, \text{Pe}, \frac{z \text{FE}_0}{\text{RT}}, \frac{c_f \kappa_0}{c_0} \right) 
\]  
(5.41)

Where;

\[
\text{Da} = \frac{i \delta}{c_0 \text{FD}_{1M}^0} 
\]  
(5.42)

\[
\text{Pe} = \frac{c_0 \text{B}_0 z_2 \text{FE}_0}{\eta D_{12}^0} 
\]  
(5.43)
Eq. 5.42 gives a dimensionless parameter that resembles a Damkohler number in nature. The grouping represents the ratio of the hydronium flux, which is imposed by the operational current of the cell, to the maximum flux of water supplied by diffusion through the membrane. If this parameter is multiplied by $\chi$, it becomes the ratio of the water flux imposed by cell operation to the flux of the hydronium imposed by cell operation. Eq. 5.43 is a dimensionless grouping that resembles a Peclet number and as such it represents the ratio of a potential-driven convective flux to the diffusive flux of water through hydronium in the membrane. For the given set of dimensionless groupings, only $Da$ and $D_{1M}^0/D_{12}^0$ vary within the range of operational parameters of the HPOGA cell. The term $\frac{zFE_0}{RT}$ contains $E_0$, which is expected to be distinct at each pressure, implying the term is dependent on pressure. However, the calculated values of $E_0$ are virtually constant with pressure making the term itself approximately constant over the range of operation. In terms of the nature of the operational variation for $Da$ and $D_{1M}^0/D_{12}^0$ the former varies with pressure and current density while the latter varies only with differential pressure.

Dehydration of the anode due to high current operation is a concern when operating the HPOGA. As the current density increases the water at the anode is consumed more rapidly to produce oxygen and eventually the water transport through the membrane is insufficient to replenish the anode. While there is electro-osmotic drag and potential-driven convection driving the water away from the anode, the sole driving force for replenishment is diffusion where the membrane structure, hydronium molecules, and possibly oxygen molecules, impede the water molecules. As oxygen pressure in the system increases the dry out behavior the anode occurs at lower current densities. When considering the operation of the test cell it is apparent that only the current density and the oxygen pressure are varied. This makes the two aforementioned
dimensionless groupings, $Da$ and $D_{1M}^0 / D_{12}^0$, of particular interest since they capture changes in the physics with changing current density and pressure.

The polarization curves shown in figure 5.4a measured for different oxygen pressures can be collapsed by means of the dimensional analysis. Eq. 5.27 can be recast in dimensionless form using table 5.2.

$$V^* = I + \phi^* + \frac{iAR_{ext}}{E_0}$$

(5.44)

Using the Damkohler number definition given by eq. 5.42 to represent the dimensionless current and the definition of the dimensionless cell voltage given by eq. 5.44 results in the dimensionless polarization curves plotted in figure 5.5.

Figure 5.5 [162]: Dimensionless polarization curves. The ratio $D_{1M}^0 / D_{12}^0$ of each curve is given in the legend. It can be seen that the limiting current density occurs at a roughly constant Damkohler number of $0.196 \pm 0.004$.  

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As seen in figure 5.5, the curves collapse reasonably well as a function of the Damkohler number. The existing spread may be attributed to each curve having a distinct diffusion coefficient ratio (outlined in the legend of figure 5.5). This ratio varies from 0.399 to 0.232 which is almost a variation of two fold and the curves still collapse reasonable well. Figure 5.5 also shows that the dehydration occurs at roughly the same Damkohler number for each pressure. This value is about $Da = 0.196 \pm 0.004$ regardless of the diffusion coefficient ratio $D_{im}^0/D_{12}^0$.

The implication is the ratio of the limiting current density to the water membrane diffusion coefficient is approximately constant over the range of pressures studied which is reasonable given that the mass transport limiting behavior is controlled by the water’s sole means of arriving at the reaction sites: water diffusion.

The dimensionless voltage in figure 5.5 can be fit as a function of the Damkohler number as given by eq. 5.45.

$$V^* = 1.68Da^{1.15} + 0.976 + \frac{0.0305}{(0.196 - Da)^{0.100}} \quad \text{(for } 0.0221 \leq Da \leq 0.196) \quad (5.45)$$

The correlation given by eq. 5.37 is valid for $0.0221 \leq Da \leq 0.196$. Below $Da = 0.0221$ the effects of activation overpotential will begin to dominate. The correlation does mimic the onset of dry out approaching the critical Damkohler number of $Da = 0.196$ but beyond it is not valid due to dry out. The coefficients in eq. 5.45 were obtained using a least squares routine in which the error between the experimental data points associated with the HPOGA and the correlation function was minimized. The standard deviation between the experimental data and the correlation was calculated as 0.0049. The diffusion coefficient ratio, $D_{im}^0/D_{12}^0$, was not included in the correlation due to its minimal impact on the result. It is important to note that this correlation is only valid so long as other dimensionless parameters appearing in the governing
equations are not altered.

Figure 5.6 shows the predicted limiting current density as a function of oxygen pressure obtained using the limiting Damköhler number highlighted in figure 5.6.

![Figure 5.6: Plot of the limiting current density as a function of pressure. The solid line is the calculated limiting current density obtained using the limiting Damköhler number. The dotted lines in the figure represent the limits of $\chi = 0.5$ and 3.](image)

The shaded region indicates the operational parameters that would be impossible for the electrolyzer due to dry out of the anode. The effect of electro-osmotic drag can be investigated through the adjustment of the parameter $\chi$. Figure 5.6 shows the limits of $\chi = 0.5$ and 3 represented by the dotted lines. Setting $\chi = 0.5$ means there is no influence of electro-osmotic drag on the system since $\chi$ is then equal to just the stoichiometric requirement of water due to the reaction occurring at the electrode (see eq. 5.9). The upper limit represents the scenario in which
the electro-osmotic drag coefficient is set to the completely saturated condition, $c_{od} = 2.5$ [7].

The nature of the electro-osmotic drag significantly impacts the system as shown in figure 5.6 where the limiting current density rises by about 37% and when $\chi = 3$ the limiting current density falls by about 27% for each differential oxygen pressure. This is to be expected when looking at eq. 5.9 since the electro-osmotic drag effect effectively increases the required water flux through the membrane to satisfy the reactions occurring at the anode. The stoichiometry requires 0.5 water molecules to pass through the membrane for each hydronium molecule. If the electro-osmotic drag effect is included, and set to 1, then the water flux is tripled due to enhanced water concentration gradients in the membrane caused by increased dry out. In this way electro-osmotic drag has a strong and direct influence on the dehydration behavior of the membrane as illustrated in Figure 5.6.

**5.4 Conclusions:**

Species transport within a high-pressure oxygen-generating PEM water electrolyzer, with liquid water supplied to the cathode of the cell, was analyzed using the DFM. This type of setup is unique compared to hydrogen-generating water electrolyzers that have been studied since the water must first cross the membrane before reacting at the anode of the cell to produce oxygen. The simulation results were compared to experimental linear region performance data for Hamilton Sundstrand’s HPOGA, a high-differential pressure oxygen-generating cell. In order to make this comparison a simplified prediction method of a cell voltage curve was employed where the membrane diffusion coefficient and the external cell resistance became fitting parameters. A meniscus model was used at the oxygen-MEA interface, which took up the over 20 MPa pressure drop across the MEA. It was found that the diffusion coefficient and the
external resistance of the cell both varied linearly with increasing oxygen pressure, with the membrane diffusion coefficient decreasing with increasing oxygen pressure and the external cell resistance increasing with increasing oxygen pressure. It was reasoned that the pressure dependency of the membrane diffusion coefficient could be attributed to additional mechanisms such as species cross-over or interfacial mass transfer at the anode. The resulting membrane diffusion coefficient was found to fall within the range of values found in the literature. The trend in the external cell resistance was expected since the preload on the cell would decrease with increasing oxygen pressure causing increasing contact resistance between components. The values were also fairly close to those determined experimentally by Hamilton Sundstrand. In order to investigate the physics of membrane dehydration the governing equations were cast in a dimensionless form in order to investigate how pressure and current density, two operational parameters which were varied during the operation of the HPOGA, affected dry-out in the cell membrane. Of all the dimensionless groupings to emerge from the analysis only the dimensionless parameter resembling a Damkohler number and the ratio of the membrane diffusion coefficient to the species diffusion coefficient changed with pressure. It was found that at a value of Da = 0.196 ± 0.004 the Damkohler number represented the mass limiting (i.e. dry out) effects of the cell regardless of the diffusion coefficient ratio which varied by a factor of two over the differential oxygen pressure range. The effect of electro-osmotic drag on membrane hydration was also a concern given its direct and significant effect on the required water flux for a given operating current density. It was found that changing the dimensionless parameter \( \chi \) from \( \chi = 0.5 \) and 3 (absence of electro-osmotic drag and electro-osmotic drag for a membrane equilibrated with liquid water) shifted the limiting current density by +37% and -27% respectively. This result shows that electro-osmotic drag is as crucial an element in the overall
water balance in the electrolyzer as it is in the fuel cell environment.
Chapter 6: Generalization and Applicability of Effective Medium Theory

*Partially adapted from [196]

6.1 Overview

Chapter 1 mentions some of the classical EMTs which still see widespread use today. More recently these classic EMTs have been subjected to further generalizations in terms of shape and anisotropy as well as modification to make them more appropriate for specific problems. A commonly cited shortcoming of BUT is that it is only applicable for a two component mixture. Duan et al. list this shortcoming in their development of a generalized Maxwell equation which accounts for anisotropy in terms of shape, orientation, and spatial distribution while allowing for multiple inclusions [197]. Jayannavar and Kumar, however, were able to extend a version of BUT to a three component composite [198]. In their work, two of the components were spherical inclusions and the third was the continuous backbone. It was demonstrated that in certain limits the BUT could be recovered while in others BST was recovered making the resulting EMT a sort of hybrid between the two.

Following with the theme of combining BUT and BST, Schwartz developed an equation for the electrical conductivity of perfectly aligned ellipsoids [199]. This concept was further iterated on by Hornby et al. [200] as well as Jakobsen et al. [201]. Both of those works focused on calculating effective elastic properties of sediment beds. The distribution of orientations for the individual inclusions was measured experimentally and included in the theoretical equations to determine the anisotropic properties.
The BST was generalized for anisotropic mixtures by Berthier, Fokker, and Stroud [202-204]. Berthier investigated the effect of shape as well as the distribution of particles on the calculated effective parameter [202]. Fokker included the effects of anisotropic particle orientation and was able to compare well with homogenization theory but only studied 2-D anisotropic systems [203]. Stroud was able to generalize BST for ellipsoidal particles with preferential orientation [204]. In that work the properties of individual particles were also allowed to be anisotropic.

The only work surveyed here which appears to focus completely on the BUT approach in terms of anisotropy is that of Giordano [205]. In that work inclusions of ellipsoids were considered which were either randomly oriented or perfectly aligned in terms of the major axis of each ellipsoid.

It is stressed here that the above list of existing literature on the topic of EMT is by no means exhaustive; it is simply a sampling of existing treatments most closely associated with the approach explored here. The listed theories above are primarily either based on Bruggeman’s symmetrical theory or unsymmetrical theory. The symmetrical and unsymmetrical theories are formulated for different problems. The unsymmetrical theory considers a discontinuous inclusion material within a continuous matrix and builds up the volume fraction from there. The symmetrical theory assumes the material type particles are randomly dispersed and in contact with each other. In this work we will be concerned with the former mixture type, thus the basis for the development presented in this work is the BUT. The focus in this chapter is towards accounting for the effects of anisotropy by allowing for preferential orientation of the individual inclusions, which are spheroidal in shape, based on a defined distribution function. While the concept of applying a distribution function is not a new concept [200,201], the developed
equations in this work provide a convenient set of analytical expressions for a large subset of possible distributions allowing for rapid analysis of appropriate systems. The effect of starting with Maxwell’s development vs. Maxwell-Garnett’s is also investigated as, while they give the same result for spheres, they do not give equivalent results once shape or anisotropy is considered. In the process of exploring both of these approaches, an expression for the far field potential of a spheroid in an infinite medium was derived which directly relates the far field potential to the spheroid internal E-field. The derivation continues by extending the number of inclusion types to N species in a manner similar to the work of Jayannavar and Kumar who extended Bruggeman’s theory to two spherical inclusion types within a continuous matrix.

6.2 Theoretical Development for Anisotropic Distributions of a Single Inclusion Type

The aim of this section will be develop an analytical-based equation which can calculate the effective parameter for a heterogeneous mixture containing a single type of inclusion within a continuous matrix material. For the purposes of the derivation the electrical conductivity will be the parameter of interest but the analog of the resulting equations can be derived for any instance in which the Laplace equation can be used to describe the fundamental physics (ex. thermal conductivity, mass diffusivity, dielectric constants, etc.). Figure 6.1 provides a 2-D representation of the type of structure being considered but the analytics will be developed in 3-D.
Figure 6.1 [196]: 2-D cross section of the material being considered.

As shown in figure 6.1 the development is restricted to spheroidal shaped inclusions of conductivity $\sigma_1$, embedded in noncontiguous fashion, in a continuous matrix with a conductivity $\sigma_0$. In an effort to keep the derivation organized the theoretical development of this section will be divided into four subsections as follows:

1. The known analytical expression for the potential field surrounding a single ellipsoidal inclusion of conductivity $\sigma_1$ embedded in an infinite medium of conductivity $\sigma_0$ will be simplified for the far field condition, i.e. at a great distance from the origin. A relationship will then be made between the far field potential and the internal E-field of the inclusion. This relation will be useful in relating the average far field potential to the average internal E-field for a distribution of ellipsoids in the dilute limit via the Maxwell development [93]. Subsequent development will be restricted to the case of a spheroid.

2. With the far field potential expression obtained, a distribution function will be introduced to orient the spheroidal inclusions. Using the distribution function, the average far field potential and internal E-field vector of a collection of spheroids will be computed.
3. The average far field potential will be used in the Maxwell development [93] while the average internal E-field vector will be used with the Maxwell-Garnett approach [94] to obtain the two possible dilute limit approximations of the effective conductivity.

4. To extend to higher volume fractions the Bruggeman unsymmetrical approach [96] will be utilized on both the resulting dilute limit expressions to obtain a final equation for the effective conductivity for a preferentially oriented mixture containing one type of inclusion.

6.2.1 Far Field Potential:

The development begins by first considering an ellipsoid of conductivity $\sigma_1$ contained in an infinite medium of conductivity $\sigma_0$. The coordinate axis is affixed to the volumetric center of the ellipsoid so that the x, y, and z directions align with the semi-principal axes of the ellipsoid. As shown in figure 6.2 the x-axis is aligned with the major principal axis of the ellipsoid, a. Also shown in figure 6.2, a uniform E-field is applied to the system at some arbitrary orientation relative to the coordinate system chosen.
Figure 6.2 [196]: Ellipsoid of conductivity $\sigma_1$ in an infinite medium of conductivity $\sigma_0$. The semi-principal axes $a$, $b$, and $c$ align with the $x$, $y$, and $z$ axes of the ellipsoid fixed coordinate system respectively. A uniform E-field is applied with an arbitrary orientation relative to the spheroid.

The analytical solution for the external potential field (Laplace solution) is available via Stratton [206].

$$
\phi^+ = -(E_{0x}x + E_{0y}y + E_{0z}z)
$$

$$
\phi^+ = \left[ \frac{E_{0x}xA}{1 - A} \int_0^\infty \frac{ds}{(s + a^2)R_s} + \frac{E_{0y}yA}{1 - B} \int_0^\infty \frac{ds}{(s + b^2)R_s} + \frac{E_{0z}zA}{1 - C} \int_0^\infty \frac{ds}{(s + c^2)R_s} \right]
$$

(6.1)

Where;
\[ A = \frac{abc}{2} \left( \frac{\sigma_0 - \sigma_1}{\sigma_0} \right) \]

\[ R_s = \sqrt{\left( s + a^2 \right) \left( s + b^2 \right) \left( s + c^2 \right)} \]

The variable, \( s \), in eq. 6.1 is a dummy variable while the variable, \( \xi \), acts as a distance measure and is related to the family of ellipsoids all concentric about the origin in the ellipsoidal coordinate system. The first groupings of terms on the right hand side of eq. 6.1 is due to the imposed uniform E-field vector mentioned previously while the second grouping is the potential contribution due to the presence of the ellipsoid inclusion. This second term is a complex function relating to the shape of the ellipsoid and also depends on the relative orientation of the imposed E-field to the ellipsoid. Both terms also depend on the location of the field point which is the position in space which the potential is being calculated.

To simplify the above equation for the far field first consider the equation of an ellipsoid.

\[ \frac{x^2}{1 + \frac{a^2}{\xi}} + \frac{y^2}{1 + \frac{b^2}{\xi}} + \frac{z^2}{1 + \frac{c^2}{\xi}} = \xi \quad (6.2) \]

As \( \xi \) becomes very large the ellipsoid approaches the shape of a sphere and the left hand side of eq. 6.2 approaches \( r^2 \) in the spherical coordinate system. This very simple observation implies that, so long as one considers a distance very far from the origin, \( \xi \) in eq. 6.1 can be replaced by \( r^2 \) where \( r \) is just the distance from the center of the ellipsoid (the origin) to the field point. Further simplification of eq. 6.1 can be made by recognizing that the quantity \( (s + a^2)R \), approaches \( s^{5/2} \) as \( \xi \) approaches \( \infty \). Applying these far field conditions to eq. 6.1 results in eq. 6.3.
\[ \phi^f = -(E_{0x}x + E_{0y}y + E_{0z}z) + \frac{abc}{3r^3} \left( \frac{\sigma_1 - \sigma_0}{\sigma_0} \right) \left[ \frac{E_{0x}x}{D_x} + \frac{E_{0y}y}{D_y} + \frac{E_{0z}z}{D_z} \right] \]  (6.3)

The \( D_x, D_y, \) and \( D_z \) in eq. 6.3 represent the integrals shown in eq. 6.4.

\[
D_x = \left. -A \int_0^\infty \frac{ds}{s + a^2} \right|_{R_s} = 1 + \frac{(\sigma_1 - \sigma_0)}{\sigma_0} L_4
\]

\[
D_y = \left. -A \int_0^\infty \frac{ds}{s + b^2} \right|_{R_s} = 1 + \frac{(\sigma_1 - \sigma_0)}{\sigma_0} L_2
\]

\[
D_z = \left. -A \int_0^\infty \frac{ds}{s + c^2} \right|_{R_s} = 1 + \frac{(\sigma_1 - \sigma_0)}{\sigma_0} L_3
\]

(6.4)

The \( L_i \) terms in eq. 6.4 are the depolarization factors and are exclusively functions of the shape of the ellipsoid. The behavior is such that;

\[
L_4 + L_2 + L_3 = 1
\]  (6.5)

In the case of spheroids, which the derivation will soon be restricted to, \( L_2 = L_3 \) so only one depolarization parameter needs to solved for. Fricke [95] provided an expression for \( M \) which is equal to \( L_2 + L_3 \). The expression is reworked here to give \( L_1 \).

\[
L_1 = 1 - \frac{\psi}{2} \frac{\sin(2\psi)}{\sin^3(\psi)} \cos(\psi) \quad \text{for } a < b \quad \text{where } \psi = \cos \left( \frac{a}{b} \right)
\]

\[
L_4 = 1 - \left[ \frac{1}{\sin^2(\psi')} - \frac{1}{2 \sin^3(\psi')} \ln \left( \frac{1 + \sin(\psi')} {1 - \sin(\psi')} \right) \right] \quad \text{for } a > b \quad \text{where } \psi' = \cos \left( \frac{b}{a} \right)
\]  (6.6)

\[
L_4 = \frac{1}{3} \quad \text{for } a = b
\]
In examining eq. 6.3 it is easy to recognize that the bracketed term is actually the dot product of the internal E-field of the ellipsoid and the field point vector (see Stratton section 3.27, eq. 35 [206]). This will prove extremely useful later on. Eq. 6.3 can then be rewritten in vector form.

$$\phi^{+f} = -\vec{E}_0 \cdot \vec{r} + \frac{abc}{3r^3} \frac{(\sigma_1 - \sigma_0)}{\sigma_0} (\vec{E}_i \cdot \vec{r})$$  \hspace{1cm} (6.7)$$

An important point to make here is that the internal E-field vector is not normally parallel to the imposed uniform E-field due to the shape factor of the ellipsoid. However, there are two instances in which it will be. This is either when the imposed E-field aligns with one of the semi-principle axes or when the ellipsoid is a sphere, in which case the two E-fields will always be parallel regardless of the imposed E-field’s orientation.

An important check on eq. 6.7 is the simplification for the spherical case ($a = b = c = R$). In this scenario the parameters $D_i$ are all equal as shown.

$$D_x = D_y = D_z = 1 + \frac{\sigma_1 - \sigma_0}{3\sigma_0}$$  \hspace{1cm} (6.8)$$

Simplifying eq. 6.7 gives the well-known expression for a sphere in a uniform E-field.

$$\phi^+ = -\vec{E}_0 \cdot \vec{r} + \frac{1}{2\sigma_0 + \sigma_1} \frac{R^3}{r^3} (\vec{E}_i \cdot \vec{r})$$  \hspace{1cm} (6.9)$$

The final term in parenthesis of eq. 6.9 reduced to the dot product of the imposed E-field and the field point vector since all the denominators of the bracketed term in eq. 6.3 were equal, for a sphere, allowing the common denominator to be pulled out of the brackets. Eq. 6.9 shows that even after the far field simplification is applied, the exact solution for the spherical particle is
This is because the far field approximation makes use of the characteristic where, in the elliptical coordinate system, the $\xi = \text{constant}$ surface approaches the shape of a sphere as $\xi$ becomes very large. Due to the nature of the simplification it still provides the exact solution for the external potential field at any distance from the particle for, and only for, the spherical case (when $a = b = c$). All other ellipsoidal shapes will have far field approximations which are valid only very far from the embedded particle.

As mentioned previously, the remainder of the derivation will be restricted to spheroidal shaped inclusions, i.e. $a \neq b = c$. This makes the far field potential expression:

$$\phi^f = -E_0 \cdot \bar{r} + \frac{ab^2}{3r^3} \left( \frac{\sigma_1 - \sigma_0}{\sigma_0} \right) (\bar{E}_i \cdot \bar{r})$$  \hspace{1cm} (6.10)

Where;

$$\bar{E}_i \cdot \bar{r} = \frac{E_{0x} x}{D_x} + \frac{E_{0y} y + E_{0z} z}{D_y}$$  \hspace{1cm} (6.11)

6.2.2 Orientation and Averaging

With an expression obtained for the far field potential for a spheroid particle inclusion in an infinite medium the next step can be taken involving averaging the far field potential and internal E-field vector for a collection of spheroids oriented according to a distribution function. This problem requires introducing a new fixed coordinate system, deemed the inertial coordinate system, since the equations in the previous section were developed for a coordinate system relative to the spheroid. This inertial reference frame will also be the coordinate system which
the distribution function will be defined relative to. Figure 6.3 shows the inertial reference frame with one of the spheroids oriented relative to it in terms of a polar ($\theta$) and azimuthal ($\beta$) angle. Note that the x-axis is the (major) axis of symmetry for the spheroid.

Using figure 6.3 the imposed E-field vector and the field point can readily be defined in terms of the inertial coordinate system.

$$\vec{E}_0 = E_{0\zeta} \hat{i}_\zeta + E_{0\eta} \hat{i}_\eta + E_{0\rho} \hat{i}_\rho$$  \hspace{1cm} (6.12)$$

$$\vec{r} = r_{\zeta} \hat{i}_\zeta + r_{\eta} \hat{i}_\eta + r_{\rho} \hat{i}_\rho$$  \hspace{1cm} (6.13)$$

Figure 6.3 [196]: Visual representation of the inertial reference frame. The x-axis of the spheroid affixed coordinate system is oriented relative to the inertial frame using spherical coordinates.
Since these two vectors have nothing to do with the inclusions they remain constant during the averaging process. In order to define the internal E-field vector in terms of the inertial reference frame a relationship between the coordinate system attached to the spheroid (x, y, z) and the fixed reference frame (ζ, η, ρ) needs to be defined. Starting with the x-axis the unit vector can be written in terms of the ζ, η, ρ coordinates.

\[ \hat{i}_x = \sin \theta \cos \beta \hat{i}_\zeta + \sin \theta \sin \beta \hat{i}_\eta + \cos \theta \hat{i}_\rho \]  
(6.14)

Due to the axis of symmetry of the spheroid the unit vectors for the y and z-axis only need to be defined such that they are orthogonal to the x-axis in the inertial coordinate system. Other than that restriction their specific orientation is irrelevant as it will not affect the end result. This is because once the x-axis of the spheroid is fixed relative to the imposed E-field, rotating it about the x-axis will not alter the physics of the system due to the symmetry of the spheroid about its major axis. Taking advantage of this behavior the y unit vector can be defined as the cross product between the x unit vector and the ρ unit vector divided by the resulting magnitude.

\[ \hat{i}_y = \frac{\hat{i}_\rho \times \hat{i}_x}{|\hat{i}_\rho \times \hat{i}_x|} = -\sin \beta \hat{i}_\zeta + \cos \beta \hat{i}_\eta \]  
(6.15)

Finally, to ensure there is an orthogonal triplet the z unit vector can be obtained as the cross product of the x and y unit vectors.

\[ \hat{i}_z = \hat{i}_x \times \hat{i}_y = -\cos \theta \cos \beta \hat{i}_\zeta - \cos \theta \sin \beta \hat{i}_\eta + \sin \theta \hat{i}_\rho \]  
(6.16)

Using the above definitions of the x, y, and z unit vectors the internal E-field vector can be rewritten in terms of the inertial coordinate system.
\[
\bar{E}_i = \frac{E_0 \cdot \hat{i}_x}{D_x} \hat{i}_x + \frac{1}{D_y} \left( (\bar{E}_0 \cdot \hat{i}_y) \hat{j}_y + (\bar{E}_0 \cdot \hat{i}_z) \hat{k}_z \right)
\]

\[
= \left[ E_0 \zeta \left( \frac{\sin^2 \theta \cos^2 \beta}{D_x} + \frac{\sin^2 \beta + \cos^2 \theta \cos^2 \beta}{D_y} \right) + E_0 \eta \sin^2 \theta \sin \beta \cos \beta \left( \frac{1}{D_x} - \frac{1}{D_y} \right) \right] \hat{i}_x
\]

\[
+ E_0 \rho \sin \theta \cos \theta \cos \beta \left( \frac{1}{D_x} - \frac{1}{D_y} \right) \hat{i}_z + \left[ E_0 \zeta \sin^2 \theta \sin \beta \cos \beta \left( \frac{1}{D_x} - \frac{1}{D_y} \right) \right] \hat{i}_x
\]

\[
+ E_0 \rho \sin \theta \cos \theta \cos \beta \left( \frac{1}{D_x} + \frac{1}{D_y} \right) + E_0 \eta \sin \theta \cos \theta \sin \beta \left( \frac{1}{D_x} - \frac{1}{D_y} \right) \hat{i}_y
\]

\[
+ \left[ E_0 \zeta \sin \theta \cos \theta \cos \beta \left( \frac{1}{D_x} - \frac{1}{D_y} \right) + E_0 \eta \sin \theta \cos \theta \sin \beta \left( \frac{1}{D_x} - \frac{1}{D_y} \right) + E_0 \rho \left( \frac{\cos^2 \theta}{D_x} + \frac{\sin^2 \theta}{D_y} \right) \right] \hat{i}_y
\]

(6.17)

With an expression obtained for the internal E-field vector in terms of the fixed reference frame obtained, all the requirements have been met to begin averaging the far field potential and internal E-field vector for a collection of spheroids. In order to orient the spheroids a distribution function must be introduced. This function, written as \( P(\theta, \beta) \), can be characterized by imagining a unit sphere which encloses the origin of the inertial coordinate system. Each spheroid’s x-axis (associated with the major axis) will intercept the unit sphere at a different point. The distribution function can be defined as the number of intersections of the x-axes of the different spheroids per unit surface area of the sphere. With this being the case the distribution function must follow the identity given by eq. 6.18 where \( N \) is the total number of spheroids.

\[
N = \int_A P(\theta, \beta) \sin \theta d\theta d\beta
\]

(6.18)
In the present study we restrict the distribution function to be symmetric about the polar axis making it invariant when changing the azimuthal angle, i.e. $\partial P/\partial \beta = 0$. The following specific distribution is then introduced.

$$P(\theta) = \begin{cases} 
K(m)\sin^{-m} \theta & \text{for } m \leq 0 \\
K(m)|\cos^{m} \theta| & \text{for } m > 0 
\end{cases}$$

(6.19)

The function $K(m)$ is simply a normalization constant ensuring that eq. 6.14 is true. Figure 6.4 shows the distribution function for a few values of the parameter $m$ as well as one special case, referred to as the equal angular distribution ($m = 1$).
Figure 6.4 [196]: The distribution function, eq. 19, as a function of m. a) Negative values of m produce a peak of increasing intensity with increasing m at 90° while b) positive values produce peaks at 0 and 180°. The equal angular distribution (m = 1) has peaks of infinity at 0 and 180°. Note: the peak of m = -2 is smaller than that of m = 2 due to the presence of the sine term in eq. 18.

As shown in figure 6.4, m = 0 gives an isotropic distribution. This means that the area based density of the collection of spheroid’s x-axes will be a constant over the surface of the previously
described unit sphere. As \( m \) increases it can be observed from figure 6.4b that the spheroids tend to align with the polar axis of the fixed reference frame. As \( m \) decreases the opposite trend is observed in figure 6.4a where all the spheroids tend to orient towards the \( \zeta, \eta \) plane with no preferential orientation in that plane (due to the distribution function being independent of \( \beta \)).

The mentioned equal angular distribution corresponds to \( P(\theta) = \frac{N}{2\pi} |\cos \theta| \). The reason it is referred to as the equal angular distribution is due to the density of \( x \)-axis intersections per angular coordinate being constant in this special case as opposed to the density per unit area of the unit sphere being constant. Combining eq. 6.18 and 6.19 yields the following relation which can be used to calculate the normalization constant, \( K(m) \).

\[
\frac{N}{2\pi} = \frac{K(m)}{2\pi} \int_0^\pi \sin^{1-m} \theta d\theta \quad \text{for} \quad m \leq 0
\]
\[
K(m) = \frac{1}{2\pi} \int_0^\pi |\cos^m \theta| \sin \theta d\theta \quad \text{for} \quad m > 0
\]  

(6.20)

Using the above equations the average, \( \langle \cdot \rangle \), of any arbitrary vector or scalar, \( A \), can be defined.

\[
\langle A \rangle = \frac{1}{N} \int_0^{2\pi} \int_0^\pi P(\theta) A \sin(\theta) d\theta d\beta = \frac{K(m)}{N} \int_0^{2\pi} \int_0^\pi A \sin^{1-m}(\theta) d\theta d\beta \quad \text{for} \quad m \leq 0
\]
\[
= \frac{K(m)}{N} \int_0^{2\pi} \int_0^\pi A |\cos^m \theta| \sin \theta d\theta d\beta \quad \text{for} \quad m > 0
\]  

(6.21)

Eq. 6.21 can be used to calculate the average far field potential or the internal E-field. In fact, taking the average of eq. 6.10 in the dilute limit (assuming the potentials of each spheroid do not interfere with each other) and assuming \( a \) and \( b/a \) are constant for each spheroid results in only the internal E-field varying. This implies a very direct relationship between the average internal E-field and the average far field potential given by eq. 6.22 where the average internal E-field vector may be calculated via eq. 6.21.
\[
\langle \phi^+ f \rangle = -E_0 \cdot \hat{r} + \frac{ab^2}{3\rho^3} \left( \frac{\sigma_1 - \sigma_0}{\sigma_0} \right) (\langle \bar{E}_i \rangle \cdot \hat{r})
\]  
\hspace{1cm} (6.22)

With this in mind the focus will be directed towards calculating the average internal E-field vector. This average can be calculated by inserting eq. 6.17 and 6.19 into eq. 6.21. The result is different for each \( m \). It is possible to organize these results and generalize the equations such that the average can be expressed as a function of \( m \) which is true for any value of \( m \).

\[
\langle \bar{E}_i \rangle = \begin{cases} 
\frac{1}{3-m} \left[ \frac{1}{2} \left( \frac{2-m}{D_x} + \frac{4-m}{D_y} \right) (E_{0\zeta} \hat{\zeta} + E_{0\eta} \hat{\eta}) + \frac{1}{m+3} \left( \frac{1}{D_x} + \frac{m+2}{D_y} \right) (E_{0\varphi} \hat{\varphi} + E_{0\rho} \hat{\rho}) \right] & \text{for } m \leq 0 \\
\frac{1}{m+3} \left[ \frac{1}{D_x} + \frac{m+2}{D_y} \right] (E_{0\zeta} \hat{\zeta} + E_{0\eta} \hat{\eta}) + \frac{1}{D_x} + \frac{2}{D_y} \right] (E_{0\varphi} \hat{\varphi} + E_{0\rho} \hat{\rho}) & \text{for } m \geq 0 
\end{cases}
\]
\hspace{1cm} (6.23)

As expected, eq. 6.23 shows that, in general, the average internal E-field vector is not parallel to the imposed E-field. They will be parallel though when either the spheroids are spheres, or the imposed E-field aligns with the \( \zeta, \eta \) plane or the \( \rho \)-axis (a trait taken advantage of later on). For the purpose of convenient notation the average internal E-field vector is generalized where \( \langle \bar{E}_i \rangle_j \) represents the \( j \) component of the average of the \( \bar{E}_i \) vectors.

\[
\langle \bar{E}_i \rangle_j = G_j (m, D_x, D_y) E_{0j} \hat{i}_j
\]  
\hspace{1cm} (6.24)

Where;

\[
G_{\zeta} = G_{\eta} = \begin{cases} 
\frac{1}{2(3-m)} \left( \frac{2-m}{D_x} + \frac{4-m}{D_y} \right) & \text{for } m \leq 0 \\
\frac{1}{m+3} \left( \frac{1}{D_x} + \frac{m+2}{D_y} \right) & \text{for } m \geq 0 
\end{cases}
\]
\[ G_{\rho} = \begin{cases} \frac{1}{3-m} \left( \frac{1}{D_x} + \frac{2-m}{D_y} \right) & \text{for } m \leq 0 \\ \frac{1}{m+3} \left( \frac{m+1}{D_x} + \frac{2}{D_y} \right) & \text{for } m \geq 0 \end{cases} \]

For convenience some select values of the functions are tabulated in table 6.1

Table 6.1 [196]: Summary of results for average internal E-field vector.

<table>
<thead>
<tr>
<th>m</th>
<th>j</th>
<th>( G_j(m,D_x,D_y) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 (isotropic)</td>
<td>( \zeta, \eta )</td>
<td>( \frac{1}{3} \left( \frac{1}{D_x} + \frac{2}{D_y} \right) )</td>
</tr>
<tr>
<td></td>
<td>( \rho )</td>
<td>( \frac{1}{3} \left( \frac{1}{D_x} + \frac{2}{D_y} \right) )</td>
</tr>
<tr>
<td>-2</td>
<td>( \zeta, \eta )</td>
<td>( \frac{1}{5} \left( \frac{2}{D_x} + \frac{3}{D_y} \right) )</td>
</tr>
<tr>
<td></td>
<td>( \rho )</td>
<td>( \frac{1}{5} \left( \frac{1}{D_x} + \frac{4}{D_y} \right) )</td>
</tr>
<tr>
<td>2</td>
<td>( \zeta, \eta )</td>
<td>( \frac{1}{5} \left( \frac{1}{D_x} + \frac{4}{D_y} \right) )</td>
</tr>
<tr>
<td></td>
<td>( \rho )</td>
<td>( \frac{1}{5} \left( \frac{3}{D_x} + \frac{2}{D_y} \right) )</td>
</tr>
<tr>
<td>-\infty (fan-like)</td>
<td>( \zeta, \eta )</td>
<td>( \frac{1}{2} \left( \frac{1}{D_x} + \frac{1}{D_y} \right) )</td>
</tr>
<tr>
<td></td>
<td>( \rho )</td>
<td>( \frac{1}{D_y} )</td>
</tr>
</tbody>
</table>
An important check on the above expressions for the internal E-field is whether they reduce to the correct expression when spheres are considered. In the case of a sphere the average internal E-field should simply be the expression for a single sphere in a uniform E-field, independent of \( m \), and it should be parallel to the imposed E-field. Inspecting eq. 6.23 results in the following expression for the average internal E-field in the case of spherical inclusions.

\[
\langle \vec{E}_i \rangle = \left( 1 + \frac{(\sigma_i - \sigma_0)}{3\sigma_0} \right)^{-1} \vec{E}_0
\]

(6.25)

Eq. 6.25 is equivalent to the internal E-field vector given by Stratton [206] (section 3.24, eq. 30) for a single sphere embedded in an infinite medium with a uniform imposed E-field.

### 6.2.3 Dilute Limit Approximations

With an expression for the average internal E-field for the defined distribution function in hand the next step in the development is to employ the dilute limit approximations of the
effective conductivity as outlined by Maxwell and Maxwell-Garnett [93,94]. Beginning with Maxwell, the general concept is outlined in figure 6.5.

Figure 6.5 [196]: Equating of the far field potentials at point r for the mixture of interest (top) and the pseudo homogeneous material (bottom) as performed in the Maxwell approach.
The top picture in figure 6.5 is the system of interest. It shows a collection of inclusions randomly distributed in a pseudo spherical control volume. The matrix material extends throughout the pseudo control volume and beyond it in all directions to infinity. The lower picture shows a single sphere made of a pseudo material of conductivity $\sigma_m$ and volume $V_S$ where the volume of this sphere is equal to the volume of the pseudo sphere in the top picture. The effective conductivity of the top mixture can be obtained by equating the far field potentials of both scenarios at the same point in space.

$$-\vec{E}_0 \cdot \vec{r} + \frac{Nab^2}{3r^3} \left( \frac{\sigma_1 - \sigma_0}{\sigma_0} \right) \langle \vec{E}_i \rangle \cdot \vec{r} = -\vec{E}_0 \cdot \vec{r} + \frac{R^3}{r^3} \vec{E}_0 \cdot \vec{r} \left[ \frac{\sigma_m - \sigma_0}{\sigma_m + 2\sigma_0} \right]$$

(6.26)

The immediate question comes to mind as to whether or not eq. 6.26 is appropriate because the average far field potential expression has been derived by assuming all the inclusions are centered at the origin when, in fact, they are not in figure 6.5. However, if one thinks in terms of the far field position the approximation is appropriate. Since the magnitude of $r$ is much greater than the distance between any individual inclusion and the origin it effectively appears as though all the inclusions are located at the origin when observing them from the field point position. This also raises questions about the interference of the potential fields but, as will be discussed later on, the inclusions are far enough from each other so they do not interfere. Essentially, in the current model the inclusions are extremely far apart from each other and the field point is incredibly far away from the space that they all occupy.

Another important issue to point out with eq. 6.26 is the shape of the control volume. In order for the equality to be true, the directivity pattern of the mixture and the sphere made of the pseudo material $\sigma_m$ must be the same. This will always be true since the pseudo material is allowed to be anisotropic however, solving for the effective conductivity will only be
straightforward when the average internal E-fields and the imposed E-fields are aligned. This will occur during those special cases described previously, when the imposed E-field is aligned with the \( \rho \)-axis or the \( \zeta, \eta \) plane. To determine the effective conductivity, which is a tensor containing only diagonal nonzero terms, the imposed E-field is aligned with each of the axes of the inertial coordinate system one at a time. Any arbitrary E-field can be considered by breaking it up into its components relative to the inertial coordinate system. By taking each component in turn, the corresponding average E-field in the material is co-linear with the imposed E field.

Using Ohm’s law, the corresponding currents \( (J_\zeta, J_\eta, \text{ and } J_\rho) \) can be calculated by the following and are co-linear with the imposed E field:

\[
\langle J_\zeta \rangle = \sigma_{m}^{\zeta \zeta} \langle \vec{E}_\zeta \rangle \\
\langle J_\eta \rangle = \sigma_{m}^{\eta \eta} \langle \vec{E}_\eta \rangle \\
\langle J_\rho \rangle = \sigma_{m}^{\rho \rho} \langle \vec{E}_\rho \rangle
\] (6.27)

Or, in matrix form:

\[
\langle \vec{J} \rangle = [\sigma_{m}] \langle \vec{E} \rangle
\] (6.28)

Each of the conductivity scalars in eq. 6.27 then represents a diagonal component in the effective conductivity tensor, with the off diagonal terms being equal to zero as given by eq. 6.29. The resulting current for an arbitrarily oriented imposed E-field can be calculated by vectorially adding the components \( J_\zeta, J_\eta, \text{ and } J_\rho \). In essence, the inertial coordinate system axes can be considered as the principal axes of the effective conductivity tensor for the distribution function form chosen here.
\[ \tilde{\sigma}_m = \begin{bmatrix} \frac{\epsilon^\infty}{m} & 0 & 0 \\ 0 & \sigma_{\eta\eta} & 0 \\ 0 & 0 & \sigma_{\rho\rho} \end{bmatrix} \]  

(6.29)

Taking the above logic, it is easy to solve for the effective conductivity using eq. 6.24 and 6.26.

\[
\sigma_{jjm} = \sigma_0 \frac{2f}{3} \left( \frac{\sigma_1 - \sigma_0}{\sigma_0} \right) G_j + 1 \\
1 - \frac{f}{3} \left( \frac{\sigma_1 - \sigma_0}{\sigma_0} \right) G_j
\]  

(6.30)

The volume fraction term, \( f \), appears by recognizing that \( f = NV_I/V_S = Nab^2/R^3 \).

As mentioned earlier, the Maxwell approach makes the restricting assumption of non-interference among the inclusions. In computing the potential fields, the inclusions were all assumed to be in an infinite medium of the matrix material of conductivity \( \sigma_0 \). This means the effective conductivity formula given by eq. 6.30 is only valid in extremely dilute mixtures so that the individual inclusions are extremely far apart from each other. The final section will attempt to modify eq. 6.30, as well as the Maxwell-Garnett result which is also a dilute limit approximation, to deal with this limitation by applying the Bruggeman unsymmetrical approach.

Before proceeding to the Maxwell-Garnett treatment, it is useful to first check the limit of spherical inclusions for eq. 6.30. In this limit we would expect eq. 6.30 to reduce to the well-known scalar effective conductivity equation derived by Maxwell. In this scenario, the depolarization factors are all equal to 1/3 so once again eq. 6.8 applies. Upon a straightforward substitution of the eq. 6.8 into eq. 6.30 the Maxwell equation is indeed obtained.

\[
\sigma_m = \sigma_0 \frac{2\sigma_0 + \sigma_1 + 2f_i (\sigma_1 - \sigma_0)}{2\sigma_0 + \sigma_1 - f_i (\sigma_1 - \sigma_0)}
\]  

(6.31)
Next, the Maxwell-Garnett approach is taken to obtain another expression for the effective conductivity in the dilute limit. In this approach, the behavior of the material is considered from within the mixture as opposed to going to the far field as illustrated by figure 6.6.

\[
\mathbf{J}_i = \sigma_i \mathbf{E}_i
\]

\[
\langle \mathbf{J} \rangle = \sigma_m \langle \mathbf{E} \rangle
\]

Figure 6.6 [196]: Maxwell-Garnett approach to solving for the effective conductivity. In this scenario, details on the top are used to calculate the average flux, E-field, and the effective conductivity in the pseudo-material on the bottom.
In figure 6.6 the details in the mixture are utilized to calculate the approximate average flux and E-field existing within the mixture which are then, in turn, used to calculate the effective conductivity. The average E-field and flux are taken as simple volumetric averages as shown below.

\[
\langle E \rangle = (1 - f)E_0 + f\langle E_i \rangle 
\]

(6.32)

\[
\langle J \rangle = \sigma_0(1 - f)E_0 + f\sigma_1\langle E_i \rangle 
\]

(6.33)

It is worth noting that eq. 6.32 takes the weighted average of the E-field, as done in [205], by assuming that the E-field within the mixture at all points surrounding the inclusions is \( E_0 \). This assertion is generally only reasonable in the dilute limit condition. Using the above definitions with \( \langle J \rangle = \tilde{\sigma}_m\langle E \rangle \) the effective conductivity can be calculated.

\[
\sigma_m = \sigma_0 + f(\sigma_1 - \sigma_0)\frac{\langle E_i \rangle}{(1 - f)E_0 + f\langle E_i \rangle} 
\]

(6.34)

The same approach can now be taken as was used in the Maxwell approach to determine the components of the effective conductivity matrix (i.e. applying the imposed E-field along each of the inertial coordinate system axes thereby aligning \( \langle E_i \rangle \) and \( E_0 \)). The result is given by eq. 6.35.

\[
\sigma_{mj}^{ij} = \sigma_0 + f(\sigma_1 - \sigma_0)\frac{G_j}{(1 - f) + fG_j} 
\]

(6.35)

It is important to note that eq. 6.35 also reduces to eq. 6.31 for spherical inclusions. The Maxwell and Maxwell-Garnett approaches give the same result for spheres but not for spheroids.
When the limits of each are analyzed it is clear that the Maxwell-Garnett result has the desired limits at $f = 0$ and $1$ while the Maxwell result does not necessarily have the correct limit at $f = 1$ when shape and anisotropy are considered. While this may seem to make a case that the Maxwell-Garnett approach is superior, the Maxwell-Garnett approach is also subject to the dilute limit and thus the higher volume fractions of inclusions violates the assumptions of the model just as with the Maxwell approach. The next section attempts to deal with this limit and also shows that, to a first order approximation, the Maxwell and Maxwell-Garnett results are actually equivalent.

6.2.4 Extension to Higher Volume Fractions

Bruggeman employed the unsymmetrical treatment in an attempt to deal with the dilute limit restriction by recursively operating within the dilute to build up the total volume fraction of the inclusion material. The process starts with a pure matrix material then adds in a small amount of inclusions in line with the dilute limit assumption. The effective conductivity of the resulting mixture is then computed via one of the dilute limit approximations and resulting pseudo material with that effective conductivity is then treated as the matrix in a new problem where another small amount of inclusion material is added. This process can be repeated over and over to obtain any volume fraction of inclusion material desired. Figure 6.7 illustrates the first few discrete steps of the process for the single inclusion type.
Figure 6.7 [196]: First few steps in Bruggeman’s unsymmetrical formulation considering a single type of inclusion.

This concept can be performed mathematically by differentiation of the dilute limit approximations (eq. 6.30 and 6.35) where df represents the differential volume fraction of added inclusion.
\[ \frac{df}{d} = \frac{3\sigma_0}{G_j(\sigma_1 - \sigma_0)} \left[ \frac{\sigma_{m}^{\text{jj}} - \sigma_0}{\sigma_{m}^{\text{jj}} + 2\sigma_0} \right] \]  
\[ (6.36) \]

\[ df = d \left[ \frac{\sigma_{m}^{\text{jj}} - \sigma_0}{\sigma_{m}^{\text{jj}} - \sigma_0 + G_j(\sigma_1 - \sigma_{m}^{\text{jj}})} \right] \]  
\[ (6.37) \]

The right hand sides of the equations are differentiated with respect to the effective conductivity. Amazingly, carrying out the differentiation, and taking the limit as \( df \to 0 \) (\( \sigma_0 = \sigma_{m}^{\text{jj}} \)), for either dilute limit approximation results in the same equation.

\[ df = \frac{d\sigma_{m}^{\text{jj}}}{G'(\sigma_1 - \sigma_{m}^{\text{jj}})} \]  
\[ (6.38) \]

Where the \( G' \) variable refers to the new definitions of \( D_x \) and \( D_y \):

\[ D_x' = 1 + \frac{(\sigma_1 - \sigma_{m}^{\text{jj}})}{\sigma_{m}^{\text{jj}}} L_1 \]  
\[ D_y' = 1 + \frac{(\sigma_1 - \sigma_{m}^{\text{jj}})}{\sigma_{m}^{\text{jj}}} L_2 \]  
\[ (6.39) \]

The reason for this result can be illuminated by considering the other way this could have been accomplished which involves expanding eq. 6.30 and 6.35 in a Taylor series and retaining only first order terms. It turns out that the Taylor series expansion to the first order is the same for either the Maxwell or Maxwell-Garnett expressions.

A change of variables is required in eq. 6.38. Consider again the discrete scenario described in figure 6.7. Due to the recursive nature of the BUT, every time some new inclusion material is added in one of the steps, some inclusion and original matrix material (of conductivity
\( \sigma_0 \) is replaced. To correct for this, and represent the volume fraction of pure inclusion material, an expression is introduced which represents the process described.

\[
(1 - \alpha) d'f = d\alpha \tag{6.40}
\]

Using eq. 6.40 the differential equation given by eq. 6.38 can be rewritten.

\[
\frac{d\alpha}{1-\alpha} = \frac{d\sigma_{m}^{ij}}{G'_j \left( \sigma_1 - \sigma_{m}^{ij} \right)} \tag{6.41}
\]

The resulting BUT formulation given by eq. 6.41 can be solved analytically using partial fraction expansion or numerically subject to \( \alpha = 0, \sigma_{m}^{ij} = \sigma_0 \). The numerical method is favored here since the analytical solution is somewhat unwieldy and implicit in nature.

Once again we perform the check on eq. 6.41 in the limit of spherical inclusions. For this case we expect eq. 6.41 to reduce to Bruggeman’s original unsymmetrical equation. In this scenario the depolarization factors are all equal to 1/3 so;

\[
D'_x = D'_y = D'_z = D' = 1 + \frac{(\sigma_1 - \sigma_{m})}{3\sigma_{m}} \tag{6.42}
\]

Substituting the above relations into eq. 6.41 yields the differential equation

\[
\frac{d\alpha}{(1-\alpha)} = \frac{2\sigma_{m} + \sigma_1}{3\sigma_{m} \left( \sigma_1 - \sigma_{m} \right)} d\sigma_{m} \tag{6.43}
\]

The result given by eq. 6.43 can be analytically solved, subject to the condition \( \alpha = 0, \sigma_{m} = \sigma_0 \), and results in the well-known Bruggeman unsymmetrical formula, as required.
\[1 - \alpha = \frac{\frac{1}{\sigma_0^3} (\sigma_m - \sigma_1)}{\frac{1}{\sigma_m^3} (\sigma_0 - \sigma_1)}\]  

6.2.5 Discussion and Observations of Results for a Single Inclusion Type

In order to look into the effects of orientation based anisotropy on the effective conductivity the results of eq. 6.44 are plotted for select cases of \(m = -\infty, -2, 0, 1, 2, \infty\) (see in table 6.1). The cases studied include oblate and prolate spheroids in the case of excellent conductor and insulating inclusions as shown in figures 6.8 and 6.9 below. Results are normalized by the matrix conductivity and the parameter \(b/a\) represents the aspect ratio, minor axis to major axis, of the spheroid (\(b/a < 1\) prolate; \(b/a > 1\) oblate; \(b/a = 1\) sphere).
Figure 6.8 [196]: Normalized $\zeta$, $\eta$ component anisotropic effective conductivities for oblate ($b/a > 1$) and prolate ($b/a < 1$) spheroids in the case of highly conducting and insulating inclusions. From top left to bottom right: $b/a = 20, \sigma_1/\sigma_0 = 100; b/a=1/20, \sigma_1/\sigma_0 = 100; b/a=200, \sigma_1/\sigma_0 = 1 \times 10^{-10}; b/a=1/20, \sigma_1/\sigma_0 = 1 \times 10^{-10}$. Legend: $m = -\infty$ (triangles), $m = -2$ (squares), $m = 0$ (solid line), $m = 2$ (circles), $m = \infty$ (diamonds), equal angular (dotted line).
Figure 6.9 [196]: Normalized ρ component anisotropic effective conductivities for oblate (b/a > 1) and prolate (b/a < 1) spheroids in the case of highly conducting and insulating inclusions. From top left to bottom right: b/a = 20, \( \sigma_1/\sigma_0 = 100 \); b/a=1/20, \( \sigma_1/\sigma_0 = 100 \); b/a=20, \( \sigma_1/\sigma_0 = 1\times10^{-10} \); b/a=1/20, \( \sigma_1/\sigma_0 = 1\times10^{-10} \). Legend: \( m = -\infty \) (triangles), \( m = -2 \) (squares), \( m = 0 \) (solid line), \( m = 2 \) (circles), \( m = \infty \) (diamonds), equal angular (dotted line).

The results shown in the above figures are somewhat extreme cases, chosen for the purpose of emphasizing the effects of anisotropy by pushing the inclusion shapes towards either rods or
disks with either highly conducting or insulating properties. As the conductivity ratio of the matrix to inclusion approaches 1 or the shape of the inclusions approach spheres the effects of anisotropy will naturally diminish. For the purpose of exploring trends the extreme cases plotted provide a convenient means to highlight the behavior and show that the effects of anisotropy can be significant due to the large variation between the isotropic results and the various anisotropic cases. The solid line \((m = 0)\) and the diamonds \((m = \infty)\) in figures 6.8 and 6.9 represent the cases studied by Giordano for isotropic and perfectly aligned spheroids [205].

For the purposes of the following discussion, the degree of anisotropy is being measured as the magnitude of the difference between \(\sigma_{\rho\rho}\) and \(\sigma_{\zeta\zeta}, \sigma_{\eta\eta}\). As shown in figures 6.8 and 6.9 the case of perfectly oriented spheroids \((m = \infty)\) exhibits the greatest degree of anisotropy with the fan-like distribution \((m = -\infty)\) giving the second largest degree of anisotropy. This result makes sense given the fact that the \(m = -\infty\) distribution has all the major axes of the spheroid inclusion lying within the \(\zeta, \eta\) plane but with no preferred orientation in that plane (due to the distribution function being independent of \(\beta\)) while the \(m = \infty\) distribution, as suggested above, has all the spheroids completely aligned with each other and the \(\rho\)-axis. This same line of reasoning extends to the \(m = -2\) and \(m = 2\) distributions as they are both equal increments towards the aforementioned extremes.

An interesting result shown in figures 6.8 and 6.9 is that some of the resulting effective conductivities for certain components are equal for different distributions. Specifically, \(\sigma_{\zeta\zeta}, \sigma_{\eta\eta} = \sigma_{\rho\rho}\) for \(m = \infty\) and \(-\infty\) respectively, \(\sigma_{\zeta\zeta}, \sigma_{\eta\eta} = \sigma_{\rho\rho}\) for \(m = 2\) and \(-2\) respectively, and \(\sigma_{\zeta\zeta}, \sigma_{\eta\eta} = \sigma_{\rho\rho}\) for \(m = -\infty\) and the equal angular distribution respectively. In the case of \(\sigma_{\zeta\zeta}, \sigma_{\eta\eta} = \sigma_{\rho\rho}\) for \(m = 2\) and \(-2\) it is clear, when examining the definition of \(G_j\) in eq. 6.24, that this equality will hold for any value, \(A\), where \(\sigma_{\zeta\zeta}, \sigma_{\eta\eta} = \sigma_{\rho\rho}\) for \(m = A\) and \(-A\) respectively. This includes the case of \(\sigma_{\zeta\zeta},\)
\( \sigma_{\eta \eta} = \sigma_{\rho \rho} \) for \( m = \infty \) and \(-\infty\) respectively. The occurrence of these equalities may be attributed, in part, to the selection of the distribution function which is not the only distribution function which can be used. However, the coincidence does provide an opportunity to explore some of the behavior of the derived equations. In attempting to understand the cause of the equality, the physical picture of the system can be analyzed by considering a point of view of the mixture parallel to the axis related to the directional component of the effective conductivity tensor of interest. In the case of \( \sigma_{\zeta \zeta} \), \( \sigma_{\eta \eta} = \sigma_{\rho \rho} \) for \( m = \infty \) and \(-\infty\) respectively, one may consider a line of view for the \( m = \infty \) case which is along the \( \zeta \)-axis and a line of view for the \( m = -\infty \) case which is along the \( \rho \)-axis as depicted in figure 6.10a.

Figure 6.10 [196]: a) visual representation of inclusion distribution from \( \zeta \)-axis for \( m = \infty \) and from the \( \rho \)-axis for \( m = -\infty \). b) Visual representation of inclusion distribution from \( \zeta \)-axis for \( m = -\infty \) and from the \( \rho \)-axis for the equal angular distribution. In these representations all inclusions
are centered at the origin for viewing purposes. The inclusions shown here are prolate (the major axis is the long axis).

For the $m = \infty$ case, along the described viewing line, one would expect to see a “forest” of spheroids whose major axes all align perpendicular to the viewing line. In the $m = -\infty$ case, again all the major axes of the spheroids are perpendicular to the viewing line described but with no preferential alignment about the viewing line. Since the predicted effective conductivity components are equal, it implies that this relative alignment of the major axes of the spheroids does not affect the conductivity. The same line of reasoning can be applied for any $A$, such that $\sigma_{\zeta\zeta}, \sigma_{\eta\eta} = \sigma_{\rho\rho}$ for $m = A$ and $-A$ respectively since both cases are equal incriminates towards the aforementioned extremes. For the final case involving $m = -\infty$ and the equal angular distribution consider viewing lines along the $\zeta$-axis and $\rho$-axis respectively of the mixtures being considered (see figure 6.10b). For $m = -\infty$, once again all the major axes of the spheroids lie within the $\zeta, \eta$ plane where the current viewing line has the major axes either perpendicular to the viewer or aligned in the extremes with an equal probability of any angle in between. For the equal angular case the same sort of distribution exists in terms of how the major axes of the spheroids are oriented either along the viewing line or perpendicular to it. However, similar to the previous comparisons, the spheroids do not have the same orientation about the viewing line. Once again it is this trait that appears to be the primary difference between the distributions and does not affect the calculated conductivity.

In studying the general trend of the calculated directional effective conductivities with varying volume fraction of inclusions it is apparent that some have more gradual behavior than
others. For highly conducting, disk-like, oblate spheroids, all of the directional conductivities change relatively rapidly in relation to \( \sigma_{pp} \) for \( m = \infty \) for increasing volume fraction. If one considers a line passing through the mixture parallel to the \( \rho \) direction for \( m = \infty \) the reason becomes clear. For highly conducting disk-like oblate spheroids which are perfectly aligned, passing through each in the \( \rho \) direction provides a boost in the conductivity over a razor thin distance. The overall increase in effective conductivity in that direction will only be substantially increased when there is a large amount of such inclusions added, i.e. higher volume fractions. For the same highly conducting disk-like oblate spheroids the most rapid change in conductivity with increasing volume fraction occurs for \( \sigma_{pp} \) for \( m = -\infty \) and \( \sigma_{\zeta\zeta}, \sigma_{\eta\eta} \) for \( m = \infty \). Here the relationship is almost linear and the conductivities are equal for the reasons already discussed. Also, in this instance the oblate spheroid’s major axes are all perpendicular to the direction being considered (the \( \rho \) direction for the \( m = -\infty \) distribution and anywhere in the \( \zeta, \eta \) plane for the \( m = \infty \) distribution). For very high aspect ratios, each oblate spheroid will provide a very thin pathway for conduction through the mixture in the direction being considered. This will create an almost linear transition from the matrix conductivity to the inclusion conductivity. The same geometrical arguments can be applied to the case of insulating, disk-like, oblate spheroids. In this case the most gradual decrease in conductivity occurs for \( \sigma_{pp} \) for \( m = -\infty \) and \( \sigma_{\zeta\zeta}, \sigma_{\eta\eta} \) for \( m = \infty \). In the case of \( \sigma_{pp} \) for \( m = \infty \), there is a sharp drop off in the calculated directional effective conductivity as volume fraction increases since, when considering again the \( \rho \) direction, each oblate spheroid has its major axis aligned with this direction, and thus, it’s “face” perpendicular to the direction being considered so it effectively acts as a non-conducting wall.

Turning to the case of the rod-like, prolate spheroids, with high conductivity, the distribution for \( m = \infty \) gives a linear dependence on \( \sigma_{pp} \). The same logic as with the oblate
spheroids applies. The highly conductive rods are running parallel to the direction being considered which gives as linear transition between the matrix conductivity and the inclusion conductivity. This applies to the insulating rods as well. For the highly conducting rods, there is a slow rise in the conductivity for $\sigma_\rho$ for $m = -\infty$ and $\sigma_\zeta$, $\sigma_\eta$ for $m = \infty$. Again, parallels can be drawn in comparison to the oblate spheroids. When the thin rods are perpendicular to the direction of interest, a great many of them will be required to build up the effective directional conductivity. What is unique in the case of the prolate, rod-like, spheroids in terms of general behavior has to do with the insulating inclusions. For insulating inclusions there is minimal anisotropy displayed in the results and there are no strongly decreasing conductivity trends with increasing volume fraction. This can be explained by realizing that the rods are unable to set up an effective barrier to current flow in the way that the disk shaped inclusions can.

Some final considerations should be made before moving on in regards to the limitations of the derived equations which are based on BUT. While BUT does attempt to deal with the dilute limit problem it is done in an approximate way. If the discrete process depicted by figure 6.7 is again considered, it is obvious that each time a new inclusion is embedded in the mixture, the interference with other inclusions and their detailed spatial relationship is left unaccounted for. The basis of the entire derivation is the Laplace solution for a single inclusion in an infinite medium. What’s interesting is that recursively operating in the dilute limit and applying Maxwell or Maxwell-Garnett’s result repeatedly does not break the spirit of EMT since all EMTs attempt to replace a complex heterogeneous mixture with a homogeneous pseudo one processing a single effective conductivity. However, the lack of rigorous accounting for interference and detailed spatial relationships of the inclusions must be kept in mind. This precludes the ability to account for percolation-like phenomena, which can be extremely important in mixtures processing large
discrepancies in the conductivities of their components. The percolating nature of a mixture can be important since, if there is no continuous pathway for electron conduction (in the case of electronic conductivity), the mixture can have effective zero conductivity for nonzero volume fractions of conductive material. Two mechanisms can give rise to percolation behavior in electronically conducting systems. These are geometric connectivity of the conducting phase and electron tunneling which occurs when electrons jump between conducting particles through a very thin insulating barrier. The tunneling effect is dominating when the geometric connectivity is essentially non-existent and can only occur over very short ranges, on the order of a few nanometers. Certain classes of materials actually do exhibit these properties such as carbon nanotube composites [207-209] or carbon black-polymer composites [210-212]. Toker et al. noted that the tunneling network and the geometric connectivity network are actually closely related due to the dominant contribution of the “nearest neighbor” tunneling between particles [213]. This implies a firm grasp of geometric connectivity percolation behavior will help address the issue of tunneling when tunneling is important. As stated previously eq. 6.41 does not account for percolation like behavior and should be used cautiously in the cases where percolation may be important. The magnitude of any resulting error is related to the mixture being considered but is expected to increase as the percolation limit is approached. Extension of the theories presented here are beyond the scope of this thesis but the future work section describes some preliminary work which is being done to attempt to analytically predict such behavior.
6.3 Extension of Anisotropic Effective Medium Theory to Account for N Inclusion Types

The purpose of this next section is to take the EMT developed in the previous section for a single inclusion type and extend it to N number of inclusion types contained in a continuous matrix of conductivity $\sigma_0$. In deriving the governing equations of section 6.2 one type of inclusion material of conductivity $\sigma_1$ was considered in a continuous matrix of conductivity $\sigma_0$. Here, N inclusions of unique conductivities $\sigma_k$ are considered to be embedded in a matrix of conductivity $\sigma_0$. In addition, each inclusion type will have its own unique orientation distribution, given by eq. 6.19, and spheroidal shape. For purposes which will become evident later, the distributions of each inclusion type are restricted to have the same principle axis.

6.3.1 Dilute Limit Approximations for N Inclusion Types

We begin the process in much the same way as before, by starting with the dilute limit approximation methods set forth by Maxwell and Maxwell-Garnett. Starting with the Maxwell approach, consider the physical picture of figure 6.5 but with multiple inclusion types. For multiple types of inclusions, the total far field potential can be expressed using the superposition principle where the second term on the right hand side of eq. 6.45 below is the summation of the contribution of the different inclusion types.

$$\phi_T^f = -\bar{E}_0 \cdot \bar{r} + \frac{1}{3r^3} \sum_{k=1}^{N} n_k a_k b_k^2 \left( \frac{\sigma_k - \sigma_0}{\sigma_0} \right) \left( \langle \bar{E}_i \rangle_k \cdot \bar{r} \right)$$  \hspace{1cm} (6.45)

This approach is reminiscent of the original Maxwell method for spherical inclusions. Ultimately, the total far field potential in the original Maxwell problem is taken to be the
summation of the individual contributions from each spherical inclusion in the suspension. As was the case before for a single inclusion type there are two spheres imagined (see figure 6.5). One sphere contains all the inclusions within a continuous matrix of conductivity $\sigma_0$ while the other sphere is made of a pseudo homogeneous material of conductivity $\sigma_m$. The matrix material of conductivity $\sigma_0$ extends beyond these spheres to infinity in all directions. By equating the far field potential of the two spheres at the same field point one can solve for the conductivity of the pseudo homogeneous material, $\sigma_m$, which is the effective conductivity. Eq. 6.46 gives the equality of interest.

$$\frac{1}{3} \sum_{k=1}^{N} n_k a_k b_k^2 \frac{(\sigma_k - \sigma_0)}{\sigma_0} \left( \langle \vec{E}_i \rangle_k \cdot \vec{r} \right) = R^3 \vec{E}_0 \cdot \vec{r} \left[ \frac{\sigma_m - \sigma_0}{\sigma_m + 2\sigma_0} \right]$$ (6.46)

Assuming the condition is satisfied that all the inclusion types share the same principle axis of the distribution function then the resulting effective conductivity tensor will have off diagonal components equal to zero as depicted in eq. 6.29. If this is the case the solution procedure will be the same as for the single inclusion type, i.e. aligning the imposed E-field with one of the inertial coordinate system’s axes at a time and solving for the relevant component of the effective conductivity tensor. This results in eq. 6.47.

$$\sigma^j_j = \sigma_0 \frac{3\sigma_0 + 2f_I \sum_{k=1}^{N} x_k (\sigma_k - \sigma_0) G_{k,j}}{3\sigma_0 - f_I \sum_{k=1}^{N} x_k (\sigma_k - \sigma_0) G_{k,j}}$$ (6.47)

Where;

$$f_k = \frac{n_k a_k b_k^2}{R^3} = x_k f_I$$ (6.48)
For the case of a single inclusion type which is spherical (N=1, $x_1=1$), eq. 6.47 reduces to eq. 6.31 as it must.

As before the Maxwell-Garnett approach may be used where figure 6.6 gives the visual representation of the equality between the actual mixture being considered and the pseudo material. Again the difference here is there is more than a single inclusion type to consider. The weighted averages of the E-field in the mixture and the flux are then;

$$\langle \vec{E} \rangle = (1 - f_I) \vec{E}_0 + f_I \sum_{k=1}^{N} x_k \langle \vec{E}_i \rangle_k$$  \hspace{1cm} (6.49)

$$\langle \vec{J} \rangle = \sigma_0 (1 - f_I) \vec{E}_0 + f_I \sum_{k=1}^{N} x_k \sigma_k \langle \vec{E}_i \rangle_k$$  \hspace{1cm} (6.50)

To determine the effective conductivity tensor from eq. 6.49 and 6.50, the definition $\langle \vec{J} \rangle = \sigma_m \langle \vec{E} \rangle$ is once again used. The result after aligning the imposed E-field with each of the inertial coordinate system’s axes is given by eq. 6.51.

$$\sigma_m^{ij} = \sigma_0 + \frac{f_I \sum_{k=1}^{N} x_k (\sigma_k - \sigma_0) G_{k,j}}{1 - f_I + f_I \sum_{k=1}^{N} x_k G_{k,j}}$$  \hspace{1cm} (6.51)

It is important to note that eq. 6.47 and 6.51 reduce to eq. 6.30 and 6.35 for single inclusion types. They are also subject to all the same behavior and shortcomings as their single inclusion type counterparts. This includes the fact that they are the same equation to a first order approximation by way of a Taylor series expansion. The next section applies the BUT procedure to extend the theories to higher volume fractions.
6.3.2 Extension to Higher Volume Fractions for N Inclusion Types

The extension to higher volume fractions of eq. 6.47 and 6.51 via BUT can be done in the same way as before but with an added subtlety. When differentiating either equation, the values, $x_k$, which represent the proportions of each inclusion type to the total inclusion amount, are taken to be constant. If considering the discrete and recursive steps outlined in section 6.2.4 this simply means the different inclusion types are added in the same proportions at each step. Differentiation of eq. 6.47 and 6.51 then leads to eq. 6.52 and 6.53.

\[
\frac{df_I}{d\sigma} = \frac{3\sigma_0^2}{(\sigma_m + 2\sigma_0)^2} \sum_{k=1}^{N} x_k (\sigma_k - \sigma_0) G_{k,j} \quad (6.52)
\]

\[
\frac{df_I}{d\sigma} = \sum_{k=1}^{N} x_k (\sigma_k - \sigma_0) G_{k,j} \quad (6.53)
\]

Taking the limit as $df_i \to 0$ ($\sigma_0 = \sigma_m$) and performing a similar change of variable as described by eq. 6.40 gives the final expression.

\[
\frac{d\alpha_I}{(1-\alpha)} = \frac{d\sigma_m^{jj}}{\sum_{k=1}^{N} x_k (\sigma_k - \sigma_m^{jj}) G_{k,j}'} \quad (6.54)
\]

Where the $D_{x,k}'$ and $D_{y,k}'$ associated with $G_{k,j}'$ are given by;
\begin{equation}
D'_{x,k} = 1 + \frac{(\sigma_k - \sigma_m)}{\sigma_m} L_{1,k} \\
D'_{y,k} = 1 + \frac{(\sigma_k - \sigma_m)}{\sigma_m} L_{2,k}
\end{equation}

Unfortunately, eq. 6.55 is not readily solvable due to the presence of the summation term but it is easy to solve numerically just like eq. 6.41.

Eq. 6.55 reduces to eq. 6.44 for a single spherical inclusion type and it also reduces to the formula derived by Jayannavar and Kumar [198] for two spherical inclusion types as it should since the method of defining volume fractions and proportions of inclusions, i.e. eq. 6.48, was adopted from the work of Jayannavar and Kumar. It is also worth mentioning that this characteristic causes eq. 6.54 to reduce to the symmetrical Bruggeman result for two spherical inclusion types with a \( f_I = 1 \). As a further check on eq. 6.54 it is found that it also reduces to the case of perfectly aligned spheroids in the BST limit given by Davidson and Tinkhan [214] when \( f_I = 1 \) in that case.

6.3.3 Discussion and Observations of Results for Multiple Inclusion Types

In order to investigate the effect of multiple inclusion a few simple mixtures are presented here. These scenarios will serve as a means to discuss a few of the characteristics of eq. 6.54 but the possible combinations of inclusion types covered by eq. 6.54 are innumerable and unfortunately cannot be generalized easily. The following examples will consider only two inclusion types contained within the continuous matrix material. The influence of differing conductivity, shape, and anisotropy will be highlighted separately.
Example 1, shown in figure 6.11, shows the results for two spherical inclusion types with different conductivities. This is the case described by Jayannavar and Kumar [198]. Figure 6.11 shows the results for $\sigma_1/\sigma_0 = 100$ and $\sigma_2/\sigma_0 = 0.01$ for different proportions of each inclusion type; $x_1 = 0, 0.25, 0.50, 0.75, 1$ and $x_2 = 1-x_1$ (Note that the volume fraction proportions must always sum to one by definition, i.e., $\sum_{k=1}^{N} x_k = 1$).

\[
\sigma_m/\sigma_0 = \left\{ \begin{array}{ll}
1 & \text{if } x_1 = 1 \\
0.75 & \text{if } x_1 = 0.75 \\
0.50 & \text{if } x_1 = 0.50 \\
0.25 & \text{if } x_1 = 0.25 \\
0 & \text{if } x_1 = 0 \end{array} \right.
\]

Figure 6.11: Results for two inclusion types of different conductivities.

It is obvious from looking at the results that the two extremes ($x_1 = 1$ and $x_2 = 1$) enclose all intermediate proportions. While this may be obvious it is important to realize that the intermediate cases are not simply weighted averages of those two extremes nor can the results in figure 6.11 be obtained by applying BUT for a single inclusion twice. In other words, the plotted results cannot be reproduced by applying BUT for inclusion type 1 and computing an effective
conductivity, call it \( \sigma_{m,1} \), then applying BUT again for inclusion type 2 with the matrix being \( \sigma_{m,1} \). Performing such an operation would have a result which depended on the order in which one considered the inclusions. As mentioned previously, the varying proportions of each inclusion type for a total inclusion volume fraction of 1 is representative of BST.

In the second example, the effect of different inclusion shapes is investigated. Here, the mixture contains two inclusion types with the same conductivity, both having isotropic distributions, but with different spheroid shapes. Inclusion type 1 has a \( b/a = 100 \) (disk-like oblate spheroids) while inclusion type 2 has a \( b/a = 0.01 \) (rod-like prolate spheroids). Figure 6.12a shows the results for insulating inclusions, \( \sigma_{1,2}/\sigma_0 = 0.01 \) while figure 6.12b shows the results for highly conductive inclusions \( \sigma_{1,2}/\sigma_0 = 100 \). The same different proportions as before are used again and plotted as different lines on the same graph.
Figure 6.12: a) Effect of shape for insulating inclusions. b) Effect of shape for highly conductive inclusions.

As before, figure 6.12a and b show that the extreme cases bracket the intermediate results in terms of varying proportions. As one might expect in this case, because the two different inclusions have the same conductivity, all the results converge to the same result for a total volume fraction of inclusion equal to 1 ($\alpha_1 = 1$). For insulating inclusions, the variation of the
conductivity with varying proportion is much greater than the case of highly conductive inclusions. This is due to the disk-like oblate spheroids setting up barriers to current flow as described in section 6.2.5. Even though the disks are randomly oriented, it is inevitable that some of them will have their major axes parallel to the current flow which will cause a sharp drop in conductivity as they effectively set up a non-conducting wall. There is no analogous situation to this for the highly conducting spheroid inclusions so the effect of varying proportion on the effective conductivity is much less pronounced.

The final example considered involves varying the anisotropy of the orientations for the two inclusion types. Here, two rod-like spheroid inclusion types with the same conductivity, $\sigma_{1,2}/\sigma_0 = 100$, are considered. Inclusion type 1 will have an orientation distribution given by $m = -\infty$ (fan-like) and inclusion type two will have an orientation distribution given by $m = \infty$ (perfectly oriented). Figure 6.13 shows the results for the same increments of proportions as shown in the other examples. Figure 6.13a gives the effective conductivity in the $\zeta,\eta$ plane while figure 6.13b gives the effective conductivity in the $\rho$ direction.
Figure 6.13: a) Effect of orientation anisotropy of the inclusions in the $\zeta,\eta$ plane. b) Effect of orientation anisotropy in the $\rho$ direction.

Once again the extremes bracket the results as one would expect in any such case and the results all converge to the same conductivity for $\alpha_I = 1$. Figure 6.13 shows that varying the proportions of inclusion types for these two extremely anisotropic distributions greatly affects the effective conductivity in both the $\zeta$, $\eta$ directions and the $\rho$ direction. Again this is not simply a weighted
average result. In the case of the $\zeta$, $\eta$ direction (figure 6.13a) adding a small amount of inclusion type 1, when there is initially only inclusion type 2, causes a great increase in the effective conductivity. This is because the perfectly oriented rods do not contribute much to increasing the conductivity in the $\zeta$, $\eta$ direction which is perpendicular to their major axes. When adding even a small amount of rods with a $m = -\infty$ orientation distribution there will be some which are parallel to the flow direction being considered so they will cause a sharp rise in the effective conductivity in that direction. The opposite is true for the $\rho$ direction where, if the mixture is composed of inclusion type 2 initially, all the inclusions are oriented parallel to the direction of interest and greatly contribute to the effective conductivity in that direction. As more or inclusion type 1 is added in place of type 2 the conductivity decreases because the inclusion type 1 spheroids are oriented with their major axes perpendicular to the direction of interest and thus do not contribute greatly to the effective conductivity in that direction. The detriment to the conductivity of adding the inclusion type 1 at the expense of inclusion type 2 is minor at first because of the strong effect of having perfectly oriented rods on the $\rho$ direction conductivity but eventually, as more and more of those perfectly oriented rods are replaced, the conductivity suffers greatly.

It is important to remember that the previous examples are a sparse subset of scenarios for which eq. 6.54 is applicable. In each example only one property was varied between two inclusion types at a time in an attempt to isolate the effects on the calculated effective conductivity. In reality any number of inclusion types can be considered with any of the three properties; individual conductivity, shape, or orientation varying simultaneously between inclusion types. As these different properties become more similar however, the need to distinguish between inclusion types may not be necessary. This would depend on the specific
case being investigated. The final section of this chapter presents some case studies to test the applicability of EMT to some real fuel cell materials.

6.4 Case Studies

6.4.1 Polymer Electrolyte Membrane

The first case study presented here relates back to the polymer electrolyte materials studied in chapters 3-5. In these studies, and many others involving polymer electrolyte membranes, the diffusivities were often corrected with the BUT. However, little direct justification of the use of this correction exists. The development in this chapter shows there are many possible EMT equations which can be used to correct for effective parameters so the question remains whether or not BUT in its original form is appropriate for membranes such as Nafion. Section 3.4.5 in chapter 3 gave some considerations to the applicability of EMT to the permeability of Nafion and those arguments are drawn upon here to evaluate the applicability of BUT to Nafion. The experimental data for the permeability can be recast vs. the wet porosity of the membrane using eq. 4.13 from chapter 4 along with the appropriate water uptake behavior noted in section 2.3.1 of chapter 2. Along with the carbon dioxide data in chapter 3 there is data available in the literature for hydrogen and oxygen which can be compared against [215]. As is commonly done in the literature, the membrane was treated as the spherical inclusion material and the water was treated as the matrix in the BUT development. Permeabilities for the water were taken from data for the solubility and diffusivities of the respective gases in pure water while the permeabilities of the dry membrane were taken to be that of the gases in Teflon or dry membrane measurements [137,141,216]. Figure 6.14 shows the comparison of permeability as a
function of porosity, $\varepsilon$, for each case. Additional permeation data was measured for oxygen in this work using a similar experimental rig as the one described in section 3.2 as indicated in the plot.
Figure 6.14: comparison of BUT to Nafion for various gas permeability measurements as a function of wet porosity. a) CO₂, b) O₂, c) H₂. The plus marks indicate data from these studies while the squares represent data taken from [215]. Curves represent EMT predictions.

As can be seen in figure 6.14 the comparison is favorable between the data sets and the EMT for Nafion. It is worth mentioning that the spread in the data can be somewhat large which is characteristic of the measurement techniques but also may be related to the amorphous nature of the polymer electrolyte. This study shows that, in the case of Nafion, BUT provides a rough estimate of the permeability with reasonable accuracy given the simplicity (Note that this does not necessarily mean BUT is applicable to AEM materials but it is assumed here due to the similar characteristics). In the case of correcting for diffusivities, the same correction should carry over so long as the dry membrane phase does not contribute to the transport. In the case that both phases contribute to the transport and the solubilities of the phases are not equal then the basic assumption of the EMT is violated and BUT is not applicable. This is because the concentrations at the interfaces between the two phases would not be equal at steady state and the Laplace solution that all of the EMT developments are based on are developed by setting the potential, concentration, etc. at the interface between the phases equal to each other. When considering, for instance, the ion transport in a PEM the theory should be applicable since the dry membrane phase is essentially impervious to the ions. It is interesting to note that the percolation effect discussed in the literature for Nafion and used in the chapter 5 derivations does not seem to appear in figure 6.14. In the case of hydrogen and oxygen this is likely because the gases seem to have non-zero permeability through the dry membrane phase. For carbon dioxide however, the dry phase permeability is approximately zero. It is possible that the percolation
effect is limited to the charged species transport and is associated with the ions being unable to make the leap between sulfonic acid clusters at low hydration. This is more speculative at this point however.

When considering the structure of the PEM a suspension of spherical Teflon particles in a continuous liquid water matrix is not a physical picture which many would support. Indeed, using the result of an EMT solution to work backwards to determine the characteristic structure of a material is not recommended. One reason is because EMT is approximate and different structures can produce very similar results. The fact that BUT matches fairly well to the data in figure 6.14 does not automatically indicate that the membrane is a collection of disjointed spheres. However, conversely, at volume water volume fractions upwards of only about 35% it is difficult to imagine these spheres in the theoretical structure as being totally separate from each other. If one considers the extreme when the volume fraction of the dry membrane is very high, the individual spherical particles will begin to overlap and may produce something similar in structure to physical models presented by Gierke [30] or the molecular dynamics model presented by Duan et al. [217].

One final question comes to mind when considering the gas permeability and its comparison to BUT. That question is why do the water diffusion coefficient results of chapter 1 have such a different behavior? Even if the water diffusion results are plotted as a function of wet porosity they would not follow the BUT prediction due to the presence of the Darken factor. In attempting to understand why this difference may exist consider the driving forces at work. Consider for simplicity the carbon dioxide transport through the membrane at steady state. As discussed in chapter 3 this transport occurs almost exclusively through the hydrophilic region. The diffusion of the dissolved gas is driven by a concentration gradient of carbon dioxide within
the pore volume. In the case of the water diffusion coefficient there is no water concentration gradient in the pore volume. It is all assumed to be liquid water of the same concentration (e.g. chapter 4’s derivation). The driving force is actually a gradient in the parameter $\lambda$. Even though the water diffusion coefficient is described by Fick’s law, there are chemical and mechanical interactions with the membrane that are at work which influence the diffusivity that BUT cannot account for.

6.4.2 Gas Diffusion Layers

As alluded to briefly in chapter 1, polymer electrolyte membrane fuel cells currently make use of gas diffusion layers (GDL) as a means of distributing the gaseous fuel to reaction sites, conducting electrons away from the reaction sites, and also helping to control the water balance in the MEA. A common method of creating GDLs is to start with a carbon fiber paper material and add a hydrophobic element, such as PTFE, to give it the desired hydrophobicity to control water flux through the MEA. One popular carbon paper to use as a base is the series provided by Toray. This carbon paper is characterized by an array of planar fibers which has a distribution very much like the fan-like ($m = -\infty$) distribution mentioned in section 6.2.2. The carbon fibers are held together with a binder material. To describe the anisotropic transport in these carbon papers and subsequent GDLs a study by Tomadakis and Sotirchos [218] has been adopted by several authors [219-221]. Tomadakis and Sotirchos performed a numerical study on various fiber structures in the Knudsen and regular diffusion regimes. This study involved applying a Monte Carlo simulation to determine effective diffusivities of their structures using the mean-square displacement of random walkers in the interior of the fiber distributions. They
performed this study for three orientations: completely random, planar orientation, and perfectly aligned fibers. In terms of studying gas diffusion layers, the second option has been used in studies related to the Toray paper but they all are useful to compare with the derived theories of this chapter. To compare with the EMT derived in section 6.2, distributions of rod-like prolate spheroids (b/a = 1/100000) were considered where the spheroids had zero diffusivity (D₁ = 0). The values of m used were m = 0, -∞, and ∞ when comparing to completely random, planar orientation, and perfectly aligned fibers respectively. Figure 6.15 shows the comparison between the results of Tomadakis and Sotirchos and the EMT theory presented here for the normalized effective diffusivities as a function of porosity.
Figure 6.15: Comparison between the results of Tomadakis and Sotirchos [218] and the EMT developed in this chapter. a) Completely random fiber orientation (m = 0). b) Fibers with a planar or fan-like distribution (m = -∞). c) Perfectly aligned fibers (m = ∞). It is important to
note in this case study that the porosity is $1-\alpha$ from the theory presented in previous sections of this chapter.

The results in figure 6.15 show that the EMT captures the trend of the simulation results quite well in all cases. It should be reiterated here that the cases of completely random fiber orientation and perfectly aligned fibers have been previously covered in the EMT literature [205] however, as far as the author is aware few, if any, comparisons have been made to other theories or experiments. The fan-like distribution ($m = -\infty$) is unique to this work. When looking at the agreement in figure 6.15 it is clear that as the material becomes more anisotropic, the agreement towards lower porosity decreases. This is connected to the percolation issue discussed in section 6.2.5. Since these results deal with a two component mixture where one component is conducting to transport (in this case the empty space between the fibers) and the other is not (the solid fibers themselves) one would expect that percolation-like phenomena would occur. As discussed before, the nature of the percolation is related to the specific structure and the results in figure 6.15 provide an example of how orientation affects the percolation limit. In the case of randomly orientated fibers the percolation limit is almost absent since long, straight fibers which are randomly oriented cannot easily set up a total blockade through the mixture. The other extreme is the perfectly oriented fibers which can totally block flow in the direction perpendicular to the fibers without filling the whole volume quite easily. An analogy that leads to that conclusion is to consider tightly packed columns. If the columns all touch they cannot be passed but at the same time, there is space between them. Conversely, those columns would never be able to totally block the direction which is parallel to them which is why the parallel direction diffusivity in figure 6.15 does not exhibit a percolation limit.
A more recent series of studies show a somewhat different behavior in the diffusivity when considering a carbon paper material like Toray [222,223]. In these works, an electrochemical diffusimetry technique was developed to experimentally measure the effective diffusion coefficients of through and in plane GDL materials. The technique involved flooding the GDL with an electrolyte and measuring the effective ionic conductivity. Then an analogy was drawn to diffusion due to the analogous potential flows exhibited by both phenomena. Different porosities were tested by compressing the membrane. The results show a much harsher drop off in the effective diffusivity as porosity decreases as well as a greater degree of anisotropy. It was noted by the authors that a major contributor to the decreased diffusivity were skins that formed from the binder material being spread between the fibers. This additional effect can be included in the EMT analysis in the form of another inclusion type. In the present study, the comparisons are restricted to the carbon paper results before the addition of PTFE. These skins will be modeled as disk-like inclusions in the EMT equations with preferential orientation of their major axes along the principle distribution axis. In order to evaluate the EMT the following is needed:

1. The volumetric percentage of skin material to total material.
2. The aspect ratio of skin material.
3. The best fit orientation distribution function of the skin material.

These three items were calculated by performing a rough stereology study on available images of the material in the literature. Figure 1 from reference [223] is the cross sectional image used. The skins were identified as long, thin traces of binder in the cross section that ran between the fibers. The original image was thresholded using ImageJ in order to calculate the volume fraction of the skin material. As a rough check on whether the figure was representative of the actual material...
the total volume fraction of solid versus pore was calculated. A porosity of 79.0% was obtained. The uncompressed porosity reported in [223] is 75.4%. This amounts to a discrepancy of about 5% but there was some extra whitespace due to thresholding error in the manipulated images. The average skin thickness appeared to be about 3 microns which is roughly in agreement with the statement made by Zhou et al. [224] who also noted the presence of the skin structures. Using the result the volumetric percent of solid material associated with skins was determined to be about 6.3% ($x_{\text{skin}} = 0.063$) and the distribution function parameter, $m$, which best matched the behavior of the skins was $m = 15.3$. The value of 6.3% is not unreasonable since the total binder has been reported as 30% of the solid volume and most of the binder does not form these skin-like structures [223]. Note that the remaining binder material is then treated as spherical inclusions in the mixture separate from either the skins or the fibers. The last unknown, the aspect ratio of the skins was the most difficult to identify and also the most subjective. The shapes of the skins are being approximated as disk-like but in reality they are fairly amorphous. The disk shape was chosen due to sharing some of the same characteristics of the skins, i.e. a large surface area to volume ratio. Relative aspect ratios of these disks were approximated by examining SEM images available in the literature [225] of the through plane direction of the carbon paper. The surface area of what appeared to be continuous, unbroken skins spanning multiple fibers was measured. The average surface area was then compared to the thickness value mentioned above and an aspect ratio of 50 was settled on.

Using the results of the image analysis the comparison can be made to the experimental data performed by Fluckiger et al. [223]. Figure 6.16 shows this comparison for varying porosity of Toray TGP-H-060 carbon paper.
Examining the results in comparison to figure 6.16 it is clear that the updated EMT captured the correct trend when accounting for the skin structures. Both the through and in plane diffusivity have decreased and the degree of anisotropy has increased. However, there are some discrepancies between the data and the EMT results. In plane diffusivity exhibits greater differences between predictions and experiments and both sets of curves seem to have slightly different curvature. Part of the reason for this discrepancy may have to do with the compression of the GDL which has been shown to cause structural damage [226]. This may alter the behavior of the transport in the GDL which is unaccounted for in the EMT. Additionally, as noted before, the actual measurements were of the ionic conductivity of the GDL flooded with an electrolyte.
It is unclear if the wetting behavior of the electrolyte influences the results and double layer charging effects due to the electrical conductivity of the fibers complicates things. On the EMT end, assumptions were made regarding the shapes of the inclusions which may be responsible for some of the discrepancies. Also, the values necessary to characterize the skins are estimated from limited data. However, as stated previously, the aspect ratio is the most subjective measurement, as well as the most sensitive, and a variation of upwards of 25% on that parameter does not result in significant variations in the calculated results.

An important result of this study thus far shows the powerful nature of the developed EMT capability. Many specific models have been developed that compute the values of the diffusivity for GDLs and in many cases they fit the specific data sets quite well. However, many of those models are empirical or semi-empirical. The EMT used here is able to predict the diffusivity with a few roughly measured parameters as input and the trends are captured and the agreement to the experimental data is reasonable. Also, as demonstrated thus far, as the structure becomes more complex the EMT can adapt by adding different types of materials, effectively “building” the desired structure from a set of predefined shapes and orientation distributions. If appropriate characterizations of the PTFE loading on the carbon paper can be made then the EMT can be further modified to compare with the finished GDL material. Furthermore, one might expect thin GDLs to have through pores, i.e. large pores which penetrate the entire through plane direction. In this case the through plane direction diffusivity would be greatly enhanced. This effect can be accounted for through the inclusion of perfectly oriented rod-like inclusions with the same diffusivity as the matrix (empty space).

One final study on the Toray carbon paper is that of the thermal conductivity. Up front, it is important to note the limitation in the EMT in this regard. Through plane conductivity in GDL
materials is believed to be related primarily to the contact points between individual fibers [226,227]. As the compression is increased the conductivity increases due to an increase in these contact points. Fundamentally, BUT which is the basis of the developments in chapter 6 cannot account for these contacts between the particles so in the case that the effective parameter is dictated primarily by that type of behavior it is not an appropriate theory to apply as it will simply predict a zero conductivity unless the volume fraction of the solid material is 1 (assuming negligible thermal conductivity of the empty space between the solid phases). However, in the case of in plane thermal conductivity the EMT developed in this chapter does predict a finite conductivity greater than zero for intermediate volume fractions. This is due to the extremely small aspect ratio of the fibers and the fact that they all lay in the same plane. In the theoretical picture, a single fiber can traverse the entire mixture giving it a thermal connection from end to end. There have been a few numerical studies of these conductivities involving discretization of the energy equation for planar fiber structures [228,229]. Experimental measurements are uncommon but at least one study of the in plane thermal conductivity of Toray carbon paper exists [230]. Figure 6.17 shows the comparison between the numeric models, experimental data, and the EMT approach.
Figure 6.17: Comparison between the literature results and the EMT for the in plane thermal conductivity of Toray carbon paper. Circles taken from [229], plus marks taken from [228], and red diamond experimental data point taken from [230].

Figure 6.17 shows excellent agreement between data available in the literature and the EMT result for the in plane thermal conductivity as a function of porosity. This gives validity to the claim that the thermal conductivity in the in-plane direction is primarily the result of conduction along the individual fibers and the interaction of the fibers with each other has a negligible effect.

6.4.3 Freeze Cast Solid Oxide Fuel Cell Electrode

Within the solid oxide fuel cell community there has been a push to develop structured ceramic materials to maximize desired transport characteristics. One such material is the freeze
cast Ni-GDC electrode produced by Chen et al. [231,232]. These structures are produced by a freeze-drying tape-casting method which results in a highly anisotropic pore structure. As noted by Chen et al. the pores have an acicular morphology which penetrates through the thickness of the electrode to maximize gas diffusion in the anode. These long thin pores have a preferential alignment with the casting direction. The case study presented here shows a preliminary comparison between conductivity data provided by Professor Fanglin Chen’s group at the University of South Carolina and the EMT developed in the previous sections. The electrical conductivity of the Ni-GDC freeze cast samples were taken along the surface in the casting direction. Silver paste was used to attach leads to the sample surface. Conductivity measurements were made between 500 and 700 °C on a sample with a 6:4 starting weight ratio of NiO-GDC. After reduction the sample had a porosity of about 50%. To compare to this data BST for spherical particles was first applied to the Ni-GDC solid mixture. BST was selected to compute the effective electrical conductivity of the Ni-GDC mixture due to the fact that neither the Ni nor the GDC is expected to preferentially surround the other material. Once the electrical conductivity of the solid mixture was computed the pores were considered using the developed BUT based theory of section 6.2. The pore shapes were approximated as disk-like with an aspect ratio, b/a, of 10. The disks were considered to be highly aligned towards the principal axis with m = 11. These parameters were obtained by examining XCT image data provided by Professor Fanglin Chen’s research group and performing a similar analysis to the one detailed in section 6.4.2. It is stressed here that in this preliminary comparison a detailed numerical analysis of the image data has not yet been performed but stereology studies of numerous cross sections was done. Figure 6.18 shows the initial comparison between the electrical conductivity data and the prediction.
Figure 6.18: Preliminary comparison between experimentally measured electrical conductivity for a freeze cast solid oxide fuel cell electrode and the previously derived EMT.

The two predicted curves in figure 6.18 represent the electrical conductivity in the casting direction along the surface (the $\zeta$-$\eta$ direction in the EMT development) and the orthogonal direction (the $\rho$ direction in the EMT development). As can be seen in the figure the experimental data is bracketed by the prediction but favors the orthogonal direction. There are several possible causes for the discrepancy. First, as was echoed in the previous sections of this chapter, percolation is unaccounted for in the BUT component of the prediction. If there is a strong effect of percolation between the pores then an over prediction of the electrical conductivity...
conductivity would be expected. Second, the assumption of disk shaped pores may be an oversimplification. The pore morphology may be better approximated by the ellipsoid family of shapes. To explore this possibility the theory derived in this chapter would need to be generalized for ellipsoids. Finally, the thickness of the electrode and the pore radii (assuming a disk shape) are on the same order since, as mentioned before, individual pores penetrate through the thickness of the electrode. The EMT was derived assuming a bulk material so this characteristic is not explicitly accounted for. Further investigation is required to understand which of these possible issues may be a major contributor to the discrepancy seen in figure 6.18 and this outcome sets the stage for further avenues which require exploration in the developed EMT.

6.5 Conclusions

The work presented in this chapter derived an expression for the effective conductivity (but can be applied to thermal conductivity, diffusivity, dielectric constants, etc.) of a mixture based on BUT where a class of distributions was defined in order to study the effects of anisotropic orientation. The provided development gives a convenient set of analytical expressions for calculating the effective conductivities of mixtures which can be reasonably described with the predefined distribution function. The final expression was obtained from two starting points; the Maxwell methodology as well as the Maxwell-Garnett approach. An expression for the far field potential of a single ellipsoid was derived and used in the Maxwell approach and it was discovered that despite the Maxwell approach using the far field potential it was still directly dependent on the average internal E-field when considering any of the
orientation distributions of the inclusions much like with the Maxwell-Garnett methodology. Additionally, it was shown that the far field potential was directly related to the internal E-field for the single ellipsoid case and to the average of the internal E-fields for the case of a distribution of ellipsoids. This property facilitated the application of the Maxwell approach to the case of a distribution of ellipsoids/spheroids. The resulting expressions for the Maxwell and Maxwell-Garnett effective conductivities were different, but resulted in the same equation when the BUT methodology was applied. The resulting BUT level equation, which extended the validity of the equations beyond the dilute limit, was then used to study the effects of anisotropy in the cases of oblate and prolate spheroidal shaped inclusions.

After considering a single inclusion type, the theory was extended to calculating the effective conductivity for N types of inclusions. The resulting expression allows for each inclusion type to have a unique orientation distribution, shape, and conductivity. The orientation distribution of each inclusion type is restricted to share the same principle axis and the shapes of the inclusions are all restricted to spheroids. A few simple mixtures were considered involving two inclusion types with different conductivities, shapes, or orientation distributions to demonstrate the potential effect of multiple inclusions on the calculated effective conductivity.

Finally, a few case studies were examined. First the original BUT was compared with experimental data for Nafion gas permeabilities. This helped confirm the applicability of BUT for correcting transport coefficients in polymer electrolyte membrane modeling. Next, the newly developed theories were tested against another polymer electrolyte membrane fuel cell component which is highly anisotropic; the gas diffusion layers. The study was restricted to just the base carbon paper component before PTFE loading but the concept of “building” complex structures from the developed theory was demonstrated and tested against experimental data.
from the literature. The favorable results confirmed the predictive power of EMT. One final preliminary study of freeze cast solid oxide fuel cell electrodes highlighted possible avenues for further development of the presented EMT.
Chapter 7: Conclusions and Remarks

Two basic types of polymer electrolyte fuel cells, the anion exchange membrane and proton exchange membrane fuel cells (PEMFC and AEMFC), share many similar characteristics but also offer unique advantages and challenges for researchers. Among these challenges include characterizing the nature of the transport behavior occurring in the polymer electrolyte. Polymer electrolyte membranes are a complicated heterogeneous material which requires high levels of hydration for ionic conduction. Transport behavior of water, ions, and gases are of great interest in designing fuel cell technology. Many efforts have been made during the course of the research presented in this thesis to provide a more fundamental understanding of transport processes occurring in both AEMs and PEMs as well as providing the theories and tools necessary to measure the pertinent parameters.

Among these efforts were measuring water diffusion coefficients in both PEMs and AEMs. As noted the water balance of these membranes is critical for maintaining a high level of ionic conductivity. Gas permeability measurements of carbon dioxide in Nafion were performed to help fill the gap in the literature as well as provide an understanding of the nature of gas transport in these membrane materials. This is important for understanding fuel cross over losses which contribute to the cell overpotential. AEM exposure to carbon dioxide causes decreased ionic conductivity due to the ion exchange of hydroxide for carbonate and bicarbonate. A transient ion exchange model was derived to help explain the trends in experimental data available in the literature. Hamilton Sundstrand’s high pressure oxygen generating electrolyzer (HPOGA) was also the subject of modeling work. The dusty fluid model (DFM) was applied to the electrolyzer membrane, Nafion 1110, to describe membrane transport and performance under
a high differential gas pressure. Finally, due to the overwhelming presence of effective medium theory (EMT) in the literature for modeling purposes a study was performed to help generalize these theories to more complex materials and evaluate their performance in some case studies. The next section provides a bulleted list of the key findings and contributions of these works as well as a list of existing and planned literary contributions.

7.1 Key Findings and Contributions

Key findings and contributions are broken down by chapters as follows:

Chapter 2: Calculation of Water Diffusion Coefficients

- A methodology of measuring water diffusion coefficients was developed and applied to Nafion 117 and SnowPure Excellion I-200. The results for Nafion 117 compared very well to NMR data from the literature giving more confidence for both results. The SnowPure Excellion I-200 calculation is the first reported.
- It was demonstrated that other test cell transport resistances must be carefully monitored to accurately calculate the water diffusion coefficient from water flux data. In this study, the pressure drop was shown to have an important effect and its impact on the water flux curves was characterized.
- The concept of the maximum achievable flux was introduced to aid in the designing of future experiments. The derived equation represents the maximum flux that may be achieved in the event that the humidities of both flow channels become equal. If the experimental data falls on that line it will not be useful in the developed methodology of chapter 2.
Chapter 3: Transport of Carbon Dioxide through Nafion 117

- A range of temperature and relative humidities was run for carbon dioxide permeation through Nafion 117. This type of comprehensive study has not been previously available for carbon dioxide transport through Nafion.
- The measurements were performed transiently allowing for the resolution of the permeability into the solubility and diffusivity.
- It was found that the assumptions made by the homogeneous model, a time lag model commonly applied to these systems, led to some inconsistent observations in the results when calculating the solubility and diffusivity. The bicontinuous model was introduced which is more generalized in that the transport may occur simultaneously through both the hydrophilic and hydrophobic domains in the membrane. By comparing this model to the homogeneous model the inconsistencies in this case were resolved and further generalizations for other types of systems were obtained.

Chapter 4: Transient Ionic Conversion of an Anion Exchange Membrane Exposed to Carbon Dioxide

- A model was developed to provide fundamental insight into the transient ion exchange process that occurs in AEMs exposed to carbon dioxide. It was validated with existing data in the literature. This model will be useful in determining the ion exchange behavior under different operating conditions.
The rate limiting mechanisms were found to be a combination of carbon dioxide diffusion and the forward reaction converting carbon dioxide and hydroxide into bicarbonate.

It was found that carbon dioxide absorption through the interface was a fast process compared to the kinetics and transport occurring within the membrane making Henry’s law as a boundary condition appropriate.

The ion dissociation reactions were also determined to be fast compared with the reactions occurring within the bulk solution and the carbon dioxide transport in the membrane.

Chapter 5: Membrane Transport in a High Pressure Oxygen Generating Electrolyzer

The DFM was applied to a high pressure electrolyzer to model the performance and species transport in the polymer electrolyte. To the author’s knowledge, this is the first such study involving DFM and an operating high pressure oxygen generating electrolyzer.

The governing equations of the system were non-dimensionalized and the results showed that dry out of the cell, and subsequent discontinued operation, occurred at a roughly constant Damköhler number of 0.196 ± 0.004 for the conditions studied.

The effect of the electro-osmotic drag coefficient was also investigated. Varying the drag coefficient from 0 to 2.5, which is characteristic of no drag effect and electro-osmotic drag in a liquid equilibrated membrane, varied the dry out limiting current density of the cell by +37% and -27% respectively.

Due to the high differential gas pressure applied to the MEA a meniscus concept was developed to investigate the nature of the pressure drop across the membrane. The
membrane pore was modeled via a wavy wall approach and it was found that the meniscus could theoretically take the full pressure imposed by the oxygen gas.

Chapter 6: Generalization and Applicability of Effective Medium Theory

- A generalized EMT was developed which applies to multi-inclusion materials with anisotropic orientations of the individual inclusions. The formulas were able to be cast into simple functions of the parameter m which accounts for the preferential orientation of the inclusions. Versions of Bruggeman’s unsymmetrical and symmetrical theories previously derived in the literature were recovered as special cases of the generalized equations.

- A Case study utilizing literature data as well as data from chapter 3 showed the validity of Bruggeman’s unsymmetrical theory (BUT) for Nafion gas permeability. This outcome was shown to carry over for diffusivity in certain cases when coupled with the arguments of chapter 3 for the bicontinuous model.

- The developed equations were shown to be applicable to gas diffusion layer (GDL) diffusivities and helped separate the importance of the binder skins which form for GDLs created with Toray carbon paper. Studies were restricted to the Toray carbon paper which serves as a base for many GDLs. Furthermore, one of the weaknesses of the current EMT was highlighted since it cannot predict through plane thermal or electrical conductivity which relies heavily on percolation behavior not accounted for in the model. The in plane thermal conductivity was successfully predicted, however, which shows fiber interaction in that case is not important.

- Preliminary comparisons were made to a highly anisotropic freeze cast solid oxide fuel cell electrode. In a first attempt the electrical conductivity measured by Professor Fanglin
Chen’s research group for the casting direction of their samples was over predicted by the developed EMT. Several possible reasons were detailed for the discrepancy including percolation behavior, pore shape, and pore size. This outcome sets the stage for further research to be performed in the EMT development.

Literary contributions (first authorship for above work only) both published and planned for the immediate future are as follows:

- **Published**

- **In Preparation**
  - Full manuscript detailing chapter 3 studies
  - Full manuscript detailing chapter 4 studies
  - Letter describing multi-inclusion extension of section 6.3
Full manuscript detailing current case studies in chapter 6 as well as future planned case studies

7.2 Recommendations and Future Work

As is always the case with research, the above results do not indicate the end of fundamental understanding of the topics involved. As such, many planned immediate future endeavors and recommendations can be made regarding the work. These are bulleted below.

- Transient oxygen permeation results have also been obtained for Nafion 117 as discussed briefly in section 6.4.1. These results exhibit behavior which does not fit a simple exponential function as is characteristic of the homogeneous model. The bicontinuous model will be applied to this data set to further validate the model and its key findings.

- The developed ion exchange model in chapter 4 is currently being applied to inactive membranes, i.e. no electrodes or current. While this still provides valuable insight into the transient conversion the next logical step is to apply it for a membrane in an operational fuel cell. This is far more complex but adds the opportunity to study the so called self-purging mechanism from a theoretical standpoint.

- The results for the ion exchange model detailed in chapter 4 were produced assuming that the equilibrium constants for the dissociation reactions for both the ETFE membrane and the A201 membrane are equal and that each anionic species dissociates with equal affinity. As a next step, these assumptions should be relaxed. Dissociation equilibrium constants can be computed through a fitting exercise to the experimental data. In order to ensure the maximum accuracy of the fitted equilibrium constants it may be necessary to
perform further experimentation with varying and carefully controlled atmospheric carbon dioxide levels.

- The model for the meniscus in the HPOGA is purely theoretical at this stage. A useful study in the future would be to measure water permeation in the membrane as a function of differential gas pressure. Standard practice is to use liquid water to impose the pressure gradient which negates the meniscus effect. This type of study would help provide independent experimental evidence of the effect of the meniscus.

- The developed orientation distribution function in chapter 6 was partially selected due to the mathematical convenience it offered. In future studies the effect of the distribution function should be explored. It is not immediately obvious that a different function which exhibits similar trends will or will not have a significant impact of the results. For example, the beta distribution in statistics behaves similarly to the chosen functions in chapter 6 but is not exactly the same. This sort of study will help justify applying the simple distribution function in chapter 6 to real materials.

- In further generalizing the developed EMTs of chapter 6 the Green’s function approach should be investigated. This approach is very general and should result in the same equations of chapter 6 if the correct simplifications are made. While it is often necessary to make ingenious assumptions for the Green’s function approach to work, it is also another avenue to explore as the derivations become more complex and may be useful in exploring the previous bullet point above.

- Further work is needed on the case study involving the freeze cast solid oxide fuel cell. As noted in section 6.4.3 the discrepancy between the experimental data and the preliminary predictions is quite large. Several possible reasons for the discrepancy are
outlined in that section and each needs to be explored and will serve as an incremental improvement to the derived theories of chapter 6.

- As noted previously, EMT has widespread potential applicability which is not limited to polymer electrolyte fuel cells or even fuel cells in general. Case studies to validate the developed EMTs will be a continued topic of research.

- As discussed in chapter 6 the percolation effect is absent in the BUT approach and thus also in the developed EMTs. Further research will be done on developing analytical predictions of percolation effects to improve the EMTs presented in this thesis.
Nomenclature:

Chapter 2:

\( a \) activity of water (unitless)
\( A_c \) cross sectional area of the channel (\( m^2 \))
\( A_m \) area of the membrane/channel interface (\( m^2 \))
\( c_{d,i} \) initial concentration of the dry channel (mol/m\(^3\))
\( c_{d,1} \) concentration in the dry channel at C.V. entrance (mol/m\(^3\))
\( c_{d,2} \) concentration in the dry channel at C.V. exit (mol/m\(^3\))
\( c_f \) fixed charge concentration in the membrane (mol/m\(^3\))
\( c_{h,i} \) initial concentration of the humid channel (mol/m\(^3\))
\( c_{h,1} \) concentration in the humid channel at C.V. entrance (mol/m\(^3\))
\( c_{h,2} \) concentration in the humid channel at C.V. exit (mol/m\(^3\))
\( D(T) \) diffusion coefficient at temperature \( T \) (m\(^2\)/s)
\( D_h \) hydraulic diameter (m)
\( D_w \) water diffusion coefficient (m\(^2\)/s)
\( D_{self} \) self-diffusion coefficient of water (m\(^2\)/s)
\( D_0 \) diffusion coefficient at a reference temperature (m\(^2\)/s)
\( E \) activation energy of diffusion (J/mol)
\( Err \) error (mol/m\(^2\)/s)
\( f \) friction factor (dimensionless)
\( J_{exp} \) experimental net flux (mol/m\(^2\)/s)
\( J_{max} \) maximum net flux (mol/m\(^2\)/s)
\( J_{num} \) numeric net flux (mol/m\(^2\)/s)
\( P \) channel pressure (N/m\(^2\))
\( R \) individual gas constant (J/kg/K)
\( \mathcal{R} \)  ideal gas constant (J/mol/K)

\( T \)  temperature (K)

\( T_0 \)  reference temperature (K)

\( v_{d,i} \)  initial velocity in the dry channel (m/s)

\( v_{d,f} \)  final velocity in the dry channel (m/s)

\( v_{d,1} \)  velocity in the dry channel at C.V. entrance (m/s)

\( v_{d,2} \)  velocity in the dry channel at C.V. exit (m/s)

\( v_{h,1} \)  velocity in the humid channel at C.V. entrance (m/s)

\( v_{h,2} \)  velocity in the humid channel at C.V. exit (m/s)

\( v_{h,i} \)  initial velocity in the humid channel (m/s)

\( v_{h,f} \)  final velocity in the humid channel (m/s)

\( w \)  mass flow rate (kg/s)

\( W_c \)  channel width (m)

\( x \)  channel position (m)

Greek letters

\( \alpha, \lambda, \Lambda, \bar{A} \)  self-diffusion coefficient empirical parameter (m\(^2\)/s)

\( \beta, \beta, \bar{B} \)  self-diffusion coefficient empirical parameter (m\(^2\)/s)

\( \delta \)  membrane thickness (m)

\( \varepsilon \)  water uptake coefficient (unitless)

\( \theta \)  water uptake coefficient (unitless)

\( \lambda \)  water content (mol H\(_2\)O per mol functional group)

\( \rho \)  density of the channel mixture (kg/m\(^3\))

\( \tau_w \)  wall shear stress (N/m\(^2\))

\( \varphi \)  water uptake coefficient (unitless)
Chapter 3:

\[ A_{\text{mem}} \] Active area of the membrane (cm\(^2\))

\[ C_1 \] Concentration boundary condition (mol cm\(^{-3}\))

\[ c_{\text{CO}_2} \] concentration of CO\(_2\) measured at the detector (mol cm\(^{-3}\))

\[ D \] CO\(_2\) diffusivity (cm\(^2\) s\(^{-1}\))

\[ J \] molar flux (mol cm\(^{-2}\) s\(^{-1}\))

\[ J_{\text{SS}} \] steady state molar flux (mol cm\(^{-2}\) s\(^{-1}\))

\[ l \] membrane thickness (cm)

\[ L_3 \] shape factor (dimensionless)

\[ P \] permeability (mol cm cm\(^{-2}\) s\(^{-1}\) Pa\(^{-1}\))

\[ Q_{\text{ch}} \] flow rate in the channel (cm\(^3\) s\(^{-1}\))

\[ Q_t \] total accumulation of CO\(_2\) (mol cm\(^{-2}\))

\[ S \] solubility (mol cm\(^{-3}\) Pa\(^{-1}\))

\[ t \] time (s)

\[ t_{\text{corr}} \] time corrected for machine lag (s)

\[ t_{\text{lag}} \] time lag (s)

\[ x \] position in the membrane (cm)

\[ \Delta p \] partial pressure drop (Pa)

\[ \Delta t_{99\%} \] 99\% rise time (s)

\[ \Delta t_{m\%} \] m\% rise time (s)

\[ \varepsilon \] volume fraction of water in the membrane (dimensionless)

\[ \varepsilon_p \] percolation threshold (dimensionless)

\[ \lambda \] water content (mol H\(_2\)O per mol functional group)

Chapter 4:

\[ C_i \] species concentration (mol cm\(^{-3}\))
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_{i, \text{ref}}$</td>
<td>reference concentration (mol cm$^{-3}$)</td>
</tr>
<tr>
<td>$D_{i,H_2O}$</td>
<td>species/water diffusivity (cm$^2$ s$^{-1}$)</td>
</tr>
<tr>
<td>$D_{i}^{\text{eff}}$</td>
<td>effective species diffusivity (cm$^2$ s$^{-1}$)</td>
</tr>
<tr>
<td>$F$</td>
<td>Faraday’s constant (C mol$^{-1}$)</td>
</tr>
<tr>
<td>$IEC$</td>
<td>ion exchange capacity (mol g$^{-1}$)</td>
</tr>
<tr>
<td>$J_i$</td>
<td>species flux (mol cm$^{-2}$ s$^{-1}$)</td>
</tr>
<tr>
<td>$k_{abs}$</td>
<td>absorption coefficient (cm s$^{-1}$)</td>
</tr>
<tr>
<td>$k_H$</td>
<td>Henry’s constant (cm$^2$ N$^{-1}$)</td>
</tr>
<tr>
<td>$k_j^+$</td>
<td>forward kinetic rate constant (cm$^3$ mol$^{-1}$ s$^{-1}$)</td>
</tr>
<tr>
<td>$k_j^-$</td>
<td>reverse kinetic rate constant (s$^{-1}$, cm$^3$ mol$^{-1}$ s$^{-1}$)</td>
</tr>
<tr>
<td>$K_j$</td>
<td>Equilibrium constant (mol cm$^{-3}$, mol$^2$ cm$^{-6}$)</td>
</tr>
<tr>
<td>$L$</td>
<td>membrane thickness (cm)</td>
</tr>
<tr>
<td>$M_{H_2O(i,j)}$</td>
<td>molecular mass of water (g mol$^{-1}$)</td>
</tr>
<tr>
<td>$M_{i,k}^*$</td>
<td>reduced molecular mass (g mol$^{-1}$)</td>
</tr>
<tr>
<td>$p_{CO_2}^{\text{gas}}$</td>
<td>partial pressure of CO$_2$ (N cm$^{-2}$)</td>
</tr>
<tr>
<td>$q$</td>
<td>Bruggeman exponent</td>
</tr>
<tr>
<td>$R$</td>
<td>ideal gas constant (J mol$^{-1}$ K$^{-1}$)</td>
</tr>
<tr>
<td>$\dot{R}_i$</td>
<td>species kinetic source terms (mol cm$^{-3}$ s$^{-1}$)</td>
</tr>
<tr>
<td>$t$</td>
<td>time (s)</td>
</tr>
<tr>
<td>$T$</td>
<td>temperature (K)</td>
</tr>
<tr>
<td>$x$</td>
<td>position (cm)</td>
</tr>
<tr>
<td>$z_i$</td>
<td>Valance</td>
</tr>
</tbody>
</table>

**Greek**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha$</td>
<td>degree of dissociation</td>
</tr>
<tr>
<td>$\varepsilon$</td>
<td>Porosity</td>
</tr>
<tr>
<td>$\lambda$</td>
<td>water content</td>
</tr>
</tbody>
</table>
\( \rho_{H_2O(l)} \) density of water (g cm\(^{-3}\))

\( \rho_m \) membrane density (g cm\(^{-3}\))

\( \sigma \) ionic conductivity (S cm\(^{-1}\))

### Chapter 5:

- **A** active cell area (m\(^2\))
- **\( B_0 \)** Darcy permeability (m\(^2\))
- **c** concentration (mol/m\(^3\))
- **c\(_0\)** liquid saturation concentration (mol/m\(^3\))
- **c\(_f\)** fixed charge concentration (mol/m\(^3\))
- **c\(_i\)** concentration of species \( i \) (mol/m\(^3\))
- **c\(_{od}\)** electro-osmotic drag coefficient
- **\( D_{IM}^0 \)** average membrane diffusion coefficient (m\(^2\)/s)
- **\( D_{ij} \)** species diffusion coefficient (m\(^2\)/s)
- **\( D_{ij}^e \)** effective species diffusion coefficient (m\(^2\)/s)
- **\( D_{im} \)** effective membrane diffusion coefficient (m\(^2\)/s)
- **\( Da \)** Damkohler number (Eq. 34)
- **\( E_0 \)** y-intercept potential (V)
- **\( F \)** Faraday’s constant (C/mol)
- **i** current density (A/m\(^2\))
- **\( K_{A,C} \)** equilibrium constant for proton solvation
- **\( N_i \)** flux of species \( i \) (mol/m\(^2\)/s)
- **\( P \)** oxygen pressure (Pa)
- **\( P_c \)** capillary pressure (Pa)
- **\( Pe \)** Peclet number (Eq. 35)
Greek Symbols

$\Gamma$ derivative acid dissociation with respect to the membrane water content

$\gamma_i$ activity coefficient of species i

$\chi$ dimensionless water balance parameter

$\delta$ pore wavelength (m)

$\Delta H^0$ enthalpy change for proton solvation (kJ/mol)

$\varepsilon$ wet membrane porosity

$\varepsilon_p$ percolation limit wet porosity

$\eta$ liquid viscosity within membrane pore (N-s/m$^2$)

$\theta$ contact angle (°, rad)

$\kappa$ acid dissociation constant

$\kappa_0$ acid dissociation constant for liquid equilibration

$\lambda$ membrane water content

$\mu_i^e$ electrochemical potential of species i (J/mol)

$\sigma$ surface tension (N/m)

$\phi$ potential (V)
Φ  pore wall angle (°, rad)
ψ  pore sine wave amplitude (m)

Subscripts
1  water
2  hydronium
M  membrane

Superscripts
*  dimensionless variable

Chapter 6:

a  major spheroid axis
A  arbitrary vector
b, c  minor spheroid axes
E  electric field (E-field)
E_i  internal E-field
E_0  imposed/applied E-field
E_{0x, y, z}  imposed/applied E-field components in spheroid coordinate system
E_{0ξ, η, ρ}  imposed/applied E-field components in inertial coordinate system
f, α  volume fraction of inclusion material
\hat{i}_x, \hat{i}_y, \hat{i}_z  unit vectors in spheroid coordinate system
\hat{i}_ξ, \hat{i}_η, \hat{i}_ρ  unit vectors in inertial coordinate system
\vec{j}  electrical current
K  normalization constant for distribution function
L_1, L_2, L_3  depolarization factors
m  distribution function parameter
N  number of spheroids in distribution
P  distribution function for spheroid orientation
r  distance from origin
\vec{r}  position vector
R  radius of spherical C. V.
$s$  
  dummy variable  

$V_S$  
  spherical C. V. volume  

$V_I$  
  volume of inclusions  

$x, y, z$  
  spheroid fixed coordinates  

**Greek Symbols**  

$\beta$  
  azimuth angle in spherical coordinates  

$\varepsilon$  
  material porosity  

$\zeta, \eta, \rho$  
  inertial frame coordinates  

$\theta$  
  polar angle in spherical coordinates  

$\xi$  
  distance parameter in ellipsoidal coordinate system  

$\sigma_0$  
  matrix conductivity  

$\sigma_1$  
  inclusion conductivity  

$\tilde{\sigma}_m$  
  effective conductivity tensor  

$\sigma_{m\eta}, \sigma_{m\rho}, \sigma_{m\phi}$  
  diagonal components of effective conductivity tensor  

$\phi^+$  
  external potential  

$\phi^+ f$  
  external far field potential  

$\phi_S^+$  
  external potential of a sphere  

**Misc.**  

$\langle \rangle$  
  average of parameter
Bibliography:


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