Modeling the Momentum and Mass Transfer within a Micro-Scale Polymer Electrolyte Membrane Fuel Cell for Flows within the Slip Flow Regime

Sean Tamarun Goudy
Western Michigan University

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MODELING THE MOMENTUM AND MASS TRANSFER WITHIN A MICRO-SCALE POLYMER ELECTROLYTE MEMBRANE FUEL CELL FOR FLOWS WITHIN THE SLIP FLOW REGIME

by

Sean Tamarun Goudy

A Dissertation
Submitted to the
Faculty of The Graduate College
in partial fulfillment of the
requirements for the
Degree of Doctor of Philosophy
Department of Mechanical and Aeronautical Engineering
Advisor: Bade Shrestha, Ph.D.

Western Michigan University
Kalamazoo, Michigan
May 2010
MODELING THE MOMENTUM AND MASS TRANSFER WITHIN A MICRO-SCALE POLYMER ELECTROLYTE MEMBRANE FUEL CELL FOR FLOWS WITHIN THE SLIP FLOW REGIME

Sean Tamarun Goudy, Ph.D.
Western Michigan University, 2010

Polymer Electrolyte Membrane (PEM) fuel cell systems are heterogeneous catalytic systems. Although there are many computational models that describe the behavior of PEM fuel cells, few simulate the catalyst surface concentration of reactant gases at the catalyst layer-membrane layer interface. Most PEM fuel cell models make no distinction between the bulk concentration of reactants and the catalyst surface concentration of reactants. It is the surface concentration that is key when studying PEM fuel cell systems: the reactions occur at the surface of the catalyst.

In addition, few model the dynamics within the non-continuum flow region near the solid surfaces of the fuel cell. Microscale and nanoscale fuel cells are not completely described by continuum mechanics. At the microscale and nanoscale, more specialized tools, which account for the increased surface forces and micro length scales, are needed to understand the dynamics of these micro-devices. The model simulates the microscale dynamics of a PEM fuel cell within the slip flow regime. Special attention is given to simulating the behavior of each reactant and product near each solid surface. To correct for non-equilibrium
behavior near the solid surfaces, slip boundary conditions are used to account for velocity slip.

This analysis models a PEM fuel cell to determine both the bulk reactant concentrations and the catalyst surface concentrations at the catalyst layer-membrane layer interface and demonstrates that size has an impact on overall fuel cell performance. The model also shows a reduction of the Ohmic losses that is balanced by an increase in the parasitic losses within the fuel cell. Finally, it is shown that the bulk concentration at the membrane-catalyst layer interface is not zero.
ACKNOWLEDGMENTS

"Dieu a tant aimé le monde qu’il a donné son fils unique pour que quiconque crois en lui ne périsse point, mais a la vie éternelle." Jean 3:16

"Le Seigneur est mon berger, je ne manque de rien." Psaume 23 :1

To my family for your loving support, I am eternally grateful for you, and I love each of you dearly. Words cannot explain the love that have for you. Thank you for allowing me to sacrifice time with you to complete this goal. You are truly the most precious thing that I have on this planet.

I would like to say thank you to both Ms. Mary Murphy and Ms. Kristi Ostling, who read my articles, my chapters, and gave me insightful feedback. You are truly scholars.

To Mr. Tony Dennis, Ms. Lateshia L. Agnew, and Ms. Latonia Raines, your tremendous support and encouragement kept me going when I wanted to give up. Thank you.

To my advisors Dr. I. Sahin and Dr. S. O. Bade Shrestha, thank you for being patient. Thank you for the support through this process.

To my dear late friends Mr. Leonard Roberson and Mr. Lindbergh Scott, you taught me to love life, to dance, and to have fun. Vous êtes mes anges gardiens. Vous me manquez toujours.

Sean Tamarun Goudy
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CHAPTER I

INTRODUCTION

The global demand for energy continues to grow at an alarming rate. Much of the growth is attributable to the growth of developing countries around the world.

In December 2001, the spot price of West Texas Intermediate (WTI) crude oil averaged $19.33 per barrel. Shortly thereafter, oil prices started to trend higher. After a brief decline from $74 per barrel in July 2006 to about $55 per barrel in January 2007, oil prices then resumed their upward trajectory. They surpassed $90 per barrel in October 2007. During the run-up in crude oil prices over the past few years, some economists and energy analysts correctly expected the price of crude oil to eventually rise to $100 per barrel or more, and crude oil prices eventually closed above $100 per barrel on Feb. 19 [2008] for the first time ever (Kliesen, 2008).

Although the price of oil subsequently fell during the latter part of 2008, the real possibility of a global energy shortage still exists, and this looming shortage is only exacerbated by the emergence of developing countries, like China and India. The two largest concerns are the demands for electricity in metropolitan areas and the demand for gasoline for transportation (Tissot, 2001).

As these developing countries continue to grow and to develop, their need for energy is growing, and the needs of these developing countries along with the needs of developed countries are causing the overall energy demand to
skyrocket. If nothing changes in the near future, the demand for energy will soon outpace the output capacity of the known oil and natural gas reserves. To stave off this looming energy crisis, new energy technologies are needed that optimize our current energy usage and that address the world’s future energy requirements.

The belief is that novel renewable energy technologies will be capable of addressing the world’s ravenous thirst for energy. However, there are still many important questions to be addressed:

1. How can developing countries continue to grow as the amount of cheap energy is declining?
2. How will developed countries be able to compete with developing countries and resolve the issue of climate change?
3. Are there energy technologies that are being developed today that will have a commercial benefit for both developed countries and developing countries?
4. As the world’s sources of crude oil diminishes, what will replace oil?
5. Is coal a viable solution to the current looming energy shortage?

Fossil Fuels: A Limited Resource

Today, fossils fuels; like oil, natural gas, and coal; represents 85% to 90% of the world’s primary energy sources (Jean-Baptiste & Ducroux, 2003; Tissot, 2001). The pitfalls of a fossil fuel dependent energy supply are many. The most
obvious concerns are that fossil fuels are not renewable, and that burning these fuels releases billions of tons of pollutants into the air each year.

Although extremely important to the accomplishments of humankind during the industrial revolution, coal, oil and natural gas are not present within the Earth in limitless quantities. Researchers now believe that the proven energy reserves of oil will be almost completely consumed by the year 2020, and the current natural gas reserves will be consumed by the year 2050 (Tissot, 2001).

Only coal, which is the greatest emitter of carbon dioxide (CO₂) and of other pollutants, offers humankind the ability to sustain its current energy demands. It has been estimated that the world’s coal reserves would be capable of sustaining the world’s energy needs for centuries (Tissot, 2001). However, coal is a heterogeneous mixture of many different components, and, when burned, coal releases numerous contaminants into the environment.

Fuel Cells and Energy

The world is at the cusp of the next great revolution: The Energy Revolution. It is believed that the Energy Revolution will revolutionize the way the world generates energy. One technology that is believed to be a key facet of the Energy Revolution is fuel cell technology. Fuel cells have been touted as a potential solution, which balances the needs of developing countries with the need to find carbon neutral energy sources (Barbir, 2005). Fuel cells have the potential to meet all of the world’s energy needs without the deleterious side effects of fossil fuels.
Although there are many types of fuel cells, Polymer Electrolyte Membrane (PEM) fuel cells are believed to be the fuel cell of choice. Polymer Electrolyte Membrane (PEM) fuel cells are simple devices that convert hydrogen gas (H₂) and oxygen gas (O₂) into electrical energy releasing water as the by-product of the electrochemical process. Because PEM fuel cells use hydrogen gas to generate energy, the world may one day be able to use these devices to address all of the world’s future energy needs without the fear of climate change, but more research is needed to commercialize this technology. Although there are numerous fuel cell models within the literature that document the impact of the macroscale physical and electrochemical properties of PEM fuel cells, none currently addresses the microscale physical and electrochemical properties of these devices.

Fundamentally, a fuel cell is a method of transforming the chemical energy stored within the covalent bonds of hydrogen gas into electrical energy (Fauvarque, 2001). A fuel cell extracts the chemical energy out of hydrogen gas (H₂) and the only by-product of this electrochemical process is water. Equation 1 is the overall reaction.

\[
2\text{H}_2 + \text{O}_2 \xrightarrow{\text{Pt}} 2\text{H}_2\text{O} + \text{Energy}
\]  

(1)

Whereas fossil fuels, like crude oil and coal, are heterogeneous mixtures, hydrogen gas is a simple molecule, which when burned emits water as the by-product of the electrochemical process, and, unlike fossil fuels, which are created
over millennia, hydrogen gas (H\textsubscript{2}) can be generated by the electrolysis of water (H\textsubscript{2}O).

The basic premise is that PEM fuel cells would allow the world to transition from a carbon based economy to a hydrogen-based economy (Nehrir & Wang, 2009). The United States government strongly believes that this transition to a hydrogen economy is key to continued economic growth. For this reason, the Department of Energy (DOE) set a goal of developing this hydrogen-based economy by 2030 (Nehrir & Wang, 2009). Fuel cell technology is in indelibly linked to this future hydrogen economy.

Hydrogen gas is more than just a chemical compound that would be mined and burned. The new paradigm would be to look at the hydrogen gas molecule as an energy carrier. Specifically, the hydrogen gas molecule would be used to store energy in a compact usable form. Hydrogen gas can be generated in many different ways. Approximately, 90% of the world’s hydrogen supply is generated through the reforming of hydrogen from natural gas (Nehrir & Wang, 2009). However, hydrogen can be generated from many different processes. Ale and Shrestha (2008) explain that in a country, like Nepal, which currently imports 100% of its fuel from other countries, could use the energy from its plentiful hydroelectric power resources to produce hydrogen gas using fuel cell technology during periods of low or moderate electrical demand. The hydrogen molecule would serve as an energy carrier allowing for the use of this stored energy during periods of high electrical demand (Ale & Shrestha, 2008).
Fuel cells and a future hydrogen economy will likely develop in tandem. Fuel cells extract the energy stored within the hydrogen molecule generating energy with no negative effects on the environment, but, as was alluded to in the prior paragraph, fuel cells can be run in reserve. The electrical energy produced from another energy device can be used by a fuel cell to generate hydrogen gas. Therefore, in lieu of generating electrical energy, during periods of low demand, the excess energy supplied from other sources could be used to generate hydrogen gas, which could be stored for other uses.

Unlike fossil fuels, which emit pollutants into the environment, fuel cells use hydrogen gas to generate electrical energy, and emit only water. That is to say that no hazardous air pollutants would be generated by PEM fuel cells. Although water is a greenhouse gas, unlike other greenhouse gases, the concentration of water in the environment is regulated naturally and readily by the Earth's natural water cycle. At the point of saturation, the water in the environment is released in the form of precipitation, i.e. rain, snow, sleet, etc.

Why Fuel Cells and Not Another Renewable Technology?

Although researchers are currently studying other technologies that would also reduce the world's dependence on fossil fuels, fuel cells are believed to be far superior to the other renewable energy technologies. The other renewable energy technologies, like wind and solar, have two major flaws. They generate electricity, which cannot be easily stored, and these "... renewable resources
have a major inconvenience: they fluctuate independently from demand” (Ibrahim et al, 2008).

The benefits of hydrogen (H$_2$) as an energy source are many. Because hydrogen can be generated from the electrolysis of water and from other renewable sources, the supply of hydrogen (H$_2$) is nearly limitless. The product of the combustion of hydrogen gas is water. Hydrogen can be stored at much less cost than electricity, and the energy stored within the covalent bonds of the hydrogen molecule can be extracted quickly.

Although renewable energy technologies are potentially large untapped sources of electrically energy, electricity storage is costly (Ibrahim et al, 2008). “. . . today, the storage capacity worldwide is the equivalent of about 90 gigawatts of a total production of 3400 gigawatts, or roughly 2.6%. . .” (Ibrahim et al, 2008). In reality, the answer is not either fuel cells or another renewable technology, but it is believed that fuel cells would be used in tandem with other renewable technologies. As previously mentioned, the paradigm of dig and burn must shift to cultivate and store. Hydrogen would be used as an energy carrier. During periods of low demand, these other renewable technologies would be used to generate hydrogen, which is easily stored, and this stored hydrogen would be used during periods of increased demand by fuel cells to produce electrical energy or the hydrogen could be burned in a conventional boiler for heat.
Research Objective

In order to develop a hydrogen economy and to unleash the potential of hydrogen fuel cells, more research is needed. The major issues that fuel cell researchers are attempting to tackle center around increasing the efficiency of these devices. Mathematical modeling is one method, which is currently being used to address the aforementioned efficiency concern. Although several researchers have modeled the macrostructure of hydrogen fuel cell, few have modeled the microstructure of hydrogen fuel cells.

Unlike macro-scale processes, micro-scale processes are not completely described by continuum mechanics or other traditional mathematical tools. As the characteristic length of the device approaches the mean free path of the fluid, which in the case of a PEM fuel cell are hydrogen and oxygen, traditional continuum mechanics assumptions fail to completely describe the characteristics of the flow. The most notable change is that the experimentally determined no-slip velocity boundary condition, which is appropriate in many macro-scale systems, cannot be assumed in micro-scale flows. The Knudsen number (Kn), a parameter borrowed from rarefied gas theories traditionally used in the space industry, can be used to predict when continuum mechanics assumptions weaken and where other dynamics equations or boundary conditions must be used to correct for non-continuum behavior.

Although there are several types of fuel cells, the focus of this research will be on polymer electrolyte membrane (PEM) fuel cells. Several models exist
for micro PEM fuel cells; however, none models the dynamics within the non-continuum region near the solid surfaces of the fuel cell gas channel. Therefore, an augmented approach to understanding micro-scale polymer electrolyte membrane fuel cell design and optimization is being proposed. This research studies how slip phenomenon at the solid surfaces of the micro-scale fuel cell affects fuel cell output and fuel cell design.

The objective of this research is to develop a transient model of a microscale PEM fuel cell. This research will be limited to Knudsen numbers less than $10^{-1}$. The computational model will simulate the transport mechanisms to predict fuel cell output. The ultimate goal of this research is to develop a tool that can be used to optimize the design of micro-scale PEM fuel cells. The study looks at three research questions:

1. What is the effect of the physical geometry on the performance of the fuel cell?

2. Is there a limit to the size of fuel cells?

3. How do the microfluidic properties of the system and the phenomenon of slip flow impact the performance of PEM fuel cells?

It is hypothesized that the size of the fuel cell will influence the performance of PEM fuel cells. It is hypothesized that the Ohmic losses will be almost non-existent in microscale models. Therefore, higher current densities would be theoretically possible. It is hypothesized that there would be a physical limitation on the minimum size of PEM fuel cells. The key would be determining
the point at which the size of the fuel cell starts to affect its performance, i.e. the overpotentials start to become too large. Finally, it is hypothesized that the microfluidic properties will have little impact on the performance of the fuel cell.
CHAPTER II

FUEL CELL FUNDAMENTALS

A fuel cell is a device that can be used to extract the chemical energy stored within the covalent bonds of chemical species, like hydrogen gas, to generate electrical energy (Fauvarque, 2001). Although fuel cells are seen as the answer to today's ever growing need for cheap energy, the fuel cell is not a recent invention. Sir William Grove performed the first fuel cell experiment in 1839 (Larminie & Andrews, 2003; Hoogers, 2003). The efficiencies of these pioneering fuel cells were extremely low: typically only a few percent (Li, 2006). Since then, a number of fuel cells have been developed. Most notably during the 1950's and 1960's, as the United States and Russia competed for the coveted prize of being the first countries to conquer space travel, a new breed of fuel cells was introduced (Li, 2006). The polymer electrolyte membrane (PEM) fuel cell developed in 1955 by Willard Thomas Grubb of General Electric was used by the United States in 1965 for the Gemini space mission (Boudellal, 2007). Shortly after that mission, NASA abandoned PEM fuel cell technology (Boudellal, 2007).

Spurred on by the development of Nafion ®, the polymer membrane developed by Dupont, in the early 1970's, fuel cell research was revitalized (Viswanathan & Scibioh, 2007). However, since the pioneering work of Grove,
scientists and engineers have worked on a myriad of different fuel cells: Polymer Electrolyte Membrane (PEM) Fuel Cell, Direct Methanol Fuel Cells (DMFC), Alkaline Fuel Cells (AFC), Phosphoric Acid Fuel Cells (PAFC), Molten Carbonate Fuel Cells (MCFC), and Solid Oxide Fuel Cells (SOFC).

Each fuel cell has its own unique operating conditions based on the media used to transport ions from one side of the fuel cell to the other. Table 1 lists the types of fuel cells with the applicable operating temperatures, fuel sources, oxygen supply requirements, and mobile ions.

Polymer Electrolyte Membrane (PEM) fuel cells have a relatively low operating temperature of approximately 80°C. Within a PEM fuel cell, hydrogen gas is used as the feed. Hydrogen gas ionizes in the presence of a platinum catalyst to form hydrogen ions, which immigrate across a polymer membrane. The benefit of this relatively simple fuel cell is that the reaction occurs at near ambient conditions. However, PEM fuel cells require a relatively pure hydrogen fuel feed. A typical PEM fuel cell has an efficiency of approximately 79% at 100°C (Larminie & Dicks, 2003).

Direct Methanol fuel cells (DMFC) are low temperature fuel cells, and are virtually identical to PEM fuel cell. However, unlike PEMFC, the fuel feed is a methanol-water solution. The nominal operating temperature of a DMFC is 75°C. Within a DMFC, methanol reacts with water to form carbon dioxide and hydrogen ions. The hydrogen ions diffuse across a polymer membrane from the anode to the cathode, and bond with oxygen molecules to form water.
Table 1: Fuel Cell Summary

<table>
<thead>
<tr>
<th></th>
<th>PEMFC</th>
<th>DMFC</th>
<th>AFC</th>
<th>PAFC</th>
<th>MCFC</th>
<th>SOFC</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Polymer Electrolyte</strong></td>
<td>Ion Exchange</td>
<td>Ion Exchange</td>
<td>Ion Exchange</td>
<td>westmembrane electrolyte</td>
<td>westmembrane electrolyte</td>
<td>Ceramic</td>
</tr>
<tr>
<td><strong>Direct Methanol Fuel Cell</strong></td>
<td>30°C - 100°C</td>
<td>20°C - 90°C</td>
<td>50°C - 200°C</td>
<td>205°C</td>
<td>650°C</td>
<td>800°C - 1000°C</td>
</tr>
<tr>
<td><strong>Alkaline Fuel Cell</strong></td>
<td>westmembrane electrolyte</td>
<td>westmembrane electrolyte</td>
<td>westmembrane electrolyte</td>
<td>westmembrane electrolyte</td>
<td>westmembrane electrolyte</td>
<td>westmembrane electrolyte</td>
</tr>
<tr>
<td><strong>Phosphoric Acid Fuel Cell</strong></td>
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<td>westmembrane electrolyte</td>
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<tr>
<td><strong>Molten Carbonate Fuel Cell</strong></td>
<td>westmembrane electrolyte</td>
<td>westmembrane electrolyte</td>
<td>westmembrane electrolyte</td>
<td>westmembrane electrolyte</td>
<td>westmembrane electrolyte</td>
<td>westmembrane electrolyte</td>
</tr>
<tr>
<td><strong>Solid Oxide Fuel Cell</strong></td>
<td>westmembrane electrolyte</td>
<td>westmembrane electrolyte</td>
<td>westmembrane electrolyte</td>
<td>westmembrane electrolyte</td>
<td>westmembrane electrolyte</td>
<td>westmembrane electrolyte</td>
</tr>
<tr>
<td><strong>Prime Cell Components</strong></td>
<td>Carbon-Based</td>
<td>Carbon-Based</td>
<td>Carbon-Based</td>
<td>Graphite-Based</td>
<td>Stainless Steel</td>
<td>Ceramic</td>
</tr>
<tr>
<td><strong>Fuel Supply Requirements</strong></td>
<td>Relatively High Purity Hydrogen</td>
<td>Methanol-Water Solution</td>
<td>Pure Hydrogen</td>
<td>Methane</td>
<td>Low Purity Hydrogen</td>
<td>Methane</td>
</tr>
<tr>
<td><strong>Fuel Supply Requirements</strong></td>
<td>Relatively High Purity Oxygen</td>
<td>Relatively High Purity Oxygen</td>
<td>Pure Oxygen</td>
<td>Oxygen/Air</td>
<td>Low Purity Air</td>
<td>Low Purity Air</td>
</tr>
<tr>
<td><strong>Catalyst</strong></td>
<td>Platinum</td>
<td>Platinum/Rubidium</td>
<td>Platinum</td>
<td>Platinum</td>
<td>Nickel</td>
<td>Perovskites</td>
</tr>
</tbody>
</table>
Equation 2 shows this simple reaction. The reaction liberates energy.

\[
\text{CH}_3\text{OH} + 3\text{O}_2 \xrightarrow{\text{Pt/Ru}} 4\text{H}_2\text{O} + 2\text{CO}_2 + \text{Energy} \quad (2)
\]

Methanol is used because a gallon of methanol has much more hydrogen available for reaction than a gallon of hydrogen gas. Moreover, liquid methanol is relatively easily stored compared to liquid hydrogen. Liquid hydrogen boils at -252.7°C at 760 mmHg pressure (or 1 atmosphere). Methanol boils at 64.7°C at 760 mmHg (Perry, Don, Maloney, 1984). DMFC have comparable efficiencies to PEMFC.

Some researchers believe that methanol is a more desirable fuel than hydrogen gas, because the distribution systems for liquid fuels already exist, and there would be relatively little training required for the safe handling of methanol. However, methanol crossover or short-circuiting is a known problem for DMFC. Crossover or short-circuiting is the migration of the fuel across the membrane electrolyte assembly (MEA). Crossover results in decreased efficiency of the fuel cell. Methanol crossover in some fuel cell applications have resulted in efficiencies less than 0.1% (Prakash, Mustain, & Kohl, 2009). In addition, the chemical kinetics of methanol conversion to hydrogen ions at the anode occurs at a slower rate than the conversion of hydrogen to hydrogen ions.

Alkaline fuel cells (AFC) were the first widely used fuel cells. Like DMFC and PEM fuel cells, AFC are low temperature fuel cells. The nominal operating temperature range of an AFC can vary from 50°C to 200°C. The electrolyte is an aqueous potassium hydroxide solution (Hoogers, 2003). AFC are suitable for
small scale applications. However, unlike PEMFC or DMFC, hydroxide ions (OH\(^-\)) diffuse from the cathode to the anode, and bond with hydrogen molecules to form water (Gregory, 1972; Larminie & Dicks, 2003). As shown in Equation 3, water and oxygen react in the presence of a platinum electrode to form hydroxide ions.

\[
2\text{H}_2\text{O} + \text{O}_2 + 4e^- \xrightarrow{\text{Pt}} 4\text{OH}^- \tag{3}
\]

The hydroxide ions then react with the hydrogen gas to form water and free electrons.

\[
4\text{OH}^- + 2\text{H}_2 \rightarrow 4\text{H}_2\text{O} + 4e^- \tag{4}
\]

Equation 5 shows that the net reactions in an AFC and a PEMFC are the same.

\[
\text{O}_2 + 2\text{H}_2 \rightarrow 2\text{H}_2\text{O} \tag{5}
\]

The major obstacle for widespread use of AFC is the requirement for a relatively pure hydrogen feed, and a high purity oxygen feed. In addition, the aqueous potassium hydroxide electrolyte of alkaline fuel cells is incredibly sensitive to carbon dioxide.

Phosphoric Acid Fuel Cells (PAFC) are medium temperature fuel cells. The nominal operating temperature of a PAFC is 205°C. Although the operating temperature is high for most small scale applications, PAFC are attractive to researchers and engineers, because a pure hydrogen feed is not required. PAFC were designed to use a methane feed (Hoogers, 2003).
Molten Carbonate Fuel Cells (MCFC) are typically used in high temperature applications. The nominal operating temperature of a MCFC is 650°C. As shown in Equation 6, within the anode, hydrogen reacts with carbonate ions to form carbon dioxide, water, and free electrons.

\[
H_2 + CO_3^{2-} \rightarrow CO_2 + H_2O + 2e^{-} \tag{6}
\]

At the cathode, oxygen reacts with carbon dioxide to form carbonate ions.

\[
O_2 + 2CO_2 + 4e^- \rightarrow 2CO_3^{2-} \tag{7}
\]

The following net reaction (Equation 8) results:

\[
2H_2 + O_2 + 2CO_2 \rightarrow 2CO_2 + 2H_2O \tag{8}
\]

The net reaction shows that carbon dioxide is catalytic, because the carbon dioxide is not consumed in the reaction. As the name would suggest, a molten salt sustains the highly conductive environment.

Similar to Molten Carbonate fuel cells, Solid Oxide Fuel Cells (SOFC) are used in high temperature applications. The nominal operating temperature range of a SOFC is between 800°C to 1000°C. SOFC are best suited for large scale applications. The membrane is a ceramic oxide.
PEM Fuel Cell Basics

Of the aforementioned fuel cells, only the Polymer Electrolyte Membrane (PEM) fuel cell has been identified as the fuel cell with the most viable applications for low temperature engines. The PEM fuel cell is a device used to exploit and to use the energy stored within the covalent bonds of hydrogen gas molecules. Unlike conventional internal combustion engines, which convert chemical energy into mechanical energy, PEM fuel cells generate electrical energy via an electrochemical reaction. As shown in Equation 9, hydrogen gas, supplied at the anode, and oxygen gas, supplied at the cathode combine electrochemically in the presence of a platinum catalyst to produce water and electrical energy.

\[
2H_2 + O_2 \xrightarrow{\text{Pt}} 2H_2O + \text{Energy} \quad (9)
\]

PEM fuel cells are relatively simple devices. A PEM fuel cell has three components: an anode, a cathode, and a polymer membrane. The polymer membrane separates the anode from the cathode, and it is the membrane, which makes fuel cell possible. Figure 1 is a schematic of a typical PEM fuel cell.

Equation 10 shows that, at the anode, hydrogen gas (H_2) is oxidized in the presence of a platinum (Pt) catalyst liberating two hydrogen ions (H^+) and two electrons (e^-).

\[
H_2 \xrightarrow{\text{Pt}} 2H^+ + 2e^- \quad (10)
\]
At the cathode, oxygen gas ($O_2$) is reduced and reacts electrochemically with the hydrogen ions and the electrons.

$$O_2 + 4H^+ + 4e^- \xrightarrow{Pt} 2H_2O$$  \hspace{1cm} (11)

The uniqueness of the PEM fuel cell polymer membrane will be discussed later.

Researchers have proposed one likely mechanism, which subdivides the anode side reaction into two half-reactions (Bi & Fuller, 2008). Scientists theorized that the platinum initially liberates two electrons forming a platinum cation ($Pt^{2+}$) (Equation 12).

$$Pt \rightarrow Pt^{2+} + 2e^-$$  \hspace{1cm} (12)
The platinum cation (Pt$^{2+}$) then scavenges the two valence electrons from the hydrogen gas molecule and the platinum catalyst is regenerated (Bi & Fuller, 2008).

\[ \text{Pt}^{2+} + \text{H}_2 \rightarrow \text{Pt} + 2\text{H}^+ \quad (13) \]

A complementary reaction occurs at the cathode. As shown in Equation 14, the oxygen-oxygen covalent bond is broken, and the each oxygen atom scavenges two of the free electrons, which were liberated at the anode.

\[ \text{O}_2 + 4e^- \rightarrow 2\text{O}^{2-} \quad (14) \]

To understand why each oxygen atom scavenges two free electrons, recall that monatomic oxygen has six valence electrons in its outer orbital. The optimal number of valence electrons for monatomic oxygen is eight. The diatomic oxygen molecule (O$_2$) exists, because monatomic oxygen (O) seeks to fill its outer orbital by forming covalent bonds with other molecules (Ebbing, 1987). A covalent bond is a bond that is created when two atoms share a pair of electrons.

Fuel Cells vs. Conventional Heat Engines

Fuel cells produce far fewer pollutants than conventional engines, because the fuel in fuel cells is not burned. By-products such as nitrogen oxides (NO$_x$), sulfur oxides (SO$_x$), and carbon monoxide (CO) are formed because of incomplete combustion or because of impurities in the fuel. The United States
Environmental Protection Agency (USEPA) has identified nitrogen oxides, sulfur oxides, and carbon monoxide as pollutants (Genevey, 2001; 40 CFR 63). However, the typical byproducts of a fuel cell's electrochemical process are water, nitrogen, the oxidized fuel, unconsumed fuel, and only trace amounts of the aforementioned pollutants (Genevey, 2001). These environmental advantages make PEM fuel cells very attractive to businesses.

Another advantage of PEM fuel cells is that they have few fuel storage limitations. Although fuel cells produce electricity electrochemically, like a battery, the cell life of a fuel cell is not dependent upon its storage capacity (Gregory, 1972; Larminie & Dicks, 2003). While the cell life of a traditional lead-acid battery is directly proportional to its storage capacity, i.e. the size of the battery, a fuel cell can have an almost infinite cell life, as long as fuel is supplied (Gregory, 1972). Therefore, any very small PEM fuel cells can have a very long usable life, because the fuel can be supplied from storage systems exterior to the fuel cell. Locating the fuel storage exterior to the fuel cell is attractive to manufacturers of micro-scale electronics, because the device design is not constrained by the size of the fuel storage.

Fuel cells produce an electric current when negatively charged electrons are liberated at the anode of the fuel cell from a donor molecule and are consumed at the cathode of the fuel cell by positively charged receiver molecules. As the electrons travel from the anode to the cathode, an electric current is generated. This flow of electrons, which is called an electric current, can be used to perform work.
PEM Fuel Cell Polymer Membrane

It is the polymer membrane, which separates the anode from the cathode that translates the chemical advantage of PEM fuel cells into a physical advantage and economic advantage. Although the concept of a membrane based fuel cell was first developed in 1955 by Willard Thomas Grubb of General Electric, “Perhaps the most common PEM [polymer electrolyte membrane] in use today is Nafion® a well-researched perfluorosulfonic acid (PFSA) ionomer, which is commercially available in films varying from 25 to 175 microns thick” (Ramani, 2006). Nafion® is a polymer, which was created by Dupont™ in the 1970s (Viswanathan & Scibioh, 2007). The chemical structure of the Nafion® molecule makes Nafion® a revolutionary material. Nafion® has a polytetrafluoroethylene (PTFE) backbone with perfluorinated double ether terminated by a sulfonic acid group (Viswanathan & Scibioh, 2007). Figure 2 is a schematic of the Nafion® molecule.

Nafion is composed of a hydrophobic polytetrafluoroethylene backbone and a hydrophilic sulfonic acid terminated perfluorinated double ether functional group. The combination of a hydrophobic backbone and a hydrophilic functional group give Nafion® unique physical and electro-chemical properties. For example, Nafion® in the presence of water is a strong acid. It is the acidic nature of Nafion®, which gives the membrane a key electro-chemical property.
Specifically, hydrolyzed Nafion® is impervious to electrons. The electron resistant nature of Nafion® prevents electrons from short circuiting the fuel cell; therefore, the free electrons generated at the anode can be directed through a conductor to a load or engine to perform useful work.

The Nafion® polymer is unique because it is impervious to electrons. To understand why Nafion® is impervious to electron flow, one must examine the chemical structure of the Nafion® polymer. The polymer membrane is virtually impervious to negatively charged particles, because the de-protonated sulfonate (R-SO$_3^-$) cognate base gives the Nafion® molecule a net negative charge. The reason for the net negative charge will become clearer to the reader after reviewing the chemical-physical structure of the membrane.

The sulfonic acid terminated perfluorinated double ether functional group has an acidic hydrogen. Because of the stability of the resonance structures, the
sulfonic acid functionality is highly acidic. When the membrane is hydrated, this acidic hydrogen is liberated, and the cognate base (R-\(\text{SO}_3^-\)) remains immobilized, attached to the tetrafluorethylene backbone. The presence of the three oxygen atoms in the sulfonate cognate base helps to stabilize the negative charge. The stabilization is possible, because the sulfonate cognate base forms resonance structures. Because of the stability of the resonance structures formed by the sulfonate cognate base, the sulfonic acid functionality is highly acidic. “One of the most important postulates of resonance theory is that the greater the number of possible resonance forms, the greater the stability of the compound” (McMurry, 1988). Figure 3 is a two-dimensional (2-D) depiction of the three resonance forms of the sulfonate ion.

![Sulfonate Ion Resonance Forms](image)

Figure 3: Sulfonate Ion Resonance Forms.

(The R group is tetrafluorethylene ethyl-propyl-vinyl ether.)

When the membrane is sufficiently hydrated, the sulfonic acid functionality dissociates forming a hydrogen ion and a negatively charged sulfonate ion (R-\(\text{SO}_3^-\)). Because the polymer membrane is immobilized, only the positively charged hydrogen ions are mobile. For the aforementioned reasons, it is imperative that the membrane remain hydrated to ensure maximum functionality.
and maximum efficiency of the fuel cell. If the membrane becomes too dry, the acidic hydrogen cannot be liberated, and the functionality of the membrane is reduced and the efficiency of the fuel cell is diminished.

Fuel Cell Efficiency

As shown in Equation 15, the efficiency ($\eta$) of an engine is defined as the output work ($W$) divided by the heat input ($Q_H$) (Smith & VanNess, 1987).

$$\eta = \frac{W}{Q_H}$$  \hspace{1cm} (15)

Chemical energy may be used directly or indirectly to generate power. Traditional engines, like internal combustion engines, which are common place in automobiles, use heat generated by the burning of a fuel indirectly to produce mechanical work. Other common traditional engines are steam engines which generate energy by the burning of coal or electrical turbines which generate energy by burning natural gas to produce electricity.

For a traditional engine, the heat input ($Q_H$) is defined as the heat that the system absorbs from a high temperature reservoir. Since no system exists that can convert heat completely into work, a portion of the heat energy inputted into a traditional heat engine is lost to the ambient environment and is not available to do work. Therefore, as shown in Equation 16, the work output is merely the difference between the heat input ($Q_H$) and the heat output ($Q_C$), which is commonly called the exhaust.
The heat output \((Q_c)\) is the residual heat expelled or exhausted to a low temperature reservoir through a stack or an exhaust pipe.

Because the quantity of heat that can be used to perform work is limited, the maximum efficiency of a traditional heat engine is much less than unity (100% thermal efficiency). Specifically, the theoretical maximum is limited to the efficiency of an ideal heat engine called a Carnot engine. The maximum efficiency of a heat engine is the Carnot efficiency \((\eta_{\text{carnot}})\). Equation 17 is a simplified equation for the Carnot efficiency, which relates the efficiency of a Carnot cycle to the temperature in the hot and cold temperature reservoirs.

\[
\eta_{\text{carnot}} = 1 - \frac{T_C}{T_H}
\]  

\((17)\)

\(T_H\) and \(T_C\) are the absolute temperatures of the hot and cold reservoirs, respectively. Although the aforementioned equation might give the reader the impression that it is theoretically possible to construct a Carnot engine which is 100% efficient, due to material of construction limitations, traditional engines have maximum efficiencies less than 45%. However, the question still remains: what makes a fuel cell different from a traditional heat engine?

Unlike traditional heat engines, fuel cells use chemical energy directly to generate power. Although the efficiency \((\eta_{\text{cell}})\) of a fuel cell is also defined as the output work \((W)\) divided by the heat input,
The output work is no longer defined as the difference between the heat input \((Q_H)\) and the heat output \((Q_C)\).

To explain the difference between a traditional engine and a fuel cell, we first need to define how much chemical energy is stored within a chemical species. The internal energy \((U)\) of a chemical species is defined as "... the energy of the molecules making up the substance, which are in ceaseless motion and possess kinetic energy of translation ..." (Smith & VanNess, 1987). The First Law of Thermodynamics states that energy is neither created nor destroyed, merely converted from one form of energy to another. Therefore, as shown in Equation 19, for any closed system, the change in energy must be given by the heat \((Q)\) transfer into the system minus the work \((W)\) done by the system.

\[
\Delta U = Q - W
\]  

Equation 19

A closed system is a system that does not allow matter to be exchanged with its surroundings. If the system is capable of exchanging matter with its surrounding, the system is called an open system, and, therefore, the First Law equation is slightly changed. The system must not only perform work against its surrounding, but the matter within must have sufficient energy to push out of the system and into its surroundings. To account for the additional energy that the matter must have, the following form of the First Law is introduced.
\[ \Delta U + \Delta (PV) = Q - W \quad (20) \]

To account for this additional pressure (P) and volume (V) work, a new term called enthalpy (H) is defined in Equation 21.

\[ \Delta H = \Delta U + \Delta (PV) \quad (21) \]

Although the enthalpy of formation (\(\Delta H_f\)) is the maximum quantity of chemical energy contained within a chemical species within an open system, the heat of formation is not the maximum amount of energy which can be extracted from the chemical species. The maximum amount of usable work is defined as the Gibb's Free Energy (\(\Delta G\)). As shown in Equation 22, the Gibb's Free Energy is a function of the enthalpy (\(\Delta H\)) and the entropy (\(\Delta S\)).

\[ \Delta G = \Delta H - T\Delta S \quad (22) \]

Equation 23 shows that the output work (\(W_{cell}\)) is related to Gibb's Free Energy, and, as shown in Equation 23, the output work of the cell is a function of the electrical energy produced by the cell.

\[ W_{cell} = n_e F E \quad (23) \]

The heat input (\(Q_H\)) is defined as the change in the heat of formation, also known as the enthalpy of formation (\(\Delta H_f\)), of the input fuel. Equation 24 relates the cell efficiency to the work output of the cell and the heat of formation of the reactants.
As shown in Equation 25, the maximum efficiency of a fuel cell is given the open circuit voltage divided by the enthalpy of formation.

\[
\eta_{\text{cell max}} = \frac{\Delta G_f}{\Delta H_f}
\]  

The effect of operating temperature on the performance of a PEMFC is complex and a little confusing. In the ideal case, as operating temperature is increased, performance, or efficiency, decreases. Specifically, if one were to plot the reversible open circuit voltage (OCV), as known as the maximum electromotive force (EMF), versus temperature for the ideal reversible fuel cell case, the data show that the performance of the fuel cell decreases with temperature.

Because fuel cells are the output voltage source of an electrical circuit, some amount of heat is lost to the environment. This loss of heat is an inefficiency or irreversibility. Within the fuel cell vernacular, scientists often use the term overpotentials, in lieu of the terms losses or irreversibilities. However, within this document, all three terms will be used interchangeably.

There are four major fuel cell irreversibilities: activation losses \(V_a\), Ohmic losses \(V_o\), parasitic losses \(V_p\), and concentration losses \(V_c\). As shown in Equation 26, the fuel cell output voltage \(E_{\text{cell}}\) is defined as the open circuit voltage \(E_0\) minus the sum of the losses.
\[ E_{\text{cell}} = E_0 - V_p - V_{\text{Act}} - V_{\text{Ohm}} - V_{\text{conc}} \]  \hspace{1cm} (26)

The open circuit voltage \( (E_0) \) of a PEM fuel cell is approximately 1.229 V at standard temperature and pressure. However, in practice, the real voltage of a fuel cell varies considerably from this maximum voltage. As shown in Equation 27, the open circuit voltage \( (E_0) \) is a function of the system temperature (Ju, Meng, & Wang, 2005).

\[ E_0 = 1.23 - 0.0009(T - 298K) \]  \hspace{1cm} (27)

Figure 4 shows that the performance of the fuel cell decreases with temperature.

![Figure 4: Maximum EMF vs. Temperature for Hydrogen Fuel Cells.](image)
Although the figure shows a decrease in performance with increasing temperature for ideal fuel cell systems, real fuel cell performance typically increases with increasing temperature. Why the apparent contradiction? The answer is the existence of voltage losses, as known as overpotentials. Typically, the voltage losses of a fuel cell decrease with increasing temperature. At lower operating temperatures, these overpotentials can be quite significant. Overpotentials, or voltage losses, are caused by system irreversibilities. The four major irreversibilities are activation losses, parasitic losses (i.e. fuel crossover), Ohmic losses, and concentration losses, as mentioned earlier.

**Activation Overvoltage**

The largest of the losses is the activation losses. The activation overvoltage ($V_{act}$), which is also called an activation loss, is the loss of voltage associated with the speed of the reactions at the electrodes. "The activation loss or activation overvoltage arises from the need to move electrons and to break and form chemical bonds in the anode and the cathode" (Pukrushpan, 2005). The activation overvoltages occur at both the anode and the cathode; however, because the cathode reaction is much slower than the anode reaction, the cathode activation overvoltage is much larger than that of the anode activation overvoltage.

In 1905, Tafel observed that the activation overpotential ($V_{act}$) at the electrode is proportional to the logarithm of the current density ($i$) divided by the exchange current density ($i_0$). Equation 28 is the Tafel equation.
A typical value for the exchange rate current density is 0.67 A/m$^2$, and a typical value for the empirical constant $a$ is 0.06 V. Activation overvoltages are responsible for the initial drop in voltage that is observed when current first begins to flow from a fuel cell. The activation overvoltage is a function of the current density ($i$) (Pukrushpan, 2005). "The effects of these losses are most pronounced at low current densities (~1 to 100 mA/cm$^2$)" (Ramani, 2006). Using Tafel’s equation (Equation 28), the net cell voltage ($V$) can be calculated as follows (Equation 29):

\[
V = E - V_{\text{act}}
\]

$E$ is the maximum EMF of the cell, and $V$ is the net cell voltage after the voltage losses due to activation losses have been subtracted.

The activation overpotential is a function of the concentration or, more specifically, the pressure of the reactant gas supply. Typically, PEM fuel cells are operated at or about 80°C, so both oxygen gas and hydrogen gas can be assumed to be ideal gases. Specifically, as the pressure of reactant gases increases the activation losses decrease.

Le Châtelier’s principle states that one can drive a reversible reaction in the forward direction or in the backward direction by imposing a stress on the system (Ebbing, 1987). When a stress is applied to a reversible system, the
system is driven toward an equilibrium state that minimizes the overall energy state of the system. Le Châtelier’s principle states that if the pressure increases on a system that has more moles of gaseous reactants, then the reaction will favor the forward reaction, because the lower energy state is the state with fewer moles of gas (Ebbing, 1987). Specifically, for PEM fuel cell system, as the pressure increases, the increased pressure creates thermodynamic instability on the reactant side of the fuel reaction. Equation 30 and Equation 31 are the chemical reactions that occur at the anode and at the cathode, respectively. If the pressure is increased, the forward reaction is preferred, because the overall number of moles of reactant are reduced.

\[
\text{H}_2(g) \xrightarrow{\text{Pt}} 2\text{H}^+(aq) + 2e^- \quad (30)
\]

\[
\text{O}_2(g) + 4\text{H}^+(aq) + 4e^- \xrightarrow{\text{Pt}} 2\text{H}_2\text{O}(l) \quad (31)
\]

Given that the both reactants are gases, Le Châtelier’s principle states that if the partial pressure of the reactants is increased, then the forward reaction would be preferentially preferred over the reverse reaction (Ebbing, 1987). This is the reason why the activation losses are reduced as the pressure increases given a constant temperature. Specifically, the number of moles of gaseous species is reduced as the reaction progresses in the forward direction. Therefore, as the pressure increases, the activation overpotential or losses will be reduced.
Ohmic Overvoltage

Along with activation overvoltages, the fuel cell output voltage is also reduced as the fuel cell membrane thickness increases. Specifically, the Ohmic overvoltage is the voltage loss associated with the movement of electrons and protons within the fuel cell membrane. The Ohmic overvoltage follows Ohm’s Law (Equation 32).

\[ V_{Ohm} = i R_{Ohm} \]  

(32)

The variable \( i \) is the current density and \( R_{ohm} \) is the resistance of the membrane. As shown in Equation 33, the current density is a ratio of the current (\( I \)) to the active area (\( A \)) of the fuel cell.

\[ i = \frac{I}{A} \]  

(33)

The current density has units of amperes per centimeter squared. "The effects of these losses are perhaps most pronounced at intermediate current densities (~100 to 500 mA/cm\(^2\))" (Ramani, 2006). As shown in Equation 34, the membrane resistance is proportional to the membrane thickness (\( t_m \)), and is inversely proportional to the membrane conductivity (\( \sigma_m \)).

\[ R_{Ohm} = \frac{t_m}{\sigma_m} \]  

(34)
Amphlett et al. (1994) have shown that the membrane conductivity is a strong function of the membrane temperature, and the membrane conductivity is also proportional to the membrane hydration (as cited by Pukrushpan, 2005). Equation 35 shows the functional relationship between the membrane conductivity ($\sigma_m$) and the temperature ($T$).

$$\sigma_m = b_1 \exp \left[ b_2 \left( \frac{1}{303} - \frac{1}{T} \right) \right]$$  \hspace{1cm} (35)

The temperature ($T$) is in Kelvin, and $b_1$ is a function of membrane hydration ($\lambda_m$) (Pukrushpan, 2005). Equation 36 shows the functional relationship between the coefficient $b_1$ and the membrane hydration.

$$b_1 = b_{11} \lambda_m - b_{12}$$  \hspace{1cm} (36)

The other variables ($b_2$, $b_{11}$, and $b_{12}$) are empirically derived constants. Springer et al. (1991) derived empirical values for $b_{11}$ and $b_{12}$ for Nafion™ 117 (Springer et al., 1991).

Concentration Overvoltage

The overall voltage is also a function of the reactant concentration. Specifically, voltage dips as the concentration around the electrode drops. Concentration overvoltage is also known as mass transport loss. These losses arise from a lack of fuel at the fuel cell electrode. Specifically, fuel is diffusing much slower than the rate at which it is being used. "The effects of these losses
are most pronounced at high current densities (> 500 mA/cm²)” (Ramani, 2006). The following correlation (Equation 37) can be used to relate the concentration losses to the current density.

\[
V_{conc} = i \left( c_2 \frac{i}{i_{max}} \right)^{c_3} \tag{37}
\]

“The parameter \( i_{max} \) is the current density that causes precipitous voltage drop” (Pukrushpan, 2005).

Parasitic Overvoltage

The most common cause of voltage loss within a fuel cell comes from parasitic losses. Parasitic loss refers to the loss of voltage potential due to unwanted side reactions. The most common parasitic loss is due to fuel crossover. For this reason, there is a critical fuel cell membrane thickness, which balances the rate fuel crossover with the rate of electricity generation. If fuel cell crossover were not a problem, fuel cell membranes could be much thinner. Short circuiting occurs when hydrogen gas diffuses across the polymer membrane and reacts with the oxygen present at the cathode (Kanezaki, Li, & Baschuk, 2006).

A polarization curve, which is a plot of the fuel cell output voltage (V) versus the current density (i), used as a standard to compare the efficiencies of different fuel cells. Figure 5 is a typical polarization curve.
Figure 5: Polarization Curve.

The initial dip in the voltage near zero current density is due to activation losses associated with the breaking and reforming of chemical bonds. The gradual decline in the polarization curve is due to the Ohmic losses that are inherent in any electrical circuit. The sudden drop at the high current densities is due the mass transport limitations at the higher current density. Specifically, the rate of consumption of the reactants is much higher than the rate of transport of these reactants to the active area.

Water Generation and Transport

As previously mentioned, a PEM fuel cell extracts the energy from the reaction of hydrogen and oxygen. The end product of the fuel cell reaction is water. Because the sulfonic acid end group is an acidic hydrogen, the degree of hydration of the fuel cell has a significant impact on the operation and efficiency of the fuel cell (Barbir, 2005). When the Nafion polymer is hydrated, the sulfonic
acid end dissociates liberating a positive hydrogen ion, leaving a negatively charged sulfonate ion in its place. It is the negatively charged sulfonate ion, which makes the polymer membrane nearly impervious to electrons.

It is important to understand the generation and the movement of water within the fuel cell. Water is a product of the reaction of hydrogen gas with oxygen gas. Specifically, hydrogen gas is supplied to the anode. The hydrogen in the presence of a catalyst dissociates to form hydronium ions. The hydronium ions diffuse across the polymer membrane and react with oxygen in the cathode to form water. Because the degree of hydration of the fuel cell significantly affects the overall efficiency of the fuel cell, it is important to understand the overall water balance. Water is introduced to the fuel cell by the humidified reactants. Water is generated at the cathode, and water is exhausted at both the cathode and the anode outlet.

There are two major mechanisms for water transport within the fuel cell. Because water has a natural dipole, a water molecule has a positively charged end and a negatively charged end. Therefore, the hydronium ion (H\(^+\)) drags a water molecule with it as it diffuses across the polymer membrane. The action of the water molecule being dragged from the anode to the cathode is called electro-osmotic drag. As shown in Equation 38, the flux (\(N_{\text{osmotic}}\)) associated with the electro-osmotic drag is a function of the electro-osmotic drag coefficient (\(n_d\)), the current density (\(i\)), and Faraday's constant (\(F\)).

\[
N_{\text{osmotic}} = n_d \frac{i}{F} \tag{38}
\]
Water will also diffuse from the cathode to the anode of the fuel cell. Because water is generated at the cathode, the concentration of water at the cathode is much higher than the concentration of water at the anode. Therefore, a concentration gradient is formed (Pukrushpan, 2005). The flux (N) is defined by Fick’s law (Equation 39).

\[ N = -D_w \frac{dc_y}{dy} \]  

(39)

Fick’s law states that the flux (N) is proportional to the concentration gradient. The constant of proportionality is the diffusivity \( D_w \). Equation 40 is the functional form of the diffusivity \( D_w \), and shows the relationship between the diffusivity and the temperature (T).

\[ D_w = D_{\lambda m} \exp \left[ 2416 \left( \frac{1}{303} - \frac{1}{T} \right) \right] \]  

(40)

\[ D_{\lambda m} = \begin{cases} 10^{-6} & \\
10^{-6} (1 + 2(\lambda_m - 2)) & \\
10^{-6} (3 - 1.67(\lambda_m - 3)) & \\
1.25 \times 10^{-6} & 
\end{cases} \]  

(41)

As shown in Equation 42, the net water flux \( N_w \) is the sum of both the osmotic drag and the diffusion. (Pukrushpan, 2005).

\[ N_w = n_d i F - D_w \frac{dc_y}{dy} \]  

(42)
The voltage of the fuel cell is also affected by the hydration of the fuel.

Although the performance of ideal fuel cell decreases with increasing temperature, the performance of real fuel cell systems increases with increasing temperature, due to the existence of irreversibilities. These irreversibilities are more pronounced at lower temperatures, causing increases in voltage losses and decreases in real fuel cell performance at lower temperatures. As the operating pressure of a fuel cell system increases, the performance of the fuel cell system increases. This increase in performance is related to the kinetics of the fuel cell system and the mass transport within the system.

The Nernst Equation (Equation 43) defines how the reactant and product pressures, or concentration, affect the cell voltage (E).

\[ E = E^0 + \frac{RT}{2F} \ln \left( \frac{P_{H_2} \cdot P_{O_2}^{0.5}}{P_{H_2O}} \right) \]  

(43)

\( E^0 \) is the EMF of the cell at standard pressure, which is 1 bar. As the partial pressures of the reactants are increased, the output voltage is increased. As shown in Equation 44, the partial pressure (\( P_i \)) of a reactant and products is related to the total system pressure (\( P_T \)) by the mole fraction (\( X_i \)).

\[ P_i = P_T X_i \]  

(44)

Therefore, partial pressure is a surrogate for concentration. From inspection, the Nernst Equation shows that as the operating pressure increases
the cell performance increases. It is assumed that the concentration or mole fraction of the reactants and products is unchanged. "The increase in power resulting from operating a PEM fuel cell at higher pressure is mainly the result of the reduction in the cathode activation overvoltage..." (Larminie & Dicks, 2003).

Current density has a dramatic impact on fuel cell performance, i.e. output voltage. Specifically, as the current density increases, the output voltage decreases. Initially, the cell voltage drops sharply, then plateaus. However, as the current density increases, the cell voltage starts to drop faster. This drop in cell voltage is caused by two irreversibilities: Ohmic losses and activation losses.

When the electrode and the electrolyte membrane are in contact, a charge double layer is formed. "In electrochemical systems, the charge double layer forms in part due to diffusion effects, as in semiconductors, and also because of the reactions between the electrons in the electrodes and the ions in the electrolyte..." (Larminie & Dicks, 2003). Specifically, for the case of the cathode side of a PEMFC, electrons gather at the electrode-electrolyte interface, and hydrogen ions gather on the electrolyte side of the electrode-electrolyte interface. The presence of these ions acts like a capacitor, and energy is stored. This stored energy is not available for work: it is lost voltage.

As the gases diffuse into the electrode and react, several phenomena have been observed. The diffusion of the ions toward the electrode-electrolyte interface also causes local reduction in the concentration of the reactants. This reduction in the concentration of the reactants near the electrode reduces the performance of the cell. For the hydrogen fuel cell, water may form at the
cathode blocking or impeding the diffusion of gases to the electrode. The presence of this water reduces the performance of the cell.
As the micro-electronic industry has grown, the need for cheaper, more energy efficient power has expanded. PEM fuel cells have been heralded as possible solutions to this need. However, a major obstacle to their use is the delivery of the fuel to these micro-electro mechanical systems (MEMS). As PEM fuel cells become smaller and smaller, the techniques traditionally used to describe the transport mechanisms in macro-scale PEM fuel cell devices fail to adequately describe the transport mechanisms that are specific to micro-scale devices. Therefore, more specialized tools, which account for the increased surface forces and micro length scales, are needed to understand the dynamics of these micro-devices.

Unlike traditional macro flows, where the fluid may be assumed continuous and the surface forces are significantly smaller than the inertial forces, in micro-devices, the surfaces forces maybe several orders of magnitude more intense than the inertial forces (Tabeling, 2005). Therefore, engineers must reassess these traditional transport theories to determine when and where these traditional assumptions fail.

"Fluid dynamics is a branch of mechanics, or physics, that seeks to describe or explain the nature of physical phenomena that involve the flow of
fluids and/or gases" (Middleman, 1998). Traditional fluid dynamics, also known as continuum mechanics, describes the macroscopic behavior of fluids by modeling the macroscopic properties of the fluid. The Navier-Stokes equations are used to described the behavior of these macroscopic flows. Both the Navier-Stokes equations relate the density ($\rho$), momentum ($\rho u$), and internal energy ($e$) of the fluid to the overall behavior of the fluid.

The basic premise is that the fluid is acted upon by a force, which causes the fluid to move. These forces are divided into two types: surface forces and body forces. Surface forces act upon the surface of the fluid. Shear stress is surface stress. Shear stresses are forces that act tangentially to the surface of a fluid element. Pressure is a surface stress, which acts perpendicular to the surfaces of a fluid element. Body forces ($f_j$), such as gravity, centrifugal forces, and electromagnetic forces, affect the entire mass of the fluid element.

The Navier-Stokes equations describe the flow dynamics of continuum flows by related the aforementioned forces to point quantities; such as density, momentum, and viscosity. Equations 45, 46, and 47 are the continuity equation, the momentum equation, and the energy equation, respectively.

\[
\frac{\partial \rho}{\partial t} + \frac{\partial}{\partial x_j} (\rho u_j) = 0 \tag{45}
\]

\[
\frac{\partial (\rho u_j)}{\partial t} + \frac{\partial (\rho u_k u_k)}{\partial x_k} = \frac{\partial \sigma_{ij}}{\partial x_i} + \rho f_j \tag{46}
\]
Bird (1994) explains that the Navier-Stokes equations can be used with great accuracy as long as there are enough molecules within the fluid space such that the fluid can reasonably be assumed to be a continuum. A fluid can only be assumed to be continuous, if and only if, all of the properties of the fluid are continuous. That is to say that both the fluid’s point quantities and the fluid’s transport quantities must be continuous in order to use continuum flow models, like the Navier-Stokes equations (Nguyen & Wereley, 2002).

\[
\frac{\partial (\rho e)}{\partial t} + \frac{\partial (\rho e u_k)}{\partial x_k} = \sigma_{ij} \frac{\partial u_j}{\partial x_i} - \frac{\partial q_j}{\partial x_i} \tag{47}
\]

\ldots \text{it must be remembered that the conservation equations do not form a determinate set unless the shear stress and heat flux can be expressed in terms of the lower-order macroscopic quantities. It is the failure to meet this condition, rather than the breakdown of the continuum description, which imposes a limit on the range of validity of the continuum equations. More specifically, the transport terms in the Navier-Stokes equations of continuum gas dynamics fail when gradients of the macroscopic variables become so steep that their scale length is of the same order as the average distance travelled by the molecules between collisions} \ldots (\text{Bird, 1994, 2}).

To ensure that all of the fluid properties of a fluid are continuous, a minimum number of molecules would be required to be within the fluid volume. Because it is the interaction of molecules that is important when determining if a fluid is continuous or discontinuous, a continuous fluid is defined as a fluid that has enough molecules within the fluid space such that the molecules interact at some minimum frequency. As rule of thumb, the characteristic length scale of a
gaseous fluid must be greater than 1 micron to ensure continuum mechanics and that the characteristic length scale of a liquid fluid must be greater than 10 nanometers to ensure continuum mechanics.

In 1872, Boltzmann postulated that one could describe the properties of a fluid by understanding how the fluid's molecules interacted. Boltzmann surmised that the fluid models of Navier and Stokes were incomplete and that the Navier-Stokes equations were incapable of modeling the molecular motion of fluids. He theorized that fluid models could be and should be divided into two classifications: microscopic models and macroscopic models. Macroscopic models are empirical models that describe the gross movement and behavior of fluids. Microscopic models are statistical models that model the real behavior of the fluid.

Is there a difference between the two model classifications? Maybe? Traditional macroscopic models, like the Navier-Stokes equations, treated the fluid mass as a continuum. These models neglect the individual molecular behavior and model the overall motion of the fluid defined by the average observable properties of the fluid. Microscopic models used the individual fluid molecules to describe the flow. These models track each and every molecule to deduce the overall behavior of the fluid. One might think that these models are completely different, in actuality, the two classifications are related. Panton (1996) describes continuum models as the average of a large number of molecular interactions.
Boltzmann’s analysis emphasized the importance of the individual molecular motion. The basic assumption was that fluid behavior and motion could be predicted by modeling the behavior of the individual fluid molecules. By modeling the behavior of the individual fluid molecules, one could extract the detailed information about the overall movement and behavior of the fluid; however, as the number of molecules becomes large, the level of detail provided by such molecular models may not be required to adequately describe the fluid motion. For this reason, Boltzmann and his contemporaries Chapman and Cowling and others applied these molecular models almost exclusively to dilute gases (Bird, 1994).

Because molecules interact through collisions, the fundamental assertion of these molecular models is that each fluid molecule is like a billiard ball and that one can predict the behavior of the fluid if the frequency of bimolecular collisions is known. As shown in Equation 48, if the molecular mass \( m_i \), velocity \( u_i \) and position \( x_i \) of each fluid molecule were known prior to a bimolecular collision then the velocity \( u_i \) and position \( x_i \) after the collision could be predicted.

\[
m_1 u_1 + m_2 u_2 = m_1 u_3 + m_2 u_4
\]  

(48)

This model, known as the hard sphere model, assumes that all collision were elastic. "An elastic collision is defined as one in which there is no interchange of translational and internal energy" (Bird, 1994). The model assumes that all collisions were bimolecular. These models were originally limited to dilute gases for ease of computation. However, before delving into the details of Boltzmann’s
theories, it is important to understand how and why atoms and molecules interact.

"The behavior of all states of matter-solids, liquids, and gases-as well as the interaction among the different states depends on the forces between the molecules that comprise the matter" (Nguyen, 2002). All matter is made up of atoms or groupings of atoms called molecules. These molecules interact in very different ways. It is the intermolecular interactions that determine the phase of the substance.

The molecules that make up a solid are bounded together in a fixed orientation as crystalline solids or non-crystalline solids also known as amorphous solids or glasses (Ebbing, 1987). Crystalline solids have a fixed orientation or lattice. The structure of the lattice depends upon the type of bond that the atoms make with one another and the angle of the bond. Non-crystalline solids have no defined structure, but the movement of the molecules that makeup a non-crystalline solids are such that one could refer to these solids as extremely high viscosity liquids. However, for the purposes of this discussion, we will assume that the molecular orientation of these non-crystalline solids is fixed, because the overall rate of molecular movement in a non-crystalline solid is extremely, extremely slow.

Liquids are made up of molecules that move freely around one another. However, these molecules are still in close contact with one another. The molecules in a liquid slide by one another interacting as the molecules move. Although the orientation of these molecules is not fixed, the movement of the
molecules that make up a liquid is limited. Molecules that make up a liquid are attracted to one another by intermolecular forces, which keep the liquid molecules from flying apart.

The molecules that make up a gas interact by colliding with one another. Typically, these collisions are binary. Three or more molecules are statistically capable of colliding, especially in dense gases, but these multi-molecular collisions are much rarer than binary collisions.

The questions in each of these three scenarios are why do the molecules interact or collide and why are the phases of matter unique and different. Tabeling (2005) explains that the attraction of polar and non-polar molecules is the result of two contributions: quantum-mechanical forces and Van der Waals forces. Quantum-mechanical forces are the forces that cause atoms to bond together with other atoms to form molecules. These quantum-mechanical forces can either be attractive or repulsive.

Van der Waals forces are attractive forces, which result from dipole-dipole forces and London forces. Van der Waals forces are weak attractive electrostatic forces. Where as the energy contained within an ionic bond and a covalent bond are on the order of 100 kJ/mol to 1000 kJ/mol, the bond energy of a Van der Waals attractive force is on the order of 0.1 kJ/mol to 10 kJ/mol (Ebbing, 1987). Ebbing (1987) explains that Van der Waals forces describe how easily a material will leave the liquid or solid state. When Van der Waals intermolecular attractions are strong, a substance tends to remain in the solid or liquid phases at ambient
condition. However, for materials with very weak Van der Waals forces, these substances tend to be gaseous at ambient temperatures.

There are numerous mathematical models that have been developed to describe the intermolecular attractive forces and repulsive forces for non-polar molecules. However, the Lennard-Jones potential is widely considered the standard for modeling intermolecular interactions (Greenspan, 2005; Nguyen, 2002; Bird, 1994). The Lennard-Jones potential, proposed in 1931 by John Lennard-Jones of Bristol University, is a simple mathematical model that represents the behavior of interacting molecules (Lennard-Jones, 1931). Equation 49 shows the functional form of the Lennard-Jones potential.

\[
V_{ij}(r) = 4\varepsilon \left[ c_{ij} \left( \frac{r}{\sigma} \right)^{-12} - d_{ij} \left( \frac{r}{\sigma} \right)^{-6} \right]
\]  

(49)

In the Lennard-Jones potential equation, the distance \( r \) is the distance between two molecules \( i \) and \( j \). The characteristic length \( \sigma \) is the finite distance at which the intermolecular potential is zero, and "... \( c_{ij} \) and \( d_{ij} \) are parameters particular to the pair of interacting molecules" (Nguyen, 2002). The characteristic energy scale is \( \varepsilon \) (Nguyen, 2002).

The term with the \( r^{12} \) dependence is a phenomenological model of the pairwise repulsion that exists between two molecules when they are brought very close together. The term with the \( r^6 \) dependence is a mildly attractive potential due to the van der Walls forces between [the] ... molecules (Nguyen, 2002).
If you take the derivative of the Lennard-Jones potential equation with respect to radius of separation \( r \), the resulting equation (Equation 50) defines the magnitude of the force \( F_{ij} \) between the two molecules can be derived from the Lennard-Jones potential equation.

\[
F_{ij}(r) = -\frac{\partial V_{ij}(r)}{\partial r} = \frac{48\epsilon}{\sigma} \left[ c_{ij}\left( \frac{r}{\sigma} \right)^{-13} - \frac{d_{ij}}{2}\left( \frac{r}{\sigma} \right)^{-7} \right]
\]  

(Eq. 50)

Electrically neutral molecules are subject to two distinct forces in the limit of large distance and short distance: Van der Waals Force and Pauli repulsion.

In general, the distribution of particles within a fluid is defined by the Boltzmann equation (Karniadakis & Beskok, 2002). The Boltzmann equation (Equation 51) relates the particle frequency distribution \( f \) to the particle collision rate \( Q(f, f') \).

\[
\frac{\partial f}{\partial t} + \frac{p \cdot \partial f}{m} + F \cdot \frac{\partial f}{\partial p} = Q(f, f')
\]  

(Eq. 51)

The Boltzmann equation is valid for all flow domains. However, because of the complexity of solving the Boltzmann equation, it is usually not practical to solve the Boltzmann equation. Therefore, for simple flows, simplifying assumptions are made to reduce the complexity of the calculation (Karniadakis & Beskok, 2002).

The kinetic theory of gases assumes that the behavior of a fluid element located at some point \( r_i \) in space can be completed defined if the velocity \( u_i \), the position \( r_i \), and the internal energy of the fluid element are known. The basic
assumption is that velocity and position are independent variables. Specifically, one can define the behavior of the fluid molecules if both the position and velocity are known. As shown in Equation 52, the derivative of an arbitrary fluid property $\alpha$ can be expressed as the partial derivative of $\alpha$ with respect to $t, x, y, z, u, v, \text{ and } z$:

$$\frac{\delta \alpha}{\delta t} = \frac{\partial \alpha}{\partial t} \frac{\delta t}{\delta t} + \frac{\partial \alpha}{\partial x} \frac{\delta x}{\delta t} + \frac{\partial \alpha}{\partial y} \frac{\delta y}{\delta t} + \frac{\partial \alpha}{\partial z} \frac{\delta z}{\delta t}$$

(52)

If as before, the aforementioned equation (Equation 52) is divided by an incremental time ($\delta t$), the resulting equation (Equation 53) represents the total change in $\alpha$ in phase space.

$$\frac{\delta \alpha}{\delta t} = \frac{\partial \alpha}{\partial t} \frac{\delta t}{\delta t} + \frac{\partial \alpha}{\partial x} \frac{\delta x}{\delta t} + \frac{\partial \alpha}{\partial y} \frac{\delta y}{\delta t} + \frac{\partial \alpha}{\partial z} \frac{\delta z}{\delta t} + \frac{\partial \alpha}{\partial u} \frac{\delta u}{\delta t} + \frac{\partial \alpha}{\partial v} \frac{\delta v}{\delta t} + \frac{\partial \alpha}{\partial w} \frac{\delta w}{\delta t}$$

(53)

Similarly, a material derivative (Equation 54) can be defined for particles in phase space.

$$\frac{D\alpha}{Dt} = \frac{\partial \alpha}{\partial t} + u \frac{\partial \alpha}{\partial x} + v \frac{\partial \alpha}{\partial y} + w \frac{\partial \alpha}{\partial z} + a_u \frac{\partial \alpha}{\partial u} + a_v \frac{\partial \alpha}{\partial v} + a_w \frac{\partial \alpha}{\partial w}$$

(54)

Rewriting the aforementioned equation, setting $\alpha$ to the number of particles in phase space ($n_f$), and summing over all bimolecular collisions, Boltzmann's equation results (Fang, 2003).

Computational models of Polymer Electrolyte Membrane (PEM) fuel cells have historically simulated the anode and cathode gas channel flow dynamics assuming that the flow within the gas channel is characterized by continuum flow.
dynamics. Although this assumption makes computational simulations easier, assuming continuum flow dynamics ignores the real flow dynamics at the microscale. In actuality, as the size of the gas channel approaches the mean free path of the fluid, continuum mechanics' assumptions start to break down.

Microfluidics

This classical understanding of fluids assumes that the behavior of each individual fluid molecule can be neglected, because the behavior of the whole fluid mass is sufficient to describe the behavior and motion of the fluid, and, therefore, the average behavior of the individual fluid molecules that make up the whole (Liou & Fang, 2006). The characteristics of the individual fluid molecules are averaged out and become insignificant when observing the overall fluid process. Only the macroscale properties of the fluid mass are important. The fluid is treated as a single unit, and the individual molecular fluid properties are indistinguishable from the properties of the entire fluid. (Panton, 1996).

In contrast to continuum flows, microfluidics is the study of fluidic processes at near molecular scales. Microfluidics is the study of the true behavior of the fluid, or, more precisely, the study of the true behavior of the fluid molecules. Karniadakis and Beskok (2002) describe microfluidics as the study of the behavior of fluids when the behavior of each individual fluid particle cannot be neglected: the flow is discontinuous (Karniadakis & Beskok, 2002). For the aforementioned reason, these systems are referred to as non-continuum flows.
The science of non-continuum fluids was first introduced in the 1950’s and 1960’s at the advent of the space industry. Non-continuum flows were experienced when rockets were launched into the Earth’s upper atmosphere. These low density fluids were coined rarefied gases. (Liou & Fang, 2006).

However, while scientists and engineers were studying low densities flows in Earth’s upper atmosphere, Uhlenbeck (1972) posed a question at the 8th International Symposium on rarefied gas dynamics. Uhlenbeck (1972) understanding and acknowledging the great work of Chapman and Enskog wondered what would happen if the characteristic length (L) of the flow were comparable to the mean free path (λ) of the fluid. Uhlenbeck (1972) theorized that the Chapman-Enskog theories might be limited (Uhlenbeck, 1972). Uhlenbeck (1972) wondered if the theories developed for continuous flows could be applied to near molecular flows (Uhlenbeck, 1972).

Classical fluid dynamic theories are based on the assumptions that the ratio of the intermolecular diameter (d) to the mean free path of fluid is much less than unity,

\[ \frac{d}{\lambda} \ll 1 \]  \hspace{1cm} (55)

and that the ratio of the mean free path (λ) to the characteristic length (L) is much less than unity.

\[ \frac{\lambda}{L} \ll 1 \]  \hspace{1cm} (56)
Unlike classical continuum fluid dynamic theories, microfluidics describes the dynamics of fluids at the microscale and at the nanoscale. Microfluidics describes fluidic processes where the magnitude of the characteristic length scale ($L$) is comparable to the mean free path ($\lambda$) of the fluid.

\[ L \sim \lambda \]  \hfill (57)

The Knudsen Number ($Kn$) is used to identify the point at which a gas transitions from continuum to non-continuum mechanics. As shown in Equation 58, the Knudsen Number ($Kn$) is defined as the ratio of the mean free path ($\lambda$) of the fluid to the characteristic length ($L$) of the fluid path (Karniadakis & Beskok, 2002).

\[ Kn = \frac{\lambda}{L} \]  \hfill (58)

The basic assumption is that fluidic processes can be characterized on a fluidic spectrum with continuum flows at one end of the spectrum and free molecular flows at the opposite end. Table 2 lists a description of the flow regime and the associated Knudsen Number ($Kn$) for that particular flow regime (Karniadakis & Beskok, 2002).
Table 2: Flow Regimes and Knudsen Numbers

<table>
<thead>
<tr>
<th>Region</th>
<th>Description</th>
<th>Knudsen Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Continuum Flow Regime</td>
<td>Kn &lt; 10^{-3}</td>
</tr>
<tr>
<td>2</td>
<td>Slip Flow Regime</td>
<td>10^{-3} &lt; Kn &lt; 10^{-1}</td>
</tr>
<tr>
<td>3</td>
<td>Transitional Flow Regime</td>
<td>10^{-1} &lt; Kn &lt; 10</td>
</tr>
<tr>
<td>4</td>
<td>Free Molecular Flow Regime</td>
<td>Kn &gt; 10</td>
</tr>
</tbody>
</table>

Barber and Emerson (2001) presented a computational study on the effects of varying Kn and Re on hydrodynamic development length of micro-channels. Their basic premise was that the Reynolds's number, which is often used to describe the characteristics of fluids in continuum flows, is not sufficient to predict flow behavior for micro-channel flows. Both Re and Kn must be considered for micro-scale flows to predict flow behavior (Barber & Emerson, 2001).

As the characteristic length scale (L) of the flow approaches the mean free path (\(\lambda\)) of the fluid, the behavior of the flow changes, and the no-slip condition, which is an empirical construct commonly used in macrofluidic systems, is no longer valid (Karniadakis and Beskok, 2002). For liquid microfluidic systems, the flow is granular (Karniadakis and Beskok, 2002).

The influence of inertial forces and body forces versus the influence of surface forces on fluid behavior at the microscale versus the influence of these forces on fluid behavior at the macroscale changes. Tabeling (2005) explains
that unlike traditional continuum flow processes where the fluid may be assumed continuous and the surface forces are significantly smaller than the inertial forces which act upon the fluid (Tabeling, 2005). In microfluidic processes, the surfaces forces may be several orders of magnitude more intense than the inertial forces and body forces, which are acting upon the fluid (Tabeling, 2005). Inertial forces and body forces have less of an impact on microfluidic systems, because the magnitude of these forces is a function of the mass of the fluid.

The classical understanding of a fluid is a continuous grouping of particles that are held so tightly together that the characteristic behavior of each individual fluid particle is indistinguishable from the characteristic behavior of the fluid particles that surround it. That is to say that the fluid behaves like a continuous mass of material. More specifically, a fluid is a mass of molecules, which when a tangential shearing force is applied to the mass, the mass continuously deforms; however, when the shearing force is removed, the mass does not return to its original form (Currie, 1993).

In the classical understanding of fluid dynamics, the fluid behaves like a continuum. When one fluid particle moves, all of the other fluid particles follow its lead like a well orchestrated dance. This classical understanding of fluids assumes that the behavior of each individual fluid molecule can be neglected, because the behavior of the whole fluid mass is sufficient to describe the behavior and motion of the fluid, and, therefore, the average behavior of the individual fluid molecules that make up the whole (Liou & Fang, 2006).
Because these fluidic system behave like a continuous mass, these systems are referred to as continuum flows.

The continuum assumption simply means that physical properties are imagined to be distributed throughout space. Every point in space has finite values for properties such as velocity, temperature, stress, electric field strength, and so on. From one point to the next the properties may change value, and there may even be surface where some properties jump discontinuously (Panton, 1996).

However, the continuum assumption assumes that the individual characteristics of the fluid molecules are averaged out and become insignificant. Therefore, only the macroscale properties of the fluid mass are important. The fluid is treated as unit, and the individual molecular fluid properties are indistinguishable from the properties of the entire fluid. For this reason, we will use the terms macrofluidics, continuum flows, and classical fluid dynamics, interchangeably.

In contrast to continuum flows, microfluidics is the study of fluidic processes at near molecular scales. Microfluidics is the study of the true behavior of the fluid or more precisely the study of the true behavior of the fluid molecules. Karniadakis and Beskok (2002) describes microfluidics as the study of the behavior of fluids when the behavior of each individual fluid particles cannot be neglected: the flow is discontinuous. For the aforementioned reason, these systems are referred to as non-continuum flows.

Inertial forces and body forces have less of an impact on microfluidic systems, because the magnitude of these forces are functions of the mass of the
fluid. For example, gravity, a common body force, is defined as the force that two bodies exerts upon each other. Equation 59 gives the functional relationship relating the masses \( m_1, m_2 \) and the distance \( r \) between the two bodies.

\[
F = G \frac{m_1 m_2}{r}
\]  

(59)

Specifically, the gravitation force that two bodies exert upon each other is a product of the masses \( m_1, m_2 \) of both bodies divided by the distance \( r \) separating the two bodies.

In contrast to inertial forces and body forces, surfaces forces, like surface tension and capillarity, are not functions of mass. Surface tension is caused by weak electrostatic attractive force which bond adjacent liquid molecules together (Batchelor, 1967). The force or tension acts tangentially to the gas-liquid interface or to the liquid-liquid interface (Middleman, 1998). It is surface tension which prevents small insects, like mosquitos, from sinking into a puddle of water and allowing these small insects to literally walk on water. As detailed in Chapter 2, these weak electrostatic attractive forces are called Van der Waals forces. When a small insect floats atop of a puddle of water, the insect displaces a small section of the liquid surface, because the electrostatic bond linking the adjacent water molecules together does not break, the insect is able to walk on the water’s surface.
Microfluidic Flows vs. Macrofluidic Flows

Because of the inherent difference between macrofluidic systems and microfluidic systems, fluid dynamists and engineers have had to reassess the traditional transport theories based on continuum flows to determine when and where these traditional assumptions fail. To truly understand the study of microfluidics versus the study of macrofluidics, one must first revisit the concept of matter.

All matter is composed of microscopic particles called atoms. The atom is the smallest unit of a material, which is still uniquely that material. However, often the normal state of a material is not monatomic, but a grouping of atoms. This grouping of atoms is called a molecule. From this point forward, we will assume that the smallest unit of a material is a molecule. Although this is not strictly correct, most fluids are not monatomic materials. With the exception of the the Noble Gases, molten metals, and mercury, all other fluids are polyatomic materials or molecules.

Most molecules are on the order of $10^{-10}$ meters, which is equivalent to 0.1 nanometers (nm) (Ebbing, 1987). "A non-SI unit of length traditionally used by chemists is the angstrom (Å), which equals $10^{-10}$ meters" (Ebbing, 1987). For example, the molecular diameter of nitrogen gas ($N_2$) is approximately 0.3 nm or 3 Å (Nguyen, 2002).

Because liquids have a finite volume, the characteristic length scale ($\sigma$) for a liquid is much different than that of a gas. The characteristic length scale ($\sigma$) of
a liquid is called the intermolecular spacing or intermolecular distance (Tabeling, 2006). As shown in Equation 60, the intermolecular distance \( d \) is related to the molecular density \( n \) (Tabeling, 2006).

\[
d = n^{\frac{1}{3}} \tag{60}
\]

The intermolecular spacing for liquid water (H\(_2\)O) is 0.4 nm, and the molecular diameter for liquid water is 0.3 nm. The intermolecular spacing is defined as the point at which the Lennard-Jones Potential is minimized (Tabeling, 2006).

Because gases do not have a finite volume, the distance between gas models varies as with the size of container. Therefore, a more robust method of determining the characteristic length is required. “For gases, the fundamental scale necessary to establish dynamical properties is . . . the mean free path \( \lambda \)” (Tabeling, 2006). Equation 61 shows the functional relationship between the mean free path \( \lambda \) and temperature \( T \).

\[
\lambda = \frac{1}{\sqrt{2\pi n a^2}} = \frac{k_B T}{\sqrt{2\pi n a^2}} \tag{61}
\]

The mean free path \( \lambda \) is the average distance a gas molecule travels between collisions. As the length scale approaches the mean free path of the gas, the fluid behaves more like a group of particles and less like a continuum. The mean free path for nitrogen gas (N\(_2\)) is 60 nm (Tabeling, 2006).

As the popularity of micro-electro-mechanical systems (MEMS) has grown, the need to understand the dynamics of such systems has spawned
greater interest in non-continuum mechanics. As the fluid path becomes smaller and smaller, the degree of rarefaction becomes greater and traditional parameters, like Reynold's number (Re), do not completely describe the totality of the flow behavior. Equation 62 is the expression for the Reynold's number:

\[
Re = \frac{pu}{\mu}
\]  
(62)

where \( p \) is the density of the fluid, \( u \) is the velocity of the fluid, \( d \) is the diameter of the conduit, and \( \mu \) is the viscosity.

As the fluid path becomes smaller and approaches the mean free path, the surface effects dominate. "For example, the surface-to-volume ratio for a device with a characteristic length of 1 m is 1 m\(^{-1}\) whilst the surface-to-volume ratio for a MEMS device having a characteristic length of 1 \( \mu \)m will increase to 10\(^6\) m\(^{-1}\) (Karniadakis & Beskok, 2002). Although the physics of macroscopic flows and microscopic flows is the same, many of the traditional assumption of macroscopic flows, like the no-slip boundary condition, are not valid for microscopic flows because the molecular motion, which typically neglected at the macroscale cannot be neglected at the microscale. Therefore, other tools are needed.

To bridge the gap between continuum mechanics and free molecular flows, a different approach was needed. The Knudsen number (Kn) was used to bridge this gap for gases. The Kn is a dimensionless number, which was first introduced to describe rarefied gas flows in high altitude aircraft and which
relates the mean free path of a molecule to the characteristic length scale of the fluid space. As shown in Equation 63, the Knudsen number is defined as the ratio of the mean free path (λ) of a substance to the characteristic length (L) of the fluid path (Karniadakis & Beskok, 2002).

\[ Kn = \frac{\lambda}{L} \]  (63)

Specifically, the Knudsen number is a measure of the overall degree of rarefaction of a gas. The Knudsen number is also a measure of inertial forces, viscous forces, and the degree of compressibility of the gas. As shown in Equation 64, the Mach (Ma) number is a measure of the compressibility of a fluid.

\[ Ma = \frac{u}{c} \]  (64)

and the Reynold’s number (Re) is the ratio of inertial forces versus viscous forces.

\[ Re = \frac{\rho ud}{\mu} \]  (65)

Therefore, as shown in Equation 66, the Knudsen number can be written as a function of both the Reynold’s number and the Mach number (Nguyen, 2002).

\[ Kn = \sqrt{\frac{k \pi Ma}{2 Re}} \]  (66)
However, to actually predict the degree of rarefaction, it is the local effects, which are of most importance. Bird (1986) showed that the local Knudsen number was depended on the mean free path ($\lambda$), local density ($\rho$), and the local density gradient (Bird, 1986). Equation 67 shows the functional relationship between the mean free path ($\lambda$), the density ($\rho$), and the density gradient.

$$\text{Kn} = \frac{\lambda}{\rho} \frac{\partial \rho}{\partial x}$$  \hspace{1cm} (67)

The Kn is used to identify the point at which a gas transitions from continuum to non-continuum mechanics. "For $\text{Kn} \leq 10^{-2}$, the continuum hypothesis is appropriate and the Navier-Stokes equations can be employed using the conventional no-slip boundary conditions. Conversely, for $\text{Kn} \geq 10$, the continuum approach breaks down completely and the regime can then be described as being a free molecular flow" (Kamiadakis & Beskok, 2002).

Barber and Emerson (2001) presented a computational study on the effects of varying Kn and Re on hydrodynamic development length of micro-channels (Barber & Emerson, 2001). Their basic premise was that the Reynold's number alone is not sufficient to predict flow behavior for micro-channel flows. Both Re and Kn must be considered for micro-scale flows to predict flow behavior. The article identified four flow regions, which were defined by the value of Kn (Nguyen, 2002).

The continuum flow region is defined by $\text{Kn} \leq 10^{-3}$. Within the continuum flow regime, one can confidently use the Navier-Stokes equations to describe the
flow. The no-slip condition, no temperature-jump condition, and the no concentration slip conditions are valid, and the flow is assumed continuous, i.e. continuum mechanics applies. One can be reasonably assume that neighboring fluid elements are in thermodynamic equilibrium (Nguyen et al., 2002; Fang, 2003). Although the Knudsen number is never zero, as the Knudsen number approaches zero, viscous effects decrease. At the limit of Kn equaling zero, the flow is described by Euler's equation: the flow is inviscid.

The slip flow region is defined by $10^{-3} < \text{Kn} \leq 10^{-1}$. Within the slip flow regime, one must use caution when applying the Navier-Stokes equations. The no-slip condition is not valid, and slip at the walls of the conduit must be considered when modeling the fluid behavior (Fang, 2003). A layer within the flow known as the Knudsen layer forms. The Knudsen layer is approximately one molecular mean free path thick, and is the layer between the bulk flow and the wall of the conduit (Karniadakis & Beskok, 2002; Sharipov, 2004) “Within the Knudsen layer, the gradients of velocity, temperature, and species concentration are so steep that these values at the edge of the Knudsen layer are significantly different from those at the boundary (wall surface)” (Xu & Ju, 2005). It is this gradient that is the source of the slip. A requirement of continuum flows is that the properties of the fluid and of the flow must be continuous over the entire flow domain. As the gradient increases, this requirement is violated.

As previously mentioned, for flows with a Kn greater than $10^{-3}$ and less than $10^{-1}$, a correction must be added to the Navier-Stokes equations to account for slip at the boundary. When describing the flow, slip boundary conditions must
be incorporated (Nguyen, 2002; Karniadakis & Beskok, 2002; Fang, 2003; Xu & Ju, 2005). Equation 68 is the equation for the slip velocity ($v_s$) at a boundary.

$$v_s - v_w = \frac{2 - \sigma_v}{\sigma_v} \frac{1}{\rho} \left( \frac{2RT_w}{\pi} \right)^{1/2} \tau_s + \frac{3}{4} \frac{\Pr(\gamma - 1)}{\gamma \Pr R T_w} (-q_s)$$  \hspace{1cm} (68)

Because the no-slip condition is not valid for microfluidic systems, the flow through microfluidic systems tends to be slightly blunted. In addition, the flow through microfluidic systems is faster than the flow that would be predicted using macrofluidic theories (Koch, Evans, & Brunnschweiler, 2000).

In addition, when modeling thermal gradients within micro-scale systems, the temperature may not be continuous at the wall. Specifically, the temperature-jumps must be incorporated into the boundary conditions. Barber et al. (2001) presented findings for $Re \leq 400$ and $Kn \leq 0.1$ (Barber, 2001). Although rarefaction is important, the Navier-Stokes equations may be used to predict flow behavior; however, temperature jump boundary conditions must be used to correct for non-continuum behavior (Nguyen, 2002; Karniadakis & Beskok, 2002; Nguyen et al., 2002; Xu & Ju, 2005). Equation 69 is the equation for temperature jump.

$$T_s - T_w = \frac{2 - \sigma_T}{\sigma_T} \left[ \frac{2(\gamma - 1)}{\gamma + 1} \right] \frac{1}{R \rho} \left( \frac{2RT_w}{\pi} \right)^{1/2} (-q_n)$$  \hspace{1cm} (69)
In micro-flows or nano-flows, the concentration of any species \( C_i \) within the bulk flow of a fluid may jump as the fluid approaches the wall of the conduit. This apparent jump in concentration is called concentration slip or diffusion slip (Xu & Ju, 2005). Although there are several models that currently predict velocity slip and temperature jumps, there are relatively few papers that discuss concentration slip. These jumps in concentration can significantly affect the rate of reaction at the catalyst surface (Xu & Ju, 2005; Stockie et. al., 2003). Xu and Ju (2005) have proposed the following form of the concentration slip boundary conditions (Xu & Ju, 2005):

\[
(pY_k)_w = \sqrt{\frac{T_s}{T_w}} \rho_s \left[ 1 - \frac{4}{3} \lambda \left( \frac{\partial p}{\partial y} \right)_s \right]
\]  \hspace{1cm} (70)

\( Y_k \) is the mass fraction of the component \( k \). A model of this type can be adapted for fuel cell systems (Xu & Ju, 2005).

The transitional flow region is defined by \( 10 \geq Kn > 10^{-1} \). At \( Kn > 0.1 \), continuum mechanics does not accurately describe the flow. The fluid behaves more like a collection of point sources. The Navier-Stokes equations are not valid, and alternate techniques; like Direct Simulation Monte Carlo (DSMC) technique, the Brunette Equation, or the modified Brunette Equation; must be used to describe the flow behavior (Fang, 2003). The Navier-Stokes equations have two basic requirements. First, the flow must be continuous everywhere. This is a mathematical requirement of differential calculus. Second, the thermo-physical properties, like density and viscosity, are averaged over units that are
small compared to the characteristic length (Raju et. al., 2004). At $\text{Kn} > 0.1$, the first assumption is not satisfied.

Free molecular flows are defined by $\text{Kn} > 10$. For systems with $\text{Kn} > 10$, one can accurately describe the system as a free molecular flow (Fang, 2003). The fluid behaves like individual colliding molecules. For gaseous fluids, free molecular flows are described by the kinetic theory of gases. Unfortunately, no simple theory exists for liquids. Free molecular flows are typical of rarefied gases, and rarefied gas dynamics is an important science in the space industry.

Figure 6 identifies the different flow regions in detail with their associated Knudsen numbers. Figure 6 also lists the fluidic models that are generally accepted as appropriate for the listed regions (Karniadakis & Beskok, 2002).

Within the continuum flow regime, it is typically accepted that one use computational models, like the Navier-Stokes equations, which are suitable for continuum flows, because the molecule-molecule interactions are not as pronounced. However, statistical models, like Direct Simulation Monte Carlo (DSMC) or Molecular Dynamics (MD), are theoretically capable of describing these flows. Some of the challenges with using a statistical model for continuum flows are the computational time required for such a simulation and the memory restrictions with currently available computers. However, as computers become more powerful, some researchers may opt to use statistical methods for continuum flows. Statistical methods have been used with some success for turbulent flows.
Fluidic processes in the transitional regime and the free molecular flow regime must be simulated using statistical methods. Continuum flow methods, like Navier-Stokes, are not valid for highly rarefied flows. These methods would not be capable of resolving the molecule-molecule interactions required to accurately model these flows.

The Knudsen number is a measure of the degree of rarefaction of a gas. A rarefied gas is a gas where the molecules are sufficiently far apart that the molecules infrequently collide. Unlike continuum flows where the fluid molecules
are in close contact, the fluid particles in rarefied gas systems rarely interact. Because these fluid molecules are physically isolated from one another, the fluid molecules are thermodynamically isolated from the other fluid molecules in the rarefied gas space. Obviously, the study of rarefied gases is extremely important when designing spacecraft (Liou & Fang, 2006). Liou and Fang (2006) explain that being able to calculate and to predict the effect of rarefied gas dynamics and heat stress scenarios during reentry is critical to designing space craft thermal protective panels (Liou & Fang, 2006).

But are there substantive difference between microfluidic systems and rarefied gas systems? Microfluidic systems are very similar to traditional rarefied gas system with several unique but significant differences. Similar to traditional rarefied gas dynamics, microfluidics is the science of studying non-continuum flows. However, as previously mentioned, traditional rarefied gas system are non-continuum flows, which are typical of the low density regions of Earth’s upper atmosphere. Therefore, in traditional rarefied gas systems, it is the abundance of space that causes the infrequency of molecular collisions. In contrast to traditional rarefied gas systems, the opposite is true for microfluidic systems. It is the lack of space that causes the each fluid molecule to behave more and more autonomously. Specifically, as the size fluid path becomes smaller, there is insufficient space for all of the fluid molecules, so the molecules are forced to move further and further away from each other, and the frequency of molecule collisions becomes less and less.
As previously mentioned, the Knudsen number (Kn) is sufficient for describing the degree of rarefaction of gas, but engineers and scientists must not try to use this elementary method to predict when non-continuum flows will occur within liquid systems. The Kinetic Theory of Gases make it possible to predict the behavior of gaseous microfluidic process; however, there is no kinetic theory of liquids. "For liquids the non-continuum behavior is more difficult to detect. It is manifested as anomalous diffusion, i.e., different diffusion in the near-wall region than in the bulk, and is associated with the rheology of the liquid" (Karniadakis & Beskok, 2002). Nguyen (2002) gives the following rule of thumb for determining if a liquid may be treated as a continuum. Specifically, Nguyen (2002) states that if the characteristics length is greater than 10 nanometers, than the liquid may be assumed to behave as a continuum (Nguyen, 2002). "For a good review of the experiments to date, the reader is encouraged to refer to Gad-el-Hak's recent review article (2002)" (Nguyen, 2002).

These tools must be capable of simulating the momentum, heat, and mass transport phenomena within micro-scale systems. Xu and Ju (2005) explain "... that the temperature and velocity slips on the wall can greatly affect the energy exchange between the gas and the wall. In a microscale combustor, these slips will also affect the catalytic surface reaction due to the strongly temperature dependent Arrhenius law and transport properties" (Xu & Ju, 2005).
CHAPTER IV

LITERATURE REVIEW

Although fuel cell research was very popular in the early 1950s around the advent of the space industry, in the early 1970s, fuel cell research went dormant. The fuel cell industry and fuel cell research waned after the landmark voyages into outer space and to the moon in the 1960s. However, after the oil embargos of the mid 1970s, the seeds of a future fuel cell industry were being cultivated. In 1977, the United States Department of Energy (DOE) was created to oversee the United States’ energy interests and new energy technologies (Nehru & Wang, 2009).

Spurred on by the creation of DOE, researchers began looking for cheaper, renewable sources of energy that could be employed to service humankind. However, it was not until about 1990 after passage of the Hydrogen Research and Development Act that fuel cell research rebounded (Nehrir & Wang, 2009, 13). The Hydrogen Research and Development Act required DOE to develop policies and initiatives that would move the United States away from a fossil fuel based economy and toward a hydrogen based economy (Nehrir & Wang, 2009).

After the passage of this landmark law, PEM fuel cell research rebounded, and, today, researchers around the United States and around the world are
working on PEM fuel cell technologies. Because physical models can be quite costly, much of the research in the PEM fuel cell arena is computational. Many of the initial PEM fuel cell models of the early 1990s were one-dimensional (1-D) steady state models.

In 1992, Bernardi and Verbrugge (1992) proposed a one dimensional (1-D) model of what was called a Solid-Polymer-Electrolyte (SPE) fuel cell. Please note that the name Solid-Polymer-Electrolyte (SPE) fuel cell is another name for a Polymer Electrolyte Membrane (PEM) fuel cell; however, in lieu of changing the authors’ terminology, the term SPE fuel cell will be used throughout this portion of the literature review. Bernardi and Verbrugge (1992) were interested in studying the performance of SPE fuel cells. Specifically, the study concentrated on maintaining a fully hydrated membrane at various system conditions (Bernardi & Verbrugge, 1992). Unlike the study by Springer et al., which focused on pressure driven flows within SPE fuel cells, Bernardi and Verbrugge (1992) replied upon diffusion as the main transport mechanism (Bernardi & Verbrugge, 1992). Bernardi and Verbrugge (1992) believed that SPE fuel cell designed should be based on good computational studies coupled with solid experimental data (Bernardi & Verbrugge, 1992).

The model proposed by Bernardi and Verbrugge (1992) was approximately 1 mm thick. The model consisted of an anode and a cathode with gas diffusion layers separating the gas channel from the electrodes. The membrane was sandwiched between the anode side electrode and the cathode side electrode (Bernardi & Verbrugge, 1992). The typical thickness of the
membrane and the electrode was between 200 microns and 300 microns (Bernardi & Verbrugge, 1992).

Bernardi and Verbrugge (1992) assumed that the system was isothermal and at steady state (Bernardi & Verbrugge, 1992). The model assumed that the humidified air was used as the source of the oxygen. The model assumed that the hydrogen supplied at the anode was also humidified. The pressure at the cathode was slightly higher than the pressure within the anode to reduce the migration of water across the membrane from electro-osmotic drag (Bernardi & Verbrugge, 1992). The fuel cell was assumed to be homogeneous and isotropic (Bernardi & Verbrugge, 1992). The model was one-dimensional (1-D).

There were really three main transport processes occurring within the gas diffusion layer. First, the gas diffusion layer served as a conductor for the electrons and allowed the electrons to flow from anode side electrode to the cathode side electrode (Bernardi & Verbrugge, 1992). Second, reactant gases, i.e. hydrogen and oxygen, flow from the gas channel and to the electrode through the gas diffusion layer. Finally, water also flowed through the pores of the gas diffusion layer (Bernardi & Verbrugge, 1992).

The governing differential equations used to solve the computational domain were “. . . derived from four basic, phenomenological equations: (a.) the Nernst-Planck equation for species transport [Equation 71], (b.) a modified form of Schlögl’s velocity equation [Equation 72], (c.) the Butler Volmer equation [Equation 73 & 74], and (d.) the Stefan-Maxwell equation for gas-phase transport [Equation 75]” (Bernardi & Verbrugge, 1992).
\[ \begin{align*}
\nu &= \frac{k_r}{\mu} \int c_i \, \text{d} \phi - \frac{k_p \, dp}{\mu \, \text{d}z} \\
\nu_s^d &= -\frac{k_{p, s}^d \, dp}{\mu \, \text{d}z}
\end{align*} \] (71)

\[ \begin{align*}
i_0^+ &= i_0^\text{ref} \left( \frac{c_{O_2}}{c_{O_2}^\text{ref}} \right) \gamma_{O_2} \left( \frac{c_{H_2}}{c_{H_2}^\text{ref}} \right) \gamma_{H_2} \\
i_0^- &= i_0^\text{ref} \left( \frac{c_{H_2}}{c_{H_2}^\text{ref}} \right) \gamma_{H_2} \left( \frac{c_{H_2}}{c_{H_2}^\text{ref}} \right) \gamma_{H^+}
\end{align*} \] (73)

\[ \begin{align*}
N_{w^+}^d &= \frac{1}{4F} x_w^{\text{sat}} \left[ 1 - x_w^{\text{sat}^+} - x_{N_2} + \frac{x_{N_2}}{r_w} \right]^{-1}
\end{align*} \] (75)

"The diffusivity ratios are defined as" (Bernardi & Verbrugge, 1992).

\[ r_w = \frac{D_{w-N_2}}{D_{w-O_2}} \] (76)

\[ N_{w^-}^d = -\frac{1}{2F} \frac{x_w^{\text{sat}^-}}{1 - x_w^{\text{sat}^-}} \] (77)

Bernardi and Verbrugge, two GM researchers working in Detroit, MI, developed a model for assessing the impact of oxygen migration in porous electrodes. Bernardi and Verbrugge (1992) proposed a model, which has been
used by other researchers to develop more sophisticated models of PEM fuel cells. Since the landmark work of Bernardi and Verbrugge (1992) and others, many more PEM fuel cells models have been developed.

In 2000, Shimpalee and Dutta (2000) proposed a three dimensional (3-D), non-isothermal model of a PEM fuel cell. Shimpalee and Dutta (2000) modeled the temperature distribution within hydrogen fed PEM fuel cells (Shimpalee & Dutta, 2000). The system was assumed to be steady state and to contain multiple chemical species. Shimpalee and Dutta (2000) also performed a detailed water balance. The model accounted for the two water phases that exist within PEM fuel cells. The computational domain was solved by solving the linked equations of mass, momentum, and energy. Although the continuity equation is an equation of mass conservation, the form of the continuity equation proposed by Shimpalee and Dutta (2000) shown below included a source term ($S_m$) to account for the formation of liquid water (Shimpalee and Dutta, 2000).

\[
\frac{\partial (\rho u)}{\partial x} + \frac{\partial (\rho v)}{\partial y} + \frac{\partial (\rho w)}{\partial z} = S_m
\]  

(78)

The authors did not elaborate on the reasons for the source term in the continuity equation. The momentum equations also included source terms ($S_{px}$, $S_{py}$, and $S_{pz}$). Only the $x$-momentum equation is shown below.

\[
u \frac{\partial (\rho u)}{\partial x} + v \frac{\partial (\rho u)}{\partial y} + w \frac{\partial (\rho u)}{\partial z} = -\frac{\partial P}{\partial x} + \frac{\partial}{\partial x} \left( \mu \frac{\partial u}{\partial x} \right) + \frac{\partial}{\partial y} \left( \mu \frac{\partial u}{\partial y} \right) + \frac{\partial}{\partial z} \left( \mu \frac{\partial u}{\partial z} \right) + S_{px}
\]  

(79)
Similar to the species equations for hydrogen and oxygen, which are presented below,

\[
\begin{align*}
\frac{\partial (\rho m_{H_2})}{\partial x} + v \frac{\partial (\rho m_{H_2})}{\partial y} + w \frac{\partial (\rho m_{H_2})}{\partial z} = \frac{\partial (J_{x,n_2})}{\partial x} + \frac{\partial (J_{y,n_2})}{\partial y} + \frac{\partial (J_{z,n_2})}{\partial z} + S_{n_2} \\
\frac{\partial (\rho m_{O_2})}{\partial x} + v \frac{\partial (\rho m_{O_2})}{\partial y} + w \frac{\partial (\rho m_{O_2})}{\partial z} = \frac{\partial (J_{x,O_2})}{\partial x} + \frac{\partial (J_{y,O_2})}{\partial y} + \frac{\partial (J_{z,O_2})}{\partial z} + S_{O_2}
\end{align*}
\] (80)

Shimpalee and Dutta (2000) developed separate species equations for the gaseous water and the liquid water. The gaseous water species equation was the more complex of the two water species equations, because water in the vapor phase is assumed to be generated from the reaction of hydrogen gas and oxygen gas (Shimpalee and Dutta, 2000). Equation 82 is the water vapor species equation.

\[
\begin{align*}
\frac{\partial (\rho m_{wv})}{\partial x} + v \frac{\partial (\rho m_{wv})}{\partial y} + w \frac{\partial (\rho m_{wv})}{\partial z} = \\
\frac{\partial (J_{x,wv})}{\partial x} + \frac{\partial (J_{y,wv})}{\partial y} + \frac{\partial (J_{z,wv})}{\partial z} + S_{H_2O,v}
\end{align*}
\] (82)

\(J\) is the diffusion mass flux parameter based on Fick law (Equation 83).

\[
J_{x,wv} = -D_{x,wv} \frac{\partial m_{k,wv}}{\partial x}
\] (83)

Shimpalee and Dutta (2000) included source terms for the chemical generation of water; however, because gaseous water and liquid water are
treated as separate species, an additional species term was incorporated into the model (Shimpalee and Dutta, 2000). Equation 84 is the water vapor species equation.

\[ S_{H_2O,v} = S_{wv_p} + S_{awv_e} + S_{cwv_e} \]  (84)

The terms \( S_{awv_e} \) and \( S_{cwv_e} \) are source terms associated with any chemical reactions, which produce water (Shimpalee and Dutta, 2000). In lieu of trying to setup a very complicated thermodynamic equation that linked the two water phases, gaseous water and liquid water were treated as two different chemical species linked together by a relatively simple function of the partial pressure of water and the vapor pressure of water (Shimpalee and Dutta, 2000). The source term \( S_{wv_p} \) is the source term associated with the transformation of gaseous water into liquid water, and vice versa (Shimpalee and Dutta, 2000). Equation 85 shows how the transformation of gaseous water into liquid water depends on the partial pressure of water.

\[
S_{wv_p} = \frac{M_{H_2O} \sum_{n_{of v}} \text{mass}_{n_{of v}}}{M_{n_{of v}}} \left[ \frac{p_{sat}}{P_{wv}} - \frac{P_{wv}}{P} \right] \times C
\]  (85)

Shimpalee and Dutta (2000) showed that the liquid water species equation is similar to the gaseous water species equation; however, there is only one
source term (Shimpalee and Dutta, 2000). Equation 86 is the liquid water species equation.

\[
\begin{align*}
    u \frac{\partial (\rho m_{wl})}{\partial x} + v \frac{\partial (\rho m_{wl})}{\partial y} + w \frac{\partial (\rho m_{wl})}{\partial z} &= \frac{\partial (J_{x,wl})}{\partial x} + \frac{\partial (J_{y,wl})}{\partial y} + \frac{\partial (J_{z,wl})}{\partial z} + S_{wl, p} \\
    \text{(86)}
\end{align*}
\]

The liquid water source term is the additive inverse of the gaseous water source term (Shimpalee and Dutta, 2000). Equation 87 shows the functional relationship between the liquid water and vapor water transformational source terms.

\[
S_{wl, p} = -S_{wv, p} \quad \text{(87)}
\]

The two gaseous water terms are functions of pressure. From elementary thermodynamics, when the partial pressure of water was greater than the vapor pressure of water, then the water exists as a liquid. However, if the partial pressure was less than the vapor pressure of water, then the water was present as a gas (Shimpalee and Dutta, 2000).

Shimpalee and Dutta (2000) also performed an energy balance on the system. Equation 88 is the energy balance.

\[
\begin{align*}
    \frac{\partial (\rho u h)}{\partial x} + \frac{\partial (\rho v h)}{\partial y} + \frac{\partial (\rho w h)}{\partial z} &= \\
    \frac{\partial}{\partial x} \left( k \frac{\partial T}{\partial x} \right) + \frac{\partial}{\partial y} \left( k \frac{\partial T}{\partial y} \right) + \frac{\partial}{\partial z} \left( k \frac{\partial T}{\partial z} \right) + S_{h, p} + S_{h, e} \\
    \text{(88)}
\end{align*}
\]
The two source terms in the energy equation are the source term \( (S_{h_p}) \) associated with phase change and the source term \( (S_{h_e}) \) associated with the electrochemical reaction.

**FLUENT ®** was used to solve the computational domain. Because FLUENT ® does not calculate the migration of protons across the polymer member; a subroutine was used to simulate the migration of protons across the membrane and the flux of water across the polymer membrane (Shimpalee and Dutta, 2000). Shimpalee and Dutta (2000) studied the effect of thermal boundary conditions on the temperature distribution within the system (Shimpalee & Dutta, 2000). Their research concluded that the temperature distribution was strongly dependent upon heat generated in the electrochemical reaction and upon the boundary conditions (Shimpalee & Dutta, 2000).

Motivated by the work of Bernardi and Verbrugge (1992) and Springer, Wilson, and Gottesfeld (1993), Um, Wang, and Chen (2000) proposed a two dimensional, transient, isothermal model of a PEM fuel cell. Um et al. (2000) had two main goals. First, the authors wanted to construct a transient, multidimensional model of a PEM fuel cell, which would be based on finite volume methods (Um et al., 2000). Second, the authors wanted to study the effect of using dilute gases on the performance of PEM fuel cells (Um et al., 2000). The fuel cell was 7.112 cm long. The gas channel width was 0.0762 cm wide. The gas diffusion layer was 0.0254 cm wide. The catalyst layer was 0.00287 cm wide. The membrane was 0.023 cm thick (Um et al., 2000).
The model used many of the standard assumptions for PEM fuel cell studies. The model assumed that all gases were ideal gases. The flows were assumed incompressible and laminar. The electrodes were assumed isotropic and homogeneous. Ohmic losses due to electron flow within the conductive solid were ignored (Um et al., 2000). Although one of the stated goals of the model was to develop a transient model, Um et al. assumed that the cell temperature remained constant, i.e. the system was isothermal (Um et al., 2000). The temperature was maintained at 353 K or approximately 80°C. The authors also assumed that water is only present as a vapor (Um et al., 2000). Because the water within the model only existed as a vapor, the model assumed that water existed in a supersaturated vapor phase (Springer, Zawodzinski, & Gottesfeld, 1991).

Um et al. (2000) explained that the model expanded upon the work of Gurau, Liu, and Kakac (1998). Gurau et al. (1998) proposed "... a two dimensional model of [the] transport phenomena in PEM fuel cells" (as cited by Um et al., 2000). However, in contrast to the model by Gurau et al. (1998), "... which employs separate differential equations for [the] different subregions [of the fuel cell] ..." (as cited by Um et al., 2000), Um et al. (2000) modeled the system as a single computational domain. Um et al. (2000) developed a set of governing equations that could be used to model a computational domain and avoid the issue of interface boundary conditions (Um et al., 2000). The computational domain was solved by solving the equations of mass and momentum along with the equations for the electrochemical potential. Equations
89, 90, and 91 are the continuity equation, the momentum equation, and the species equations. The porosity ($\varepsilon$) was added to each of the equations.

The porosity ($\varepsilon$) was added to each of the aforementioned equations, because the flow domain is porous. Equation 92 is equation for the phase potential ($\Phi$).

Within the aforementioned differential equations, $u$, $p$, $X$, $\varepsilon$, $\mu^{eff}$, $D^{eff}$, and $\Phi$ are the velocity vector, pressure, reactant mole fraction, porosity, effective viscosity, effective diffusivity, and the phase potential, respectively (Um et al., 2000). As shown in Equation 93, continuous flux conditions were used at the interfaces to address any discontinues across the interfaces.

The minus (-) sign subscript meant left side and the plus (+) sign subscript meant right side (Um et al., 2000).
The kinetic source term \( S_k \) referenced in the species equation was based on the Bulter-Volmer equation. There are three species equations: one equation for each of the chemical species present within the PEM fuel cell. This treatment assumed that only hydrogen gas, oxygen gas, nitrogen gas, and water were present. Equations 94, 95, and 96 are the hydrogen gas consumption source term, the oxygen gas consumption term, and the water generation term, respectively.

\[
S_{H_2} = -\frac{j_a}{2F_{c_{Total}}} \quad (94)
\]

\[
S_{O_2} = \frac{j_c}{4F_{c_{Total}}} \quad (95)
\]

\[
S_{H_2O} = -\frac{j_c}{2F_{c_{Total}}} \quad (96)
\]

Because nitrogen does not participate in any of the critical chemical reactions, no source term was developed for nitrogen. Um et al. (2000) assumed that the anode side reaction proceeds at a much faster rate than the cathode side kinetics. For the aforementioned reason, modified forms of the Bulter-Volmer equation (Equations 97 & 98) are used.

\[
j_a = a_{j_0,a}^{ref} \left( \frac{X_{H_2}}{X_{H_2,ref}} \right)^{1/2} \left( \frac{\alpha_a + \alpha_c}{RT} F \eta \right) \quad (97)
\]
\[ j_c = -aj_{0,c}^{\text{ref}} \left( \frac{X_{O_2}}{X_{O_2,\text{ref}}} \right) \exp \left( -\frac{\alpha_c F \eta}{RT} \right) \]  

(98)

\( \eta \) is the surface overpotential, and \( j_a \) and \( j_c \) are the transfer currents at the anode and cathode, respectively.

One of the cited goals of the study was to assess the effect of hydrogen dilution on fuel cell performance (Um et al., 2000). As the hydrogen concentration was reduced, the overall performance of the fuel cell was reduced. The model was validated by comparing the model results with the experimental results of Ticianelli, Berry, and Srinivasan (1988) (Um et al., 2000). The polarization curve was used as the comparator. Um et al. (2000) acknowledge that although Ticianelli et al. (1988) did not report concentration data that the model proposed by Um et al. could be used to estimate the concentration profile within the fuel cell. An oxygen concentration profile is presented in the appendix. However, the authors acknowledged that the profile given is inconsistent with the continuous flux boundary condition at the gas diffusion layer-catalyst layer interface. The authors suggested that a mass transfer resistance must exist, which caused the sudden drop in oxygen concentration within the catalyst layer.

In 2001, Liu and Zhou (2001) proposed a 3-D model of a PEM fuel cell, which was developed to study the mass transfer and the heat transfer within the fuel cell constructed with dead-end gas channels (Liu & Zhou, 2001, para. 3). To increase mass transfer and heat transfer, the gas channel was blocked forcing the reactant gases to travel through the gas diffusion layer prior to exiting the
system on the other end of the gas diffusion layer (Liu & Zhou, 2001, para. 3). The system was assumed to be at steady state. The gas diffusion layer, the membrane, and the catalyst layer were assumed to be isotropic and homogeneous. All fluid properties were assumed constant and independent of temperature (Liu & Zhou, 2001). Validation of the model was performed by comparing the polarization curves generated from the model data to the test data referenced in Nguyen (1996). The model showed good agreement with the test data. The model concludes that when the mass transfer mechanisms are changed from diffusion to convention the reaction rate increases significantly and the catalyst is used more effectively. The study also concludes that interdigitated flow fields are superior to conventional flow fields.

In 2004, Nguyen, Berning, and Djilali (2004) developed a three dimensional (3-D) computational model of a PEM fuel cell with a serpentine gas channel (Nguyen, Berning, and Djilali, 2004). Nguyen, Berning, and Djilali (2004) assumed no losses associated with reactant gas crossover (Nguyen, Berning, and Djilali, 2004). Waste heat generation due to Ohmic losses was ignored (Nguyen, Berning, and Djilali, 2004). Water was assumed to exist as a single vapor phase throughout the system (Nguyen, Berning, and Djilali, 2004). In lieu of using the Bulter-Volmer equation, Nguyen, Berning, and Djilali (2004) used a Voltage-to-Current algorithm, which allowed for the calculation of the local activation overpotential (Nguyen, Berning, and Djilali, 2004). Nguyen, Berning, and Djilali (2004) noted that the current density near the limiting current density was not in agreement with the experimental data; however, the higher current
densities observed in single phase models at higher current densities is a known discrepancy of single phase models (Nguyen, Berning, and Djilali, 2004).

In addition, in 2004, Hum and Li (2004) developed a two-dimensional, steady state model of a PEM fuel cell. The gas diffusion layer was 200 microns thick, the catalyst layer was 10 microns thick, and the membrane was 230 microns thick. The system is assumed to be fully hydrated and isothermal (Hum & Li, 2004). The focus of the study was the evaluation of the phenomena at the catalyst layer and effect of humidification on fuel cell performance (Hum & Li, 2004). The study also compared counter current flow of reactants to co-current flow of reactants. The computational domain was solved using finite volume techniques with an alternate direction implicit algorithm (Hum & Li, 2004). The study demonstrated that the responses to the potential changes at the cathode were more pronounced than the changes at the anode (Hum & Li, 2004). In addition, the study show that there was no significant different between counter current flow of reactants and co-current flow of reactants (Hum & Li, 2004).


In 2005, Ju, Meng, and Wang (2005) proposed a steady state, three dimensional (3-D) single-phase, non-isothermal model of a PEM fuel cell to simulate the heat transfer dynamics within a PEM fuel cell using a 3-D model of the system (Ju, Meng, & Wang, 2005). PEM fuel cell can generate about the
same amount of waste heat as electrical power output (Ju, et al., 2005). The rate of heat loss correlates to be an efficiency of 50% (Ju, et al., 2005). Waste heat can significantly degrade the life and performance of a PEM fuel cell (Ju, et al., 2005). Therefore, the heat management and modeling of waste heat or temperature gradients within PEM fuel cells is essential for PEMFC design (Ju et al., 2005).

Ju et al. (2005) expanded on the work of Shimpalee and Dutta (2000) and others. While Shimpalee and Dutta (2000) assumed that the membrane was uniformly hydrated, Ju et al. studied the effect of localized temperature gradients associated with differences in membrane and electrode temperatures (Ju et al., 2005). Earlier models, like the model of Shimpalee and Dutta (2000), did not differentiate between temperature of the membrane and the electrode (Ju et al., 2005). The major drawback of these earlier models was that the heat source terms were treated as global parameters. These models ignored localized variations in temperature, which could leave to membrane failure (Ju et al., 2005).

Ju et al. (2005) used the equations of motion and energy to solve the computational domain. The conservative forms of the continuity equation, the momentum equation, and the species equations are listed below (Ju et al., 2005):

\[
\nabla \cdot (\rho \mathbf{u}) = 0 \tag{99}
\]

\[
\frac{1}{\varepsilon^2} \nabla \cdot (\rho \mathbf{u} \mathbf{u}) = -\nabla p + \nabla \cdot \mathbf{\tau} + \mathbf{S}_u \tag{100}
\]
\[ \nabla \cdot (\bar{u}C_k) = \nabla \cdot (\rho_{keff} \nabla C_k) + S_k \quad (101) \]

Equation 102 is the equation for the phase potential, and Equation 103 is the energy equation.

\[ \nabla \cdot \left( \kappa_{eff} \nabla \Phi_e \right) + S_\Phi = 0 \quad (102) \]

\[ \nabla \cdot \left( \rho C_{peff} \bar{u}T \right) = \nabla \cdot \left( \kappa_{eff} \nabla T \right) + S_T \quad (103) \]

To account for localized variations in temperature, Ju et al. (2005) defined an effective heat capacity \( C_{p_{eff}} \). As shown in Equation 104, the effective heat capacity is a function of the heat capacity of the fluid and the heat capacity of the solid.

\[ \rho C_{p_{eff}} = \varepsilon \rho C_{p_f} + (1 - \varepsilon) \rho C_{p_s} \quad (104) \]

The effective heating capacity is a function of the heat capacities of the fluid (f) regions of the system and the solid (s) matrix regions of the systems (Ju et al., 2005).

Ju, et al. (2005) studied three parameters: gas diffusion layer thermal conductivity, the feed gas relative humidity, and the operating cell voltage (Ju, et al., 2005). The study showed that gas diffusion layer thermal conductivity was strongly correlated with membrane temperature rise (Ju, et al., 2005). The study
also showed that 80% to 90% of the waste heat was generated by reactions at the cathode (Ju, et al., 2005).

In 2006, Liu, Tao, Li, and He (2006) developed a 3-D multi-component model of a PEM fuel cell. The model assumes that the system is constructed of straight parallel plates (Liu, Tao, Li, and He, 2006). The system was assumed to be isothermal and steady state. All reactants were assumed to be ideal gases. The model assumed no crossover losses (Liu, Tao, Li, and He, 2006). The model used no-slip boundary conditions (Liu, Tao, Li, and He, 2006). The Semi-Implicit Method Pressure Linked Equations (SIMPLE) was used to estimate the velocity distribution within the gas channel. Liu, Tao, Li, and He (2006) validated the model by comparing the model's polarization curve with the polarization curve generated from experimental data by Ticianelli, Berry, and Srinivasan (1988) (Liu, Tao, Li, and He, 2006). At low current densities, the model agrees quite well with the experimental data; however, at high current densities, the model predicted a much higher limiting current density than did the experimental data (Liu, Tao, Li, and He, 2006).

Mann, Amphlett, Peppley, and Thurgood (2006) presented a study on reactant gas solubility modeling. The study used the Henry’s Law to model the reactant gas concentration at the membrane-catalyst layer interface. The study concluded that the hydration of the Nafion membrane was key to predicting reactant gas concentration at the catalyst layer-membrane layer interface (Mann, Amphlett, Peppley, & Thurgood, 2006). The authors cautioned the reader that solubility data in the literature is developed for specific experimental scenarios.
and caution must be used when using these data. Specifically, the authors noted that solubility data is prone to variability (Mann, Amphlett, Peppley, & Thurgood, 2006). Experimental setup could potentially affect the solubility data that was generated. The authors noted parameters such as experimental run time, the humidification, and order of the runs might potentially have influenced the data (Mann, Amphlett, Peppley, & Thurgood, 2006). The authors discussed the solubility correlation proposed by Bernardi and Verbrugge (1991). Bernardi and Verbrugge (1991) suggest a correlation for the Henry's Law constant for Nafion for dissolved oxygen gas. Equation 105 is the correction for the Henry's Law constant proposed by Bernardi and Verbrugge (1991).

\[ H_{O_2,Nafion} = 1.33 \times 10^6 \exp\left(\frac{-666}{T}\right) \]  

Mann, Amphlett, Peppley, and Thurgood (2006) explained that Bernardi and Verbrugge (1991) referenced solubility values at 80°C and 95°C. The authors explain that the value cited by Bernardi and Verbrugge (1991) at 80°C was consistent with the cited correlation; however, the value at 95°C was not consistent.

In 2007, Park, Matsubara, and Li (2007) simulated the micro-scale flows within the microstructure of the porous electrode. The simulation by Park, Matsubara, and Li was one of the first papers published, which attempted to model the flows within the microscale porous electrode (Park, Matsubara, and Li, 2007). Park Matsubara, and Li (2007) used the porous Lattice Boltzmann model
developed by Spaid and Phelan (1997) to model reactant flows within the gas diffusion layer (GDL) of a PEM fuel cell (Park, Matsubara, & Li, 2007). Woven carbon fiber is used to construct the gas diffusion layer of a PEM fuel cell. The premise of this study is that the carbon matrix is not homogeneous, but heterogeneous. Park, Matsubara, and Li (2007) stated that the advantage of using the porous Lattice Boltzmann model to simulate reactant movement within the gas diffusion layer is that the gas diffusion layer (GDL) is heterogeneous, not homogeneous, which is the assumption that most other models use (Park, Matsubara, & Li, 2007).

In 2007, Vasileiadis, Brett, Vesovic, Kucervak, Fontes, and Brandon (2007) proposed a two-dimensional numerical model of a PEM fuel cell. The model was described as an extension of the pioneering work of Bernardi and Verbrugge (1991) (Vasileiadis et al., 2007). Bernardi and Verbrugge (1991) proposed a one-dimensional model of the PEM fuel cell; Vasileiadis et al. (2007) modeled the system in two-dimensions. The model assumed that the system was operated in a cross flow orientation. Although the Vasileiadis et al. (2007) allude to the heterogeneity of the membrane, the model assumed that the membrane is homogeneous and the hydration of the membrane is constant (Vasileiadis et al., 2007). The model also assumes that the ionic current density across the membrane is constant for voltage potential.

Vasileiadis et al. (2007) modeled the seven sections of the PEM fuel cell: two gas channels, two gas diffusion layers, two catalyst layers, and membrane layer. The model assumed that all reactant were ideal gases and were well
mixed. Vasileiadis et al. (2007) modeled both electronic potential and the ionic potential. Vasileiadis et al. (2007) used the differential forms of Ohm's Law to describe both the electronic conductivity and the ionic conductivity. The electronic conductivity \( (\Phi_s) \) within the gas diffusion layer is given by the following Laplace's Equation (Vasileiadis et al., 2007):

\[
\frac{\partial^2 \Phi_s}{\partial z^2} + \frac{\partial^2 \Phi_s}{\partial y^2} = 0 \quad (106)
\]

The electronic conductivity within the catalyst layer is given by the following Poisson's equation (Vasileiadis et al., 2007).

\[
-\sigma_{\text{eff}} \left( \frac{\partial^2 \Phi_s}{\partial z^2} + \frac{\partial^2 \Phi_s}{\partial y^2} \right) = -\left( \frac{\partial \Phi_{\text{elect}}}{\partial z} + \frac{\partial \Phi_{\text{elect}}}{\partial y} \right) \quad (107)
\]

\( \sigma_{\text{eff}} \) is the effective electronic conductivity. As shown in Equation 108, the effective electronic conductivity is defined as the product of the electronic conductivity \( (\sigma) \) multiplied by one minus the void fraction \( (\varepsilon) \) (Vasileiadis et al., 2007).

\[
\sigma_{\text{eff}} = \sigma (1 - \varepsilon) \quad (108)
\]

The electronic conductivity is effectively the inverse of the resistance, which is typically used in Ohm's Law. The ionic conductivity \( (\Phi_i) \) is defined in a similar fashion as the electronic conductivity. As shown in Equation 109, Laplace's
Equation is used to describe the ionic conductivity in the gas diffusion layer (Vasileiadis et al., 2007).

\[
\frac{\partial^2 \Phi_i}{\partial z^2} + \frac{\partial^2 \Phi_i}{\partial y^2} = 0
\]  
(109)

As shown in Equation 110, Poisson’s Equation is used to describe the ionic conductivity within the catalyst layer.

\[
-k_{\text{eff}} \left( \frac{\partial^2 \Phi_i}{\partial z^2} + \frac{\partial^2 \Phi_i}{\partial y^2} \right) = - \left( \frac{\partial \Phi_i}{\partial z} + \frac{\partial \Phi_i}{\partial y} \right)
\]  
(110)

\( k_{\text{eff}} \) is the effective ionic conductivity and is defined as the ion conductivity times one minus the void fraction. Similar to the electronic conductivity, the ionic conductivity is effectively the inverse of the resistance, which appears in the traditional form of Ohm's Law. As shown in Equation 111, Vasileiadis et al. (2007) modeled the concentration \( (c_i) \) of each species \( i \) assuming that the major modes of transport were diffusion and convection (Vasileiadis et al., 2007).

\[
-D_i \left( \frac{\partial^2 c_i}{\partial z^2} + \frac{\partial^2 c_i}{\partial y^2} \right) + \frac{\partial (c_i u_z)}{\partial z} + \frac{\partial (c_i u_y)}{\partial y} = R_i
\]  
(111)

\( R_i \) is a source term with the following functional form (Vasileiadis et al., 2007):

\[
R_i = - \frac{n}{4F} \left( \frac{\partial i}{\partial z} + \frac{\partial i}{\partial y} \right)
\]  
(112)
F is Faraday's constant, and n is the number of free electrons.

The computational domain was solved using FEMLAB® and MATLAB® (Vasileiadis et al., 2007). The model assumes that the concentration of reactant at the gas channel-gas diffusion layer boundary is constant. The model assumes that the flux of hydrogen gas and oxygen gas at the catalyst layer-membrane layer are zero at the anode and cathode, respectively. In addition, the model assumes that the flux of water across the membrane is zero.

Vasileiadis et al. (2007) validated the model by comparing the computational results to experimental data (Vasileiadis et al., 2007). The model predicts increasing current density with decreasing cell voltage. The model also predicts a sharp increase in current density close to the membrane (Vasileiadis et al., 2007). The model predicts a significant voltage drop across the membrane. Specifically, the model predicted almost no voltage drop within the anode or the cathode (Vasileiadis et al., 2007). The model also predicts the pressure distribution across the fuel cell at various voltages (Vasileiadis et al., 2007). Given that the inlet mole fraction of hydrogen is 0.6 and the inlet mole fraction of water is 0.4, the model predicts that hydrogen concentration at the catalyst layer-membrane layer interface is not zero.

In 2008, Haddad, Bouyekhf, and El Moudni (2008) proposed a 1-D dynamic model of a PEM fuel cell that simulated the mass transfer of chemical species across the polymer membrane. The model used dynamic control methodologies to manage the water transport throughout the fuel cell to maintain the desire hydration of the membrane (Haddad, Bouyekhf, and El Moudni, 2008).
The model evaluated the effect of gas consumption rate and humidification rate on the rate of migration of water and protons across the polymer membrane (Haddad, Bouyekhf, & El Moudni, 2008). The hydration of the membrane was maintained by varying the inlet gas humidity (Haddad, Bouyekhf, & El Moudni, 2008). The model assumes that the diffusion of chemical species across the fuel cell is one-dimensional. To reduce the complexity of the system, the model was isothermal; however, the model assumed that all water generated at the cathode is liquid water (Haddad, Bouyekhf, & El Moudni, 2008). Haddad, Bouyekhf, and El Moudni (2008) concluded that the model was capable of simulating the dynamics of a PEM fuel cell, and the dynamic control of the water transport translated into improved PEM fuel cell efficiency (Haddad, Bouyekhf, and El Moudni, 2008).

In 2009, Moreira and de Silva (2009) developed a practical model for evaluating the performance of PEM fuel cells. Moreira and de Silva (2009) stated that there are really two modeling methods that are currently used for the modeling of fuel cells: mechanistic models and semi-empirical models. Moreira and de Silva (2009) describe mechanistic models as models that use the Navier-Stokes equations and other equations of motion to describe the system dynamics. Moreira and de Silva (2009) stated that mechanistic models are typically difficult to use, but mechanistic models are good for simulating detailed system parameters. Semi-empirical models were described as being more user-friendly, and Moreira and de Silva suggested that semi-empirical models would typically be used by fuel cell modeler to assess quickly fuel cell performance.
The goal of the model was to reduce the computational complexity of simulating the performance of PEM fuel cells (Moreira & de Silva, 2009).

In addition, in 2009, Haddad, Benmoussa, Bourmada, Oulmi, Mahmah, and Belhamel (2009) proposed a 1-D transient model of a PEM fuel cell. Model simulated the movement of water through the system by diffusion, convection, and general migration (Haddad et al., 2009). Finite element methods were used to solve the computational domain. The study correlated current density to the mean water concentration within the fuel cell. The model concluded that adjusting the pressure gradient across the polymer membrane might be one method of ensuring membrane hydration (Haddad et al., 2009).
CHAPTER V

COMPUTATIONAL METHOD

The goal of this research was to develop a working model of a microscale polymer electrolyte membrane (PEM) fuel cell. However, before delving into the nuances of the models, a review of the physical models and numerical schemes used in the simulations is presented here. This chapter is presented as a detail review of the methods that were used to construct the models. Although the methods presented will be tailored to PEM fuel cell systems, these same methods are directly applicable to other fluidic systems.

Because fuel cells are complex systems, several simplifying assumptions are made to reduce the complexity of the system. The initial models were one dimensional (1-D) models. The details of the 1-D model will be presented. After the 1-D models were completed, two dimensional (2-D) models were also completed. The 2-D models are presented. Prior to reviewing the data generated from the models, this chapter is presented as a review of the basic modeling concepts and schemes.

As previously mentioned a fuel cell has two halves: the anode and the cathode. Hydrogen is supplied to the anode to power the fuel cell, and oxygen is flows to the cathode. A fuel cell produces electrical energy via an electrochemical reaction. The electrochemical processes occur at opposite ends of the fuel cell
Oxygen ($O_2$) is combined electrochemically with hydrogen ($H_2$) in the presence of a platinum catalyst to produce water, electrical energy, and heat (Gregory, 1972; Larminie & Dicks, 2003). Equation 113 is the overall reaction.

$$H_2 + \frac{1}{2}O_2 \xrightarrow{Pt} H_2O$$

Although it is well understood that fuel cells are dynamic systems, the system was first modeled assuming steady state conditions exist. The initial steady state model was constructed as a baseline for the models that follow. The steady state model is also used to validate the later models, which are time dependent.

To ease the level of complexity, which exists in real fuel cell systems, several simplifying assumptions have been made to lessen the computational burden. All gases are assumed to be ideal gases. Both oxygen gas and hydrogen gas can reasonably be assumed to be ideal gases at moderate pressures and moderate temperatures, because the critical temperatures of oxygen gas and of hydrogen gas are 154.6K (-118.55°C) and 33.2K (-239.95°C), respectively (Smith & Van Ness, 1987). Nitrogen is also present in the cathode gases, but nitrogen gas does not participate significantly in any of the critical fuel cell reactions. That being said, nitrogen is also an ideal gas at ambient temperatures and moderate to low pressures. Water, on the other hand, is not an ideal gas; however, for the purposes of this model, water vapor will be assumed
to be an ideal gas. When appropriate, either steam tables or known water vapor correlations will be used to correct for the non-ideality of water.

The only reactants are hydrogen (H₂), oxygen (O₂), nitrogen (N₂), and water (H₂O). Although in practice both reactant streams would be contaminated by trace amounts of other gases, it is assumed that the impact of these contaminant gases can be neglected, because the model does not model the long-term effects of such gases on the performance of the fuel cell. In the short-term, contaminants, like carbon monoxide (CO), which is a known poison to platinum catalysts, will have little impact on the overall trends generated from the model (Larminie & Dicks, 2003; Gregor, 2003). The intent of these simulations is not to simulate the life of a fuel cell, but the overall operation of the fuel cell. Therefore, catalyst fouling and catalyst deactivation are neglected.

The novelty of polymer electrolyte membrane fuel cells is that these fuel cells are capable of converting hydrogen and oxygen into electrical energy and water at relatively low temperatures (Pukrushpan, Stefanopoulou, & Peng, 2005,). Although the electrochemical reaction between oxygen and hydrogen is exothermic, to simplify the initial computation, the initial 1-D models are simulated as an isothermal process. The fuel cell temperature is set to 80°C or 353 K, which is a typical temperature referenced in the literature for PEM fuel cell systems (Hu, Fan, Chen, Liu, & Cen, 2004).

Figure 7 depicts the overall material movement for all primary species present within a PEM fuel cell.
Figure 7: Material Flow Schematic for PEM Fuel Cell.
While the transport of hydrogen (H\textsubscript{2}) and oxygen (O\textsubscript{2}) is essentially unidirectional, the transport of water through PEM fuel cell systems is quite complex. The movement of water through the fuel cell is dependent upon many factors; however, there are two principle mechanisms, which describe the movement of water within a PEM fuel cell: electro-osmotic drag and molecular diffusion.

As shown in Equation 114, at the anode, hydrogen (H\textsubscript{2}) reacts with the platinum electrode and dissociates into two hydrogen ions (H\textsuperscript{+}) and two free electrons (e\textsuperscript{−}).

\[
\begin{equation}
H_2 \xrightarrow{\text{Pt}} 2H^+ + 2e^- \tag{114}
\end{equation}
\]

Because of the natural dipole moment (\(\delta\)), which exists within a water molecule, the negatively charged end of the water molecule is attracted to the positively charged hydrogen ions (H\textsuperscript{+}). Figure 8 illustrates the overall dipole structure of a water molecule.

![Figure 8: Structure of Water Molecule Showing Electric Dipole.](image)

Water is a polar molecule with a dipole moment with a measured magnitude of 6.2 \times 10^{-30} \text{ Coulomb-meters} (Ebbing, 1987). This weak electrostatic attraction forms an electrostatic bond between the hydrogen ion and the
negatively charged end of the water molecule forming a positively charged hydronium cation ($H_3O^+$). Equation 115 is the reaction for the formation of the hydronium cation ($H_3O^+$).

\[
H^+ + H_2O \rightarrow H_3O^+ \quad (115)
\]

Because of this weak electrostatic attraction, hydrogen ions ($H^+$) drag water molecules across the polymer membrane as the hydrogen ions ($H^+$) diffuse toward the fuel cell cathode. This dragging of water molecules with hydrogen ions ($H^+$) is called electro-osmotic drag. As shown in Equation 116, the rate of water transport from the anode to the cathode is a function of the current density ($i$) and the degree of hydration of the polymer membrane (Barbir, 2005):

\[
N_{H_2O,\text{drag}} = \xi(\lambda) \frac{i}{F} \quad (116)
\]

The electro-osmotic drag coefficient ($\xi$), which is a measure of how many water molecules are being actively dragged with the hydrogen ion, is a function of the membrane hydration ($\lambda$). La Conti, Fragala, and Boyack (1977) documented drag coefficients ($\xi$) between 2 to 3 for membrane hydrations ($\lambda$) between 15 and 25 (as cited by Barbir, 2005).

Water is also transported through the fuel cell via diffusion. The diffusion of water is a function of concentration. Water molecules will diffuse from areas of high concentration, i.e. the cathode, to areas of low concentration, i.e. the anode.
Equation 117 is the equation for the diffusion of water from the cathode towards the anode.

$$N_{H_2O} = -D \frac{\Delta C_{Water}}{\Delta x}$$

Because both the hydrogen and oxygen supplied to the fuel cell may be humidified, water may also diffuse from the gas channels toward the electrolyte membrane. However, the production of water at the cathode electrode is several orders of magnitude greater than the water supplied to the reactant gases. The reactant gases are humidified to lessen or to prevent membrane dehydration.

Because of the water that is generated at the cathode electrode, it is very important that the model accurately describes the transport of water within a fuel cell. If the rate of water production and the rate of water supply are not modeled accurately, the fuel cell will flood. Flooding of the fuel cell reduces the overall efficiency of the fuel cell, because gases are significantly less soluble in water.

As previously mentioned, the only constituents are hydrogen (H$_2$), water (H$_2$O), oxygen (O$_2$), and nitrogen (N$_2$). Because nitrogen (N$_2$) does not actively participate in the cathode side reactions, the model assumes that the nitrogen concentration distribution at the cathode is established instantaneously and does not simulate the development of the nitrogen distribution. In actuality, the nitrogen distribution is established during the initial start-up of the fuel cells; however, after that initial start-up, the concentration of nitrogen within the fuel cell does not change appreciably with time.
The gas diffusion layer is porous. Because it is a porous material, it is the effective diffusivity \( D_e \) that must be used for all diffusional mass transport calculations. "The effective diffusivity accounts for the fact that not all of the area normal to the direction of the flux is available for the molecules to diffuse" (Folger, 1992). Equation 118 shows the functional dependence of the effective diffusivity on the porosity \( \varepsilon_p \), the constriction factor \( \sigma \), and the tortuosity \( \tau \).

\[
D_e = D_{AB} \frac{\varepsilon_p \sigma}{\tau}
\] (118)

The porosity \( \varepsilon_p \) is a measure of the amount of void space within a porous structure versus the total volume (Folger, 1992). The tortuosity \( \tau \) is a measure of the curviness of the void space. Specifically, the tortuosity \( \tau \) is a type of normalized distance that a molecule travels within a porous media. The tortuosity is defined as the actual distance a molecule travels from an initial point A to a point B divided by the shortest distance between the two points. The higher the tortuosity the more curves exist within the space per unit length (Folger, 1992). "The constriction factor \( \sigma \) accounts for the variation in the cross-sectional area that is normal to diffusion" (Folger, 1992). The tortuosity can vary from 1 to 10.

Folger (1992) references typical values of the constriction factor \( \sigma \), the tortuosity \( \tau \), and the porosity \( \varepsilon_p \) for porous materials: \( \sigma = 0.8 \), \( \tau = 3.0 \), and \( \varepsilon_p = 0.40 \) (Folger, 1992). The aforementioned values for the constriction factor, the tortuosity, and the porosity have been used throughout the model.
Model Parameters

Before a viable computational model can be developed, the system parameters were identified, and a parameter analysis was performed. The model parameter analysis were use to generate critical system parameters, and to refine the process assumptions that will be mentioned below.

To simplify the complexity of the problem, several simplifying assumptions have been made:

1. The anode and cathode catalysts are homogeneous and isotropic.
2. Entrance effects will be neglected for the 2-D Cases.
3. All gaseous reactants and products are ideal gases.
4. The oxygen concentration and supply rate is constant.
5. Oxygen fed to the cathode will be modeled as pure oxygen.
6. The hydrogen supply rate is constant.
7. Catalyst fouling can be neglected.
8. The polymer membrane is DuPont™ Nafion® 117.
9. All flows are laminar.
10. Density is constant.
11. Filtration velocity is constant.
12. The system is isothermal.
13. There are no body forces.
14. Viscosity is constant.
15. Differential Pressure can be estimated by the following equation:

$$\frac{\partial P}{\partial y} \approx \frac{\Delta P}{\Delta y}$$  (119)

16. Fluid is a Newtonian fluid.

17. The shear stress ($\tau_s$) at the wall or specifically near the wall is constant. This is the shear stress that appears in the slip velocity equation.

$$v_s - v_w = \frac{2 - \sigma_v}{\sigma_v} \frac{1}{\rho \left( \frac{2RT_w}{\pi} \right)^{1/2}} \tau_s$$  (120)

18. Diffusion term is appropriately zero.

$$\frac{\partial^2 v}{\partial y^2} \approx 0$$  (121)

Numerical Schemes

There are a myriad of computational schemes available for solving the equations of motion and the species equations. Because each of the differential equations, which describe the computational domain, must be solved simultaneously, the following vector equation is used to solve the computational domain (Tannehill, Anderson, & Pletcher, 1997).
\[ \frac{\partial U}{\partial t} + \frac{\partial E}{\partial x} + \frac{\partial F}{\partial y} + \frac{\partial G}{\partial z} = 0 \]  
(122)

The vector \( U \) is given by the following (Tannehill et al., 1997):

\[
U = \begin{bmatrix}
\rho \\
\rho u \\
\rho v \\
\rho w \\
E_t
\end{bmatrix}
\]  
(123)

The vector \( E \) is given by the following vector (Tannehill et al., 1997):

\[
E = \begin{bmatrix}
\rho u \\
\rho u^2 + p - \tau_{xx} \\
\rho u v - \tau_{xy} \\
\rho u w - \tau_{xz} \\
(E_t + p)u - u\tau_{xx} - v\tau_{xy} - w\tau_{xz} + q_x
\end{bmatrix}
\]  
(124)

The vector \( F \) is given by the following vector (Tannehill et al., 1997):

\[
F = \begin{bmatrix}
\rho v \\
\rho u v - \tau_{xy} \\
\rho v^2 + p - \tau_{yy} \\
\rho u w - \tau_{yz} \\
(E_t + p)v - u\tau_{xy} - v\tau_{yy} - w\tau_{yz} + q_y
\end{bmatrix}
\]  
(125)

The vector \( G \) is given by the following vector (Tannehill et al., 1997):
The specific numerical schemes will be described for the both the 1-D and 2-D cases.

Explicit MacCormack Scheme

The goal was to select a robust scheme, which allowed for maximum flexibility. Specifically, the scheme was required to be stable over a wide range of time step sizes and space step sizes. Using the aforementioned mathematical models to describe the physics of the system, several computational models were developed. The computational methods that have been used to simulate the physical domain are divided into two groups: explicit schemes and implicit schemes. Each has its advantages and disadvantages. Explicit schemes tend to be relatively easy to program; however, typically these schemes are computationally intensive and are prone to instability as the mesh size gets small. Implicit schemes are very robust. Implicit models typically are unconditionally stable. However, implicit schemes tend to be more difficult to program.

Because of the ease of computation, the explicit MacCormack scheme was selected to simulate and to solve both the 1-D fuel cell cases and the 2-D
fuel cell cases. The purpose of this review is to present the computational and numerical methods used within the simulations and to define the merits of the methods. The intended purpose is to link the selection of the method to the physics of the system.

The MacCormack method is an explicit scheme developed in the 1970's, which is used to solve the compressible Navier-Stokes equations. The scheme is divided into two parts: a predictor step and a corrector step. The predictor step (Equation 127) is used to calculate the value of $U_{i,j,k}$ at an intermediate time step.

$$U_{i,j,k}^{n+1} = U_{i,j,k}^n - \frac{\Delta t}{\Delta x} \left( E_{i+1,j,k}^n - E_{i,j,k}^n \right) - \frac{\Delta t}{\Delta y} \left( F_{i,j+1,k}^n - F_{i,j,k}^n \right) - \frac{\Delta t}{\Delta z} \left( G_{i,j,k+1}^n - G_{i,j,k}^n \right)$$ (127)

The corrector step (Equation 128) uses the information from the predictor step to calculate the value of $U_{i,j,k}$ at the next time step.

$$U_{i,j,k}^{n+1} = U_{i,j,k}^n - \frac{\Delta t}{\Delta x} \left( E_{i+1,j,k}^n - E_{i,j,k}^n \right) - \frac{\Delta t}{\Delta y} \left( F_{i,j+1,k}^n - F_{i,j,k}^n \right) - \frac{\Delta t}{\Delta z} \left( G_{i,j,k+1}^n - G_{i,j,k}^n \right)$$ (128)

The MacCormack scheme is a second order accurate explicit scheme (Tannehill et al., 1997; Hoffmann, 1989). The method is second order accurate in both space and time (Tannehill et al., 1997; Hoffmann, 1989). Tannehill et al. (1997) explains that second-order accuracy in time is required to accurately describe a transient flow (Tannehill et al., 1997). However, unlike implicit schemes, linearization of the nonlinear terms is not required for explicit computational schemes, because all of the known data are evaluated at the
known time step (Hoffmann, 1989). Only the unknown variable \( (U_{i,j,k}^{n+1}) \) is calculated at the next time step.

Unlike implicit schemes, the explicit MacCormack scheme is a conditionally stable. Because the explicit MacCormack scheme is conditionally stable, the Courant-Friedrichs-Levy (CFL) number must be selected to ensure stability through the simulation. "Because of the complexity of the compressible Navier-Stokes equation, it is not possible to obtain a closed form stability expression for the MacCormack scheme applied to these equations. However, the following empirical formula can normally be used" (Tannehill et al., 1997):

\[
\Delta t \leq \sigma \frac{(\Delta t)_{CFL}}{2 \left[ 1 + \frac{\Delta x}{Re_{\Delta}} \right]}, \tag{129}
\]

"... where \( \sigma \) is the safety factor (\( \approx 0.9 \)), \( (\Delta t)_{CFL} \) is the inviscid Courant-Friedrichs-Levy (CFL) condition (MacCormack, 1971) ..." (Tannehill et al., 1997).

\[
(\Delta t)_{CFL} \leq \frac{1}{\left( \frac{|u|}{\Delta x} + a \left( \frac{1}{(\Delta x)^2} \right) \right)}, \tag{130}
\]

"\( Re_{\Delta} \) is the minimum mesh Reynolds number given by ... “(Tannehill et al., 1997).

\[
Re_{\Delta x} = \frac{\rho |u| (\Delta x)}{\mu}, \tag{131}
\]
“... and a is the local speed of sound ...” (Tannehill et al., 1997). Equation 132 shows the depends of the local speed of sound on the pressure (P), density (ρ), and ratio (γ) of the specific heats.

\[
a = \sqrt{\frac{\gamma P}{\rho}}
\]  

(132)

The Courant-Friedrichs-Levy (CFL) number has been selected to ensure stability through the simulation. Perrin and Hu (2006) explained that given a Reynolds' numbers between 10 and 500 and small Mach numbers the complexity of the stability condition is reduced (Perrin & Hu, 2006, 169). Equation 133 gives the stability criterion.

\[
\Delta t \leq \frac{0.5 \Delta x}{c}
\]  

(133)

The variable c is an arbitrary constant, but Perrin and Hu (2006) explained that c could be the speed of sound (Perrin & Hu, 2006, 167).

Although the explicit MacCormack scheme was selected because of the ease of programming of this method, the differencing of the viscous terms (E, F, and G) must be performed carefully as not to reduce the accuracy of the method. Specifically, the programmer must ensure that if forward differencing is used for the x derivative terms within the viscous term E then backward difference must be used for derivative of the viscous term E with respect to spatial variable x (Tannehill et al., 1997). In addition, if applicable, the y and z derivatives
appearing within the viscous term $E$ must be differenced using central differencing (Tannehill et al., 1997). The same is true for the viscous terms $F$ and $G$. “Likewise, the $y$ derivatives terms appearing in $F$ and the $z$ derivative terms appearing in $G$ are differenced in the opposite direction to that used for $dF/dy$ and $dG/dz$, respectively, while the cross-derivative terms in $F$ and $G$ are approximated with central differences” (Tannehill et al., 1997). Tannehill et al. (1997) caution that the forward differencing and backward differencing should be alternated to eliminate “. . . bias due to the one-sided differencing” (Tannehill et al., 1997).

1-D MICRO-PEM Fuel Cell Model

Each of the different sections of the fuel cell will be presented separately along with the mathematical equations, which define the system. The relevant boundary and initial conditions for each will be presented after all of the mathematical models have been discussed. The model development will start with the anode models.

Anode Model

The anode is divided into three sections: the gas channel, the gas diffusion layer, and the catalyst layer. Hydrogen gas is supplied to the anode via the anode gas channel. Hydrogen gas diffuses from the gas channel through the gas diffusion layer to the platinum catalyst layer. As the hydrogen gas reaches the catalyst, the hydrogen gas ionizes in the presence of the platinum electrode.
releasing electrons ($e^-$) and hydrogen ions ($H^+$). This one-dimensional model will describe the mathematical model used to simulate both the gas diffusion layer and the catalyst layer. The gas channel is not model in the original 1-D cases.

**Anode Gas Diffusion Layer Model**

The gas diffusion layer is a porous carbon fiber web. The carbon fiber web is used to protect the catalyst layer and it is used to distribute the gaseous reactants. This web also provides structural support to the membrane electrode assembly (MEA) (Barbir, 2005). No reactions occur within the gas diffusion layer. All fuel cell properties within the anode gas diffusion layer are assumed to be functions of space and of time only, as shown in Equation 134.

$$f = f(x,t)$$

(134)

The 1-D continuity equation, the $x$ momentum equation, and two species equations are used to describe the anode gas diffusion layer dynamics. The one dimensional continuity equation is given by the following equation:

$$\varepsilon \frac{\partial \rho}{\partial t} + \frac{\partial (\rho u)}{\partial x} = 0$$

(135)

Because the gas diffusion layer is a porous material, the porosity ($\varepsilon$) is introduced to account for the presence of void spaces within the gas diffusion layer. Porosity ($\varepsilon$) is the fraction of void space available for material transport. The porosity of the gas diffusion layer varies between 0.7 and 0.8 (Barbir, 2005). As shown in
Equation 136, the density ($\rho$) is a function of both the hydrogen concentration and the water concentration.

$$
\rho = M_{H_2}C_{H_2} + M_{H_2O}C_{H_2O}
$$

(136)

The velocity ($u$) given in the 1-D continuity equation and all subsequent equations is the filtration velocity, which is given by the Darcy equation (Vorobev, Zikanov, & Shamin, 2007). Equation 137 is the Darcy equation.

$$
\frac{\partial P}{\partial x} = -\frac{\mu u}{K}
$$

(137)

The Darcy equation is a simplified form of the one dimensional momentum equation (Hwang, Chao, Chang, Ho, & Wang, 2007). The permeability ($K$) of the gas diffusion layer is constant and set to $1.12 \times 10^{-14}$ m$^2$ (Ju & Wang, 2004).

There are only two chemical species, which are transported through the anode gas diffusion layer: hydrogen gas and water vapor. Equation 138 and Equation 139 are the hydrogen and water species equations for the gas diffusion layer.

$$
\varepsilon \frac{\partial C_{H_2}}{\partial t} + \frac{\partial (uC_{H_2})}{\partial x} = \frac{\partial}{\partial x} \left( D_e \frac{\partial (C_{H_2})}{\partial x} \right)
$$

(138)

$$
\varepsilon \frac{\partial C_{H_2O}}{\partial t} + \frac{\partial (uC_{H_2O})}{\partial x} = \frac{\partial}{\partial x} \left( D_e \frac{\partial (C_{H_2O})}{\partial x} \right)
$$

(139)
There is no source term in the aforementioned equations, because no reactions take place within the gas diffusion layer. The effective diffusivity ($D_e$) is used to account for the effect of porous on the overall rate of diffusion (Equation 140).

$$D_e = D_{AB} \frac{\varepsilon \rho \sigma}{\tau}$$  (140)

The effective diffusivity ($D_e$) is a function of the binary diffusion coefficient ($D_{AB}$), the porosity ($\varepsilon$), the tortuosity ($\tau$), and the constriction factor ($\sigma$). Because the gas diffusion layer is a porous material, it is the effective diffusivity ($D_e$) that must be used for all diffusional mass transport calculations. "The effective diffusivity accounts for the fact that not all of the area normal to the direction of the flux is available for the molecules to diffuse" (Folger, 1992).

Each of the aforementioned transport equations are solved simultaneously. To facilitate the solving of the transport equations, a one-dimensional vector equation (Equation 141) is used to link each of the transport equations.

$$\frac{\partial U}{\partial t} + \frac{\partial E}{\partial x} = 0$$  (141)

The vector $U$ is composed of each of the terms from the time derivative of each of the transport equations.
The vector $E$ is composed of the convective and diffusive terms of each of the transport equations:

$$E = \begin{bmatrix} \rho u \\ uC_{H_2} - D_e \frac{\partial}{\partial x} (C_{H_2}) \\ uC_{H_2O} - D_e \frac{\partial}{\partial x} (C_{H_2O}) \end{bmatrix}$$  \hspace{1cm} (143)$$

The vector equation is solved numerically using the explicit MacCormack scheme. The explicit MacCormack scheme is divided into a predictor step and a corrector step. The predictor step (Equation 144) is initially calculated at the initial time $n$.

$$U^n_{i+1} = U^n_i - \frac{\Delta t}{\Delta x} \left( E^n_{i+1} - E^n_i \right)$$  \hspace{1cm} (144)$$

The corrector step (Equation 145) is calculated at the intermediate time step.

$$U^{n+1}_{i} = \frac{1}{2} \left[ U^n_i + U^{n+1}_{i+1} - \frac{\Delta t}{\Delta x} \left( E^{n+1}_{i+1} - E^{n+1}_{i} \right) \right]$$  \hspace{1cm} (145)$$

As previously mentioned, the explicit MacCormack scheme was selected, because the explicit MacCormack scheme is second order accurate in both space and time.
Anode Catalyst Layer Model

The catalyst layer, as known as the fuel cell electrode, is merely a layer of immobilized platinum catalyst pellets evenly dispersed on a thin layer of carbon fiber, which is pressed between the gas diffusion layer and the polymer membrane (Barbir, 2005). There are three chemical species present with the anode catalyst layer: hydrogen gas, hydrogen ions, and water vapor. At the three-phase boundary; i.e. where the gas phase, the electrode and polymer membrane meet; the hydrogen gas is ionized in the presence of a platinum catalyst forming hydrogen ions (Barbir, 2005).

\[
\text{H}_2 \xrightarrow{\text{Pt}} 2\text{H}^+(\text{aq}) + 2e^- \tag{146}
\]

Although the water is diffusing along with the hydrogen gas, the water vapor is not believed to actively participate in the reaction. However, the literature is clear that hydration of the polymer membrane is critical to the membrane's ability to transport hydrogen ions (Natarajan & Van Nguyen, 2003).

Within the catalyst layer, the transport equations are again used to describe the dynamics of the system. The continuity equation is unchanged. Equation 147 is the continuity. Equation 148 shows the functional dependence of the hydrogen concentration and water concentration on the density.

\[
\varepsilon \frac{\partial p}{\partial t} + \frac{\partial (pu)}{\partial x} = 0 \tag{147}
\]
\[
\rho = M_{H_2} C_{H_2} + M_{H_2O} C_{H_2O}
\]  

(148)

Again, the filtration velocity is given by the Darcy Equation. However, because the hydrogen is being consumed at the catalyst, a consumption term \( S_{H_2} \) is added to the hydrogen species equation (Equation 149).

\[
\varepsilon \frac{\partial C_{H_2}}{\partial t} + \frac{\partial (u C_{H_2})}{\partial x} = \frac{\partial}{\partial x} \left( D_e \frac{\partial (C_{H_2})}{\partial x} \right) + S_{H_2}
\]  

(149)

\[
S_{H_2} = -\frac{i}{2F}
\]  

(150)

Within the consumption term, \( i \) is the current density and \( F \) is Faraday's constant. The number two (2) is the number of electrons, which are liberated during the reaction. Because the water vapor is not believed to participate actively in the reaction, the water species equation (Equation 151) is unchanged.

\[
\varepsilon \frac{\partial C_{H_2O}}{\partial t} + \frac{\partial (u C_{H_2O})}{\partial x} = \frac{\partial}{\partial x} \left( D_e \frac{\partial (C_{H_2O})}{\partial x} \right)
\]  

(151)

The transport equations are again solved simultaneously. For ease of computation, the following vector equation is used to solve the equations.

\[
\frac{\partial U}{\partial t} + \frac{\partial E}{\partial x} = H
\]  

(152)
Because the derivative terms are unaffected by the addition of the consumption term, the vectors $U$ and $E$ are unchanged.

$$U = \begin{bmatrix} \varepsilon p \\ \varepsilon C_{H_2} \\ \varepsilon C_{H_2O} \end{bmatrix} \quad (153)$$

$$E = \begin{bmatrix} \rho u \\ uC_{H_2} - D_e \frac{\partial}{\partial x} (C_{H_2}) \\ uC_{H_2O} - D_e \frac{\partial}{\partial x} (C_{H_2O}) \end{bmatrix} \quad (154)$$

However, because of the presence of the consumption source term in the hydrogen species equation, the vector $H$ is introduced.

$$H = \begin{bmatrix} 0 \\ i \\ \frac{i}{2F} \\ 0 \end{bmatrix} \quad (155)$$

The vector $H$ will be used hereafter for each of the source terms.

As was the case for the gas diffusion layer, the vector equation is solved using the explicit MacCormack scheme, which is again a two-step predictor-corrector method. Equation 156 is the predictor step.

$$U_{i}^{n+1} = U_{i}^{n} - \frac{\Delta t}{\Delta x} \left( E_{i+1}^{n} - E_{i}^{n} \right) + \Delta t \left( H_{i}^{n} \right) \quad (156)$$

Equation 157 is the corrector step.
Because hydrogen is consumed in the catalyst layer, the source vector H is introduced. Appendix A describes in detail the FORTRAN program, which was used to solve each of the mathematical models.

Membrane Model

The polymer membrane is the bridge between the anode and the cathode. The polymer membrane is a perfluorocarbon-sulfonic acid supported on a tetrafluorethylene (Teflon) polymer matrix (Barbir, 2005). There are two chemical species present with the membrane: hydrogen ions (H\(^+\)) and water. Hydrogen ions (H\(^+\)) are conducted from the anode to the cathode via the polymer membrane. It has been theorized that perfluorocarbon-sulfonic acid dissociates in the presence of water liberating an acidic hydrogen (Barbir, 2005). The dissociation of the perfluorocarbon-sulfonic acid allows the hydrogen ions produced at the anode to conduct across the polymer membrane (Barbir, 2005,).

The movement of water across the polymer membrane is equally as complicated as the transport of hydrogen ions. Water is also transported across the polymer membrane via three mechanisms: electro-osmotic drag, concentration gradients, and pressure gradients.

As is the case for the anode, the transport equations are used to describe the dynamics within the polymer membrane. The primary transport equations are

\[
U_{i}^{n+1} = \frac{1}{2} \left[ U_{i}^{n} + U_{i}^{n+1} - \frac{\Delta t}{\Delta x} \left( E_{i+1}^{n+1} - E_{i}^{n+1} \right) + \Delta t \left( H_{i}^{n+1} \right) \right] \tag{157}
\]
the continuity equation and the species equations. The 1-D continuity equation is given by the following equation:

\[
\varepsilon \frac{\partial \rho}{\partial t} + \frac{\partial (\rho u)}{\partial x} = 0 \tag{158}
\]

However, within the polymer membrane, the density (\(\rho\)) is a function of the membrane hydration only.

Hydrogen is present in its ionized state and water exists as liquid water. To account for the transport of these two species, the following species equations are used to describe the transport of hydrogen ions and water within the polymer membrane.

\[
\varepsilon \frac{\partial C_{H^+}}{\partial t} + \frac{\partial (u C_{H^+})}{\partial x} = \frac{\partial}{\partial x} \left( D_e \frac{\partial (C_{H^+})}{\partial x} \right) + S_{H_2} \tag{159}
\]

\[
\varepsilon \frac{\partial C_{H_2O}}{\partial t} = \frac{\partial}{\partial x} \left( D_e \frac{\partial (C_{H_2O})}{\partial x} \right) + S_{H_2O} \tag{160}
\]

A vector equation is used to solve the transport equations simultaneously.

\[
\frac{\partial U}{\partial t} + \frac{\partial E}{\partial x} = H \tag{161}
\]

The vectors \(U\), \(E\), and \(H\) are presented below:
Appendix A describes in detail the FORTRAN program, which was used to solve each of the mathematical models and how each of the sections of the fuel cell were linked computationally.

**Cathode Model**

Similar to the anode, the cathode is divided into three sections: the gas channel, the gas diffusion layer, and the catalyst layer. Oxygen gas is supplied to the cathode via the cathode gas channel. Oxygen gas diffuses from the gas channel through the gas diffusion layer to the platinum catalyst layer. As the oxygen gas reaches the catalyst, the oxygen gas combines electrochemically with hydrogen ions (H$^+$). This one-dimensional model will describe the
mathematical model used to simulate both the gas diffusion layer and the catalyst layer.

**Cathode Gas Diffusion Layer Model**

The cathode gas diffusion layer is an isotropic, homogeneous, and porous material. Generally, there are three chemical species present in the cathode gas diffusion layer: oxygen gas, nitrogen gas, and water. Oxygen gas (O₂) is supplied to the gas diffusion layer from the gas channel. Nitrogen is present if oxygen is supplied via ambient air. Unlike nitrogen and oxygen, water (H₂O) is present in two phases. However, this 1-D model assumes that water exists only in a supersaturated vapor phase (Springer, Zawodinski, & Gottesfeld, 1991). No reactions occur within the gas diffusion layer. Similar to the anode models, the dynamics of the cathode gas diffusion layer is described using the transport equations. The continuity equation (Equation 165) has a similar form as was previously presented for the anode and polymer membrane analyses.

\[ \varepsilon \frac{\partial \rho}{\partial t} + \frac{\partial (\rho u)}{\partial x} = 0 \]  

(165)

However, the definition of the density is changed. Unlike on the anode side, the density at the cathode is defined as the sum of the mass concentration of oxygen gas and water vapor.

\[ \rho = M_{O_2}C_{O_2} + M_{H_2O}C_{H_2O} \]  

(166)
The Darcy equation (Equation 167) is again used to calculate the filtration velocity.

\[
\frac{\partial P}{\partial x} = -\frac{\mu u}{K} \tag{167}
\]

The velocity \( u \) is the filtration velocity. There are two species equations: one for oxygen and one for water. Equation 168 is the oxygen species equation, and Equation 169 is the water species equation.

\[
\begin{align*}
\varepsilon \frac{\partial \phi_{O_2}}{\partial t} + \frac{\partial (u \phi_{O_2})}{\partial x} &= \frac{\partial}{\partial x} \left( D_e \frac{\partial (\phi_{O_2})}{\partial x} \right) \tag{168} \\
\varepsilon \frac{\partial \phi_{H_2O}}{\partial t} + \frac{\partial (u \phi_{H_2O})}{\partial x} &= \frac{\partial}{\partial x} \left( D_e \frac{\partial (\phi_{H_2O})}{\partial x} \right) \tag{169}
\end{align*}
\]

A vector equation (Equation 170) is used to link the transport equations into a compact form, which will be solved numerically.

\[
\frac{\partial U}{\partial t} + \frac{\partial E}{\partial x} = 0 \tag{170}
\]

Unlike in the anode, the \( U \) and \( E \) vectors are defined as follows:

\[
U = \begin{bmatrix}
\varepsilon \rho \\
\varepsilon \phi_{O_2} \\
\varepsilon \phi_{H_2O}
\end{bmatrix} \tag{171}
\]
The explicit MacCormack scheme is used to solve the computational domain.

**Cathode Catalyst Layer Model**

At the catalyst layer, the oxygen gas is combined electrochemically with hydrogen ions to form water.

\[
\text{O}_2 + 4\text{H}^+ + 4e^- \rightarrow 2\text{H}_2\text{O}
\]  

(173)

The water is generated by the cathode reaction. Although water is generated, the basic form of the continuity equation is unchanged.

\[
\frac{\partial (\rho \text{u})}{\partial t} - \frac{\partial (\rho \text{u}^2)}{\partial x} = 0
\]  

(174)

Similar to the cathode gas diffusion layer, the density (\(\rho\)) is given by the sum of the oxygen and water concentrations,

\[
\rho = \text{M}_{\text{O}_2} \text{C}_{\text{O}_2} + \text{M}_{\text{H}_2\text{O}} \text{C}_{\text{H}_2\text{O}}
\]  

(175)

In addition, the filtration velocity is given by the Darcy Equation. However, because the oxygen is being consumed at the catalyst, a consumption source
term \((S_{O_2})\) is added to the oxygen species equation. Equation 176 is the oxygen species equation.

\[
\frac{\varepsilon}{\partial t} \frac{\partial C_{O_2}}{\partial t} + \frac{\partial (uC_{O_2})}{\partial x} = \frac{\partial}{\partial x} \left( D_e \frac{\partial (C_{O_2})}{\partial x} \right) + S_{O_2} \tag{176}
\]

\[
S_{O_2} = -\frac{i}{4F} \tag{177}
\]

Within the consumption term, \(i\) is the current density and \(F\) is Faraday’s constant. The number four (4) is the number of electrons, which are consumed during the reaction. Because water is generated at the cathode catalyst, there is a generation source term added to the species equation. Equation 178 is the water species equation.

\[
\frac{\varepsilon}{\partial t} \frac{\partial C_{H_2O}}{\partial t} + \frac{\partial (uC_{H_2O})}{\partial x} = \frac{\partial}{\partial x} \left( D_e \frac{\partial (C_{H_2O})}{\partial x} \right) + S_{H_2O} \tag{178}
\]

\[
S_{H_2O} = \frac{2i}{4F} \tag{179}
\]

The two (2) in the generation source term is the stoichiometric coefficient, and the four (4) is the number of electrons consumed.

The aforementioned transport equations are again solved simultaneously. For ease of computation, the following vector equation (Equation 180) is used to solve the equations.
\[
\frac{\partial U}{\partial t} + \frac{\partial E}{\partial x} = H
\]  

(180)

The vectors U and E are unchanged compared to the vectors defined for the cathode gas diffusion layer.

\[
U = \begin{bmatrix}
\varepsilon \rho \\
\varepsilon C_{O_2} \\
\varepsilon C_{H_2O}
\end{bmatrix}
\]  

(181)

\[
E = \begin{bmatrix}
\rho u \\
u C_{O_2} - D_e \frac{\partial}{\partial x} (C_{O_2}) \\
u C_{H_2O} - D_e \frac{\partial}{\partial x} (C_{H_2O})
\end{bmatrix}
\]  

(182)

However, because of the presence of the oxygen consumption source term in the oxygen species equation and the water generation source term in the water species equation, the vector H has the following form:

\[
H = \begin{bmatrix}
0 \\
\frac{i}{4F} \\
2i \\
\frac{4F}{4F}
\end{bmatrix}
\]  

(183)

As was the case for the gas diffusion layer, the vector equation is solved using the explicit MacCormack scheme. Equation 184 is the predictor step equation, and Equation 185 is the corrector step equation.
Appendix A describes in detail the FORTRAN program, which was used to solve each of the mathematical models.

**Boundary and Initial Conditions**

The concentration of hydrogen at the gas channel-gas diffusion layer boundary is equal to the concentration of the hydrogen in the gas channel.

\[ C_{H_2}^{GC} = \frac{P_{GC}}{RT} \]  

(186)

At ambient temperature and pressure, hydrogen behaves like an ideal gas; therefore, ideal gas dynamics are assumed throughout the model. The temperature (T) is fixed at 80°C or 353 K, and the pressure is varied from 101,325 Pascals to 506,625 Pascals. The concentration of water in the gas channel is initially set to zero.

\[ \left. C_{H_2O} \right|_{GC} = 0 \]  

(187)

As shown in Equation 188, the flux of hydrogen across the anode gas channel (GC)-gas diffusion layer (GDL) interface is continuous.
\[ \text{D}_\text{H}_2 \left. \frac{\partial C_{\text{H}_2}}{\partial x} \right|_{\text{GC, Anode}} = \text{D}_\text{H}_2 \left. \frac{\partial C_{\text{H}_2}}{\partial x} \right|_{\text{GDL, Anode}} \] (188)

As shown in Equation 189, a similar boundary condition is specified for the flux of water at the anode gas channel (GC)-gas diffusion layer (GDL) interface.

\[ \text{D}_\text{H}_2 \left. \frac{\partial C_{\text{H}_2 \text{O}}}{\partial x} \right|_{\text{GC, Anode}} = \text{D}_\text{H}_2 \left. \frac{\partial C_{\text{H}_2 \text{O}}}{\partial x} \right|_{\text{GDL, Anode}} \] (189)

Initially, the concentrations of hydrogen and water within the anode are equal to the concentration of both species in the anode gas channel.

\[ C_{\text{H}_2} \big|_{t=0} = \frac{P_{\text{GC, Anode}}}{RT} \] (190)

\[ C_{\text{H}_2 \text{O}} \big|_{t=0} = \frac{P_{\text{GC, Anode}}}{RT} \] (191)

As shown in Equation 192, at the anode gas diffusion layer-catalyst layer boundary, the molar flux (N) of hydrogen gas (H\textsubscript{2}) is constant.

\[ N = \text{D}_e \left. \frac{d}{dx} \left( C_{\text{H}_2} \right) \right|_{\text{GDL}} = \text{D}_e \left. \frac{d}{dx} \left( C_{\text{H}_2} \right) \right|_{\text{CL}} \] (192)

At the catalyst layer-membrane boundary, the flux of hydrogen gas is constant. The effective diffusivity (De) of the gas diffusion layer and the catalyst layer is 1.1028 x 10\textsuperscript{-4} m\textsuperscript{2}/s (Ju & Wang, 2004). However, the effective diffusivity
(De) of hydrogen gas within the Nafion(R) membrane is $2.59 \times 10^{-10}$ m$^2$/s (Ju & Wang, 2004). The flux ($N$) is defined by Fick's Law of molecular diffusion. The concentration of hydrogen at the membrane-catalyst interface is predicted by assuming that the flux ($N$) of hydrogen at the catalyst layer-membrane interface is constant across the interface, as shown in Equation 193.

$$D_e \frac{d}{dx} \left( C_{H_2} \right)_{CL, Anode} = D_e \frac{d}{dx} \left( C_{H_2} \right)_{Membrane}$$

Equation 193

This boundary condition allows for the estimation of the concentration of hydrogen at the interface. The flux through the membrane is assumed constant, and the concentration of hydrogen gas at the cathode end of the membrane is assumed to be zero. The assumption is that any hydrogen gas that migrates across the membrane reacts immediately and completely with the oxygen present at the cathode catalyst layer-membrane interface. The concentrations of $O_2$ and $H_2O$ within the cathode side gas channel are:

$$C_{O_2} = \frac{P}{RT}$$

Equation 194

$$C_{H_2O} = 0$$

Equation 195

As shown in Equation 196 and Equation 197, at the cathode gas diffusion layer-catalyst layer boundary, the molar fluxes ($N$) of oxygen gas ($O_2$) and water vapor ($H_2O$) are constant.
Refer to Appendix A for the details of the computation.

**Quasi 2-D Model MICRO-PEM Fuel Cell Model**

Following the construction of the 1-D models, 2-D models of the system were constructed. Figure 9 is a schematic of the 2-D computational domain.

![2D Computational Model Schematic](image)

Figure 9: 2D Computational Model Schematic.

Initially, the flow domain is solved with the gas channel for both the anode and the cathode gas channels. These data from the gas channel are used as the
input to the gas diffusion layers, and are incorporated into the boundary conditions.

A two dimensional (2-D) model of a micro-PEM fuel cell was constructed. The model is divided into seven sections: the anode gas channel, the anode gas diffusion layer, the anode catalyst layer, the polymer membrane, the cathode catalyst layer, the cathode gas diffusion layer, and the cathode gas channel. The size of the gas channel was selected to ensure that the flow within the gas channel of both the anode and the cathode was characterized as slip flow.

Both the gas channel and the gas diffusion layer of the model are 50 microns in width. The catalyst layers are 5 microns in width and the membrane is 5 microns in width. Computational framework of each section is described hereafter. Table 3 lists the dimensions of each section of the fuel cell.

Table 3: Micro PEM Fuel Cell Model Dimensions

<table>
<thead>
<tr>
<th></th>
<th>Gas Channel (microns)</th>
<th>Gas Diffusion Layer (microns)</th>
<th>Catalyst Layer (microns)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anode</td>
<td>50</td>
<td>50</td>
<td>5</td>
</tr>
<tr>
<td>Cathode</td>
<td>50</td>
<td>50</td>
<td>5</td>
</tr>
</tbody>
</table>

Table 4 shows the mean free path for each of the reactants and the equivalent Knudsen number (Kn) for a gas channel with a width of 50 microns. The micro PEM fuel cell model was constructed with a set gas channel diameter of 50 microns for both the anode and the cathode. The Knudsen number (Kn) for
the anode is 0.002, and the Kn equals 0.001 for the cathode. Table 4 is a summary of the mean free paths for each of the reactant gases.

<table>
<thead>
<tr>
<th>Reactant</th>
<th>Mean Free Path (microns)</th>
<th>Kn</th>
<th>Gas Channel Width (microns)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen</td>
<td>0.11</td>
<td>0.0022</td>
<td>50</td>
</tr>
<tr>
<td>Oxygen</td>
<td>0.06</td>
<td>0.0012</td>
<td>50</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>0.06</td>
<td>0.0012</td>
<td>50</td>
</tr>
</tbody>
</table>

**Gas Channel Model**

The 2-D continuity equation (Equation 198), and the x and y momentum equations (Equation 199 and Equation 200) are used to describe the flow dynamics within the gas channel.

\[
\frac{\partial p}{\partial t} + \frac{\partial (pu)}{\partial x} + \frac{\partial (pv)}{\partial y} = 0
\]  
(198)

\[
\frac{\partial (pu)}{\partial t} + \frac{\partial (puu)}{\partial x} + \frac{\partial (puv)}{\partial y} = - \frac{dP}{dx} + \frac{\partial}{\partial x} (\tau_{xx}) + \frac{\partial}{\partial y} (\tau_{xy})
\]  
(199)

\[
\frac{\partial (pv)}{\partial t} + \frac{\partial (pvu)}{\partial x} + \frac{\partial (pvv)}{\partial y} = - \frac{dP}{dy} + \frac{\partial}{\partial y} (\tau_{yy}) + \frac{\partial}{\partial x} (\tau_{xy})
\]  
(200)
The Semi-Implicit Method for Pressure Linked Equations (SIMPLE) was used to calculate the pressure field and velocity fields of the flow. The details of the SIMPLE method are described in a separate section.

No reaction occurs within the anode gas channel; therefore, the fluids are assumed to be ideal gases. The model assumes that the mole fraction of hydrogen and water remains constant throughout the gas channel.

Differential Equation

After applying the aforementioned simplifying assumptions to the Navier-Stokes equations, the following differential equation results.

\[ \rho \bar{u} \frac{\partial v}{\partial x} = -\frac{\partial P}{\partial y} \quad (201) \]

Boundary Conditions

Within the slip flow regime, the empirical no-slip condition is not valid, and slip at the walls of the conduit must be considered when modeling the fluid behavior (Fang, 2003). For flows within the slip flow regime, a correction must be added to the Navier-Stokes equations to account for slip at the boundary (Nguyen, 2002; Karniadakis & Beskok, 2002; Fang, 2003; Xu & Ju, 2005).

\[ v_s - v_w = \frac{2 - \sigma_v}{\sigma_v} \frac{1}{\tau_s} \left( \frac{2RT_w}{\rho \left( \frac{2RT_w}{\pi} \right)^{1/2}} \right)^{1/2} \left( \frac{3 Pr(\gamma - 1)}{4 \gamma pRT_w} \right) (-q_s) \quad (202) \]
The flow through microfluidic systems tends to be slightly blunted. In addition, the flow through microfluidic systems is faster than the flow that would be predicted using macrofluidic theories (Koch, Evans, & Brunnschweiler, 2000). The tangential momentum accommodation coefficient ($\sigma_v$) is a function of the material of construction of the wall, the wall roughness, and the fluid. It is assumed that the tangential momentum accommodation coefficient ($\sigma_v$) is 0.87 for all calculations (Karniadakis & Beskok, 2002). The tangential heat flux ($q_s$) term is zero: the system is isothermal. Because the primary fluid species are oxygen and hydrogen at 80°C, one can safely assume that even within the slip flow regime that the fluids are Newtonian; therefore, the shear stress ($\tau_s$) is defined as a function of the viscosity and the shear rate.

$$\tau_s = \mu \frac{dv}{dx} \quad (203)$$

As previously mentioned, the $y$-direction is defined as the direction of flow within the gas channel. By solving the differential equation and employing the boundary condition, the following equation results for the velocity profile.

$$v(x) = \frac{2 - \sigma_v}{\sigma_v} \frac{1}{\rho \left( \frac{2RT_w}{\pi} \right)^{1/2}} \tau_s - \frac{1}{\rho \bar{u}} \Delta P x \quad (204)$$

Next, the average velocity is calculated by summing up all of the velocities over a cross section and then dividing by the cross-sectional area:
\[
\bar{v} = \frac{\int_0^D v(x)\,dx}{\int_0^D \,dx}
\]

Performing the integration and simplifying;

\[
\bar{v} = \frac{2 - \sigma_v}{\sigma_v} \frac{1}{\rho \left( \frac{2RT}{\pi} \right)^{1/2}} \tau_s^{\text{Wall}} - \frac{D}{2\rho u} \frac{\Delta P}{\Delta y}
\]

Solving the average velocity equation for the differential pressure, the following equation results:

\[
\frac{\Delta P}{\Delta y} = \frac{2\bar{u}}{D} \left[ \left( \frac{2 - \sigma_v}{\sigma_v} \right) \frac{1}{\rho \left( \frac{2RT}{\pi} \right)^{1/2}} \tau_s^{\text{Wall}} - \frac{\bar{v}}{\rho} \right]
\]

The flow through microfluidic systems tends to be slightly blunted. In addition, the flow through microfluidic systems is faster than the flow that would be predicted using macrofluidic theories (Koch, Evans, & Brunnschweiler, 2000). The tangential momentum accommodation coefficient (\(\sigma_v\)) is a function of the material of construction of the wall, the wall roughness, and the fluid. It is assumed that the tangential momentum accommodation coefficient (\(\sigma_v\)) is 0.87 for all calculations (Karniadakis & Beskok, 2002). Because the primary fluid species are oxygen and hydrogen at 80°C, one can safely assume that even
within the slip flow regime that the fluids are Newtonian. The shear stress \( \tau_s \) is the shear stress very near the wall. For the aforementioned reasons, the shear stress will be assumed to be constant. As previously mentioned, the y-direction is defined as the direction of flow within the gas channel.

In addition to velocity slip, the concentration of any species \( C_i \) may jump as the fluid approaches the wall of the conduit. This apparent jump in concentration is called concentration slip or diffusion slip (Sharipov & Kalempa, 2004). Although there are several models that currently predict velocity slip, there are relatively few papers that discuss concentration slip. These jumps in concentration can significantly affect the rate of mass transfer (Sharipov & Kalempa, 2004; Xu & Ju, 2005). Xu and Ju (Xu & Ju, 2005) have proposed the following form of the concentration slip boundary conditions (Xu & Ju, 2005):

\[
(\rho Y_i)_w = \sqrt{\frac{\tau_s}{\tau_W}} \left[ (\rho Y_i)_{slip} - \frac{4}{3} \lambda \left( \frac{\partial (\rho Y_i)}{\partial y} \right)_{slip} \right]
\]  

\( Y_i \) is the mass fraction of the component \( i \) (Xu & Ju, 2005). Since the system is isothermal, the aforementioned concentration slip equation becomes a simple function of the characteristic length and the Knudsen number, as given by the following equation (Xu & Ju, 2005):

\[
\frac{(Y_i)_w}{(Y_i)_{slip}} = \left( \frac{y + \frac{4}{3} \text{Kn}}{L} \right) \left( \frac{1 + \frac{8}{3} \text{Kn}}{1 + \frac{8}{3} \text{Kn}} \right)
\]
Using the aforementioned equations for the concentration at the wall, the boundary conditions for hydrogen and water at the gas channel-gas diffusion layer boundary are calculated using the following equations:

\[
C_{\text{H}_2}|_{\text{GC-GDL}} = \left[ \left( \rho Y_{\text{H}_2} \right)_{\text{slip}} - \frac{4}{3} \lambda \left( \frac{\partial (\rho Y_{\text{H}_2})}{\partial x} \right)_{\text{slip}} \right] 
\]  
(210)

\[
C_{\text{H}_2\text{O}}|_{\text{GC-GDL}} = \left[ \left( \rho Y_{\text{H}_2\text{O}} \right)_{\text{slip}} - \frac{4}{3} \lambda \left( \frac{\partial (\rho Y_{\text{H}_2\text{O}})}{\partial x} \right)_{\text{slip}} \right] 
\]  
(211)

For purposes of this simulation, the porous wall is the PEM fuel cell gas channel-gas diffusion layer interface.

This boundary condition allows for the estimation of the concentration of the hydrogen concentration at the interface. The flux throughout the membrane is assumed to be constant, and the concentration of hydrogen at the cathode-membrane interface is zero.

The concentration of oxygen and water vapor in the cathode channel are a function of the mole fraction \((y)\) of the chemical species. Equation 212 and Equation 213 are the oxygen and water concentration slip equations.

\[
C_{\text{O}_2}|_{\text{GC}} = \left[ \left( \rho Y_{\text{O}_2} \right)_{\text{slip}} - \frac{4}{3} \lambda \left( \frac{\partial (\rho Y_{\text{O}_2})}{\partial x} \right)_{\text{slip}} \right] 
\]  
(212)
The flux of oxygen across the cathode gas channel (GC)-gas diffusion layer (GDL) interface is continuous, as given by the following equation:

\[
C_{H_2O}^{|_{GC}} = \left( \rho Y_{H_2O} \right)_{\text{slip}} - \frac{4}{3} \lambda \left( \frac{\partial (\rho Y_{H_2O})}{\partial x} \right)_{\text{slip}}
\]  

(213)

A similar boundary condition is specified for the flux of water at the cathode gas channel (GC)-gas diffusion layer (GDL) interface, as given by the following equation:

\[
D_{e,O_2} \left. \frac{\partial C_{O_2}}{\partial x} \right|_{GC} = D_{e,O_2} \left. \frac{\partial C_{O_2}}{\partial x} \right|_{GDL}
\]

(214)

Semi-Implicit Method for Pressure Linked Equations (SIMPLE)

In conjunction with the explicit MacCormack scheme, the Semi-Implicit Method for Pressure Linked Equations (SIMPLE) was used to resolve the flow domain in the quasi 2-D cases. SIMPLE is a computational method, which uses a guess to solve the momentum equations, called a pressure correction or segregated approach (Tannehill, Anderson, & Pletcher, 1997). This iterative method is used to solve the flow domain. An estimate for the pressure is used to solve the velocity domain. Then the velocities are inputted into the continuity
equation. When the velocities satisfy the continuity equation, the method is said to have converged. The guessed pressured \( p_0 \) is used to solve the momentum equations for the velocities. Equation 216 is the equation for the actual pressure.

\[
p = p_0 + \alpha p'
\]  

(216)

The variable \( p' \) is the pressure correction and \( p \) is defined as the actual pressure. For the initial guess, the \( p' \) is set to zero. The coefficient \( \alpha \) is the under relaxation coefficient. The coefficient \( \alpha \) was set at 0.8. Equation 217 and Equation 218 are the equations for the \( u \) and \( v \) velocities, respectively.

\[
u = u_0 + u'
\]  

(217)

\[
v = v_0 + v'
\]  

(218)

The variable \( u' \) and \( v' \) are the velocity correction factors and \( u \) and \( v \) are the true velocities. For the initial guess, the \( u' \) and \( v' \) are set to zero.

Patankar and Spalding cautioned that a staggered grid (as cited by Tannehill, 1997). Tannehill explains that use of nonstaggered grids can potential result in decoupling of the velocity and the pressure domains. This decoupling may cause wiggling in the velocity domain (Tannehill et al., 1997). After the velocities have been calculated using the guessed pressure, the pressure-correction equation is solved using the following Poisson's equation (Equation 219):
The Gauss-Siedel Method is used to solve the pressure-correction equation.

\[ \nabla^2 p' = \frac{1}{Z} (\nabla \cdot \vec{v}_0) \]  

(219)

\[ Z = \frac{\Delta t}{\rho} \]  

(220)

The Gauss-Siedel Method is used to solve the pressure-correction equation.

\[ \frac{1}{h^2} \left( p'_{i+1,j} + p'_{i-1,j} + p'_{i,j+1} + p'_{i,j-1} - 4p'_{ij} \right) = \frac{1}{2zh} \left( u_{i+1,j} - u_{i-1,j} + v_{i,j+1} - v_{i,j-1} \right) \]  

(221)

The Jacobi Method may be used in lieu of the Gauss-Siedel method; however, the convergence is much improved if the Gauss-Siedel method for solving Poisson's equation is used. The discretized form of the pressure-correction equation is put into the following form:

\[ \frac{1}{h^2} \left( p'_{i+1,j} + p'_{i-1,j} - 4p'_{ij} \right) = \frac{1}{2zh} \left( u_{i+1,j} - u_{i-1,j} + v_{i,j+1} - v_{i,j-1} \right) + \frac{1}{h^2} \left( p'_{i,j+1} + p'_{i,j-1} \right) \]  

(222)

\[ h = \Delta x = \Delta y \]  

(223)

SIMPLE requires the use a staggered grid. Specifically, the velocity components are not collocated at the same grid point. When a uniform grid is used, the location of the velocity components is located at the midway point between the grid points (Jaluria & Torrance, 2003). The aforementioned form is appropriate, because it is assumed that \( p'_{ij+1} \) and \( p'_{ij-1} \) are known. \( p'_{ij-1} \) comes from the boundary conditions or the last sweep at the \( k-1 \) time step. \( p'_{ij+1} \) is
assumed to be known at the k time step. k is the current time step. The equation results in a tridiagonal matrix and is solved using the Thomas Algorithm (Tannehill et al., 1997).

The aforementioned Poisson's equation (Equation 224) can be written in vector form.

\[ Ax = b \]  \hspace{1cm} (224)

Where appropriate, the computational model takes advantage of the reduced computational time associated with performing the LU decomposition. In the aforementioned Poisson's equation, the A matrix is a coefficient matrix and the vector x is the vector containing the unknown pressure variables. The vector b is the known information from the boundary conditions. Any matrix A can be decomposed into two matrices, such that one of the matrices is a lower triangular matrix (L) and the other is an upper triangular matrix (U), as follows.

\[ A = LU \]  \hspace{1cm} (225)

Assuming that the matrix A is a square matrix with the following form, the procedure described below can be used to decompose the matrix into an upper matrix (U) and a lower matrix (L).
The lower matrix is generated first by using a dummy variable y.

\[ y_1 = b_1 \tag{229} \]

\[ y_i = b_i - L_i y_{i-1} \tag{230} \]

\[ U_n x_n = y_n \tag{231} \]

\[ U_i x_i = y_i - B_i x_{i+1} \tag{232} \]
The reader is cautioned to remember that a matrix, whose determinant equals zero, has no inverse.

LU decomposition is a matrix decomposition, which writes a matrix as the product of a lower and upper triangular matrix. The product sometimes includes a permutation matrix as well. This decomposition is used in numerical analysis to solve systems of linear equations or find the inverse of a matrix. The benefit of the LU decomposition technique is that the LU decomposition reduces the computational resources required to invert the matrix $A$.

After the pressure correction is calculated, the next guess for the velocity domain is calculated using the initial velocity guess calculated from the momentum equation and the pressure correction calculated from the pressure-correction equation, as given by the following equations (Equation 235 & Equation 236):

$$u = u_0 - \frac{\Delta t}{2\rho\Delta x} \left( p'_{i+1,j} - p'_{i,j} \right)$$  

(235)

$$U_{n-1}x_{n-1} - B_{n-1}x_n = y_{n-1}$$  

(234)
\[ v = v_o - \frac{\Delta t}{2\rho \Delta x} \left( p_{i,j+1}^* - p_{i,j}^* \right) \] (236)

The entire method is repeated until the continuity equation is satisfied and the system of equations converges. For a full derivation of the SIMPLE method, the reader should refer to Patankar (1980). The follow method steps are used through the calculation:

1. Guess the pressure \((p^n)\) and velocity domains.

2. Solve the momentum equation for velocity.

3. Solve the Poisson's Equation (Equation 237) for the pressure correction \((p')\).

\[ \nabla^2 p' = \frac{1}{\Delta t} \left( \nabla \cdot \vec{V} \right) \] (237)

4. Calculate the new value for the pressure \((p^{n+1})\). Under relaxation is used to stabilize the simulation. The under relaxation coefficient \((\alpha)\) was set to 0.8.

\[ p^{n+1} = p^n + \alpha p' \] (238)

5. Use the calculated velocity and new value for the pressure to calculate the new values for the velocity.

6. Check for convergence.

7. If converged, stop. Otherwise, repeat starting at step 2.
A staggered velocity grid is used to prevent the occurrence of artificial oscillations in the velocity field. Collocated grids are known to cause artificial velocity oscillation in the flow domain (Patankar, 1980). Figure 10 shows the staggered grid that was used to solve the pressure and velocity domains with the gas channel.

Figure 10: Staggered Grid of Gas Channel.

The pressure is specified at the boundaries perpendicular to the direction of flow. The computational structure presented in Matyka (2003) was used as a starting point to solve the flow domain; however, the reader is cautioned that several of the equations presented in Matyka (2003) were corrected prior to
finishing the computation. The following equations represent the corrected equations; therefore, the equations will not exactly match the equations presented in Matyka (2003). Although not shown, the pressure will be specified at each grid point where the physical boundary changes direction. There is a velocity component between each pressure node to maintain the staggered velocity grid. The discretization scheme is presented below (Matyka, 2003):

\[
\begin{align*}
    u^{n+1}_{i+0.5,j} &= u^n_{i+0.5,j} + \Delta t \left( A - \left( \frac{1}{\rho} \right) \left( \frac{p_{i+1,j} - p_{i,j}}{\Delta x} \right) \right) \\
    v^{n+1}_{i,j+0.5} &= v^n_{i,j+0.5} + \Delta t \left( B - \left( \frac{1}{\rho} \right) \left( \frac{p_{i,j+1} - p_{i,j}}{\Delta x} \right) \right)
\end{align*}
\]  

(239)  

(240)

The reader is cautioned that \( A \) and \( B \) as defined in this text differ from what is presented in Matyka (2003). Matyka (2003) inserted negative signs in front of the terms \( a_1 \) and \( b_1 \). These signs were removed from the above equations. The terms \( A \) and \( B \) are defined below (Matyka, 2003):

\[
A = a_1 + (a_2 + a_3) \left( \frac{\mu}{\rho} \right) 
\]

(241)

\[
B = b_1 + (b_2 + b_3) \left( \frac{\mu}{\rho} \right) 
\]

(242)

\[
a_1 = -\Delta u^2 - \frac{(u\dot{v})^n_{i+0.5,j+1} - (u\dot{v})^n_{i+0.5,j-1}}{2\Delta y} 
\]

(243)
The clotted velocity components are defined below (Matyka, 2003):

\[
\Delta u^2 = \frac{\left( u^2 \right)_{i+1.5,j} - \left( u^2 \right)_{i-0.5,j}}{2\Delta x} \quad (244)
\]

\[
b_1 = -\Delta v^2 = \frac{\left( v^2 \right)_{i+1,j+0.5} - \left( v^2 \right)_{i-1,j+0.5}}{2\Delta x} \quad (245)
\]

\[
\Delta v^2 = \frac{\left( v^2 \right)_{i,j+1.5} - \left( v^2 \right)_{i,j-0.5}}{2\Delta y} \quad (246)
\]

\[
a_2 = \frac{(u)_{i+1.5,j}^{n} - 2(u)_{i+0.5,j}^{n} + (u)_{i-0.5,j}^{n}}{(\Delta x)^2} \quad (247)
\]

\[
a_3 = \frac{(u)_{i+0.5,j+1}^{n} - 2(u)_{i+0.5,j}^{n} + (u)_{i+0.5,j-1}^{n}}{(\Delta y)^2} \quad (248)
\]

\[
b_2 = \frac{(v)_{i,j+1.5}^{n} - 2(v)_{i,j+0.5}^{n} + (v)_{i,j-0.5}^{n}}{(\Delta y)^2} \quad (249)
\]

\[
b_3 = \frac{(v)_{i+1,j+0.5}^{n} - 2(v)_{i,j+0.5}^{n} + (v)_{i-1,j+0.5}^{n}}{(\Delta x)^2} \quad (250)
\]

\[\dot{u} = \frac{1}{2}(u_{i-0.5,j}^{n} - u_{i-0.5,j+1}^{n}) \quad (251)\]

\[\ddot{u} = \frac{1}{2}(u_{i+0.5,j}^{n} - u_{i+0.5,j+1}^{n}) \quad (252)\]
\[
\dot{v} = \frac{1}{2}(v_{i,j+0.5}^n - v_{i+1,j+0.5}^n)
\] (253)

\[
\dot{v} = \frac{1}{2}(v_{i,j-0.5}^n - v_{i+1,j-0.5}^n)
\] (254)

Poisson's equation is solved numerically using the following five-point pressure scheme (Matyka, 2003).

\[
p_{i,j}' = -\frac{b_4}{a_4} (p_{i+1,j} + p_{i-1,j}) + c_4 (p_{i,j+1} + p_{i,j-1}) + d_4
\] (255)

\[
a_4 = 2\Delta t \left[ \frac{1}{\Delta x^2} + \frac{1}{\Delta y^2} \right]
\] (256)

\[
b_4 = -\frac{\Delta t}{\Delta x^2}
\] (257)

\[
c_4 = -\frac{\Delta t}{\Delta y^2}
\] (258)

\[
d_4 = \frac{1}{\Delta x} (u_{i+0.5,j} - u_{i-0.5,j}) + \frac{1}{\Delta y} (v_{i,j+0.5} - v_{i,j-0.5})
\] (259)

Use the aforementioned iterative process for the SIMPLE algorithm until the pressure domain solves the continuity equation. The aforementioned SIMPLE algorithm was developed and validated against known flow distributions to verify the veracity of the computation. In addition, under relaxation of the pressure and
velocity components was used to stabilize the model. The under relaxation coefficient is 0.8.
CHAPTER VI

RESULTS AND DISCUSSION

Because of the growing popularity of micro-electro mechanical systems (MEMS), engineers and scientists have sought new tools to explain the dynamics within micro-scale systems. As discussed in Chapter III, micro-scale processes are not completely described by continuum mechanics. Specifically, as the characteristic length of the conduit approaches the mean free path of the fluid, traditional continuum mechanics assumptions fail to describe completely the characteristics of the flow. For example, the experimentally determined no-slip velocity boundary condition, which is appropriate in many macro-scale systems, cannot be assumed in micro-scale flows.

To bridge this gap, new parameters were needed. The Knudsen number (Kn), a parameter borrowed from rarefied gas theories, bridges the gap between continuum and non-continuum mechanics. Specifically, the Knudsen number can be used to predict, when continuum mechanics assumptions weaken, and where other dynamics equations and boundary conditions must be used to correct for non-continuum behavior.

This research improves upon prior models by incorporating the modeling of the slip phenomenon at the solid surfaces of the fuel cell. This enhanced
model will more accurately simulate the fuel cell’s performance and will be used to improve fuel cell design and to improve fuel cell performance.

The objective of this research is to develop a 2-D computational model of a micro-scale Polymer Exchange Membrane (PEM) fuel cell. This research was limited to flow within the slip flow regime, i.e. Knudsen numbers less than $10^{-1}$.

1-D Computational Model

Initially, 1-D computational models were constructed. Both the anode and cathode were modeled, and the data from these models were used to construct the 2-D models. One dimensional (1-D) models were constructed, which calculated the concentration of reactant at different gas channel pressures. Both the anode and cathode were modeled. Figure 11 through Figure 18 show the data collected for the 1-D cases at a variety of pressures and current densities.

Figure 11 is a graph of the hydrogen concentration at the anode for a gas channel pressure of 1 bar. The data show that the concentration is linear within the gas diffusion layer. However, within the catalyst layer, because of the reaction that is occurring, the graph is not linear. More importantly, the concentration at the catalyst layer-membrane layer is not zero. The data clearly show that the concentration at the catalyst layer-membrane layer interface for different current densities is not zero.

Figure 12 is a graph of the oxygen concentration at the cathode at a pressure of 1 bar. Similar to the anode, the graph is linear within the gas diffusion layer. However, the graph is non-linear within the catalyst layer.
Figure 11: Anode Hydrogen Concentration (System Pressure = 1 bar).

Figure 12: Cathode Oxygen Concentration (System Pressure = 1 bar).
The non-linearity is due to the consumption of oxygen within the catalyst layer within the cathode. Again, the concentration at the membrane-layer catalyst layer interface at the cathode is not zero.

Figure 13 is a graph of the hydrogen concentration at the anode for a gas channel pressure of 2 bar. Similar to the data for the 1 bar case, the data show that the concentration is linear within the gas diffusion layer. However, within the catalyst layer, because of the reaction that is occurring the graph is not linear. In prior models, the concentration at the catalyst layer-member layer was assumed to be zero; however, the model shows that the concentration at the catalyst layer-membrane layer interface is not zero. The percentage change in concentration in the 2 bar case is approximately half of the percentage change in concentration in the 1 bar case.

Figure 14 is a graph of the oxygen concentration at the cathode at a pressure of 2 bar. Similar to the anode, the graph is linear within the gas diffusion layer. However, the graph is non-linear within the catalyst layer. Similar to the anode case, the percentage in oxygen concentration at the cathode for the 2 bar case is approximately half of the percentage change in oxygen concentration in the 1 bar case. The percentage change in concentration was calculated at the membrane layer-catalyst layer interface.
Figure 13: Anode Hydrogen Concentration (System Pressure = 2 bar).

Figure 14: Cathode Oxygen Concentration (System Pressure = 2 bar).
Figure 15 is a graph of the hydrogen concentration at the anode for a gas channel pressure of 4 bar. Again, the data show that the hydrogen concentration is linear within the gas diffusion layer. The hydrogen concentration is linear within the gas diffusion layer, because no reactions are occurring within the gas diffusion layer, so the concentration is expected to decrease with a constant slope. However, within the catalyst layer, because of the reaction that is occurring, the graph is not linear. Again, the concentration at the catalyst layer-membrane layer is not zero.

![Anode Hydrogen Concentration Graph](image)

Figure 15: Anode Hydrogen Concentration (System Pressure = 4 bar)

Figure 16 is a graph of the oxygen concentration at the cathode at a pressure of 4 bar. Similar to the anode, the graph is linear within the gas diffusion layer, and the graph is non-linear within the catalyst layer. Similar to the anode,
the percentage change in concentration in the 4 bar case is much less than the percentage in the 1 bar case, because the flux of oxygen for a given current density is constant. In each of the models, pressure is used as a surrogate for concentration, so, as the pressure is increased, the change in concentration is reduce. Again, the concentration at the catalyst layer-membrane layer interface is used to calculate the relative change in concentration.

Figure 17 is a graph of the hydrogen concentration at the anode for the 5 bar case. Similar to the other cases, the concentration curve within the gas diffusion layer is linear. However, within the catalyst layer, the concentration of hydrogen curve is not linear. Again, the flux of hydrogen for a given current density is constant, so the percentage change in concentration relative to simulations with lower gas channel pressures is reduced.

![Graph showing the concentration of oxygen at the cathode](image)

Figure 16: Cathode Oxygen Concentration (System Pressure = 4 bar).
Figure 17: Anode Hydrogen Concentration (System Pressure = 5 bar).

Figure 18 is a graph of the oxygen concentration at the cathode at a pressure of 5 bar. Similar to prior simulations, the graph is linear within the gas diffusion layer, and the graph is non-linear within the catalyst layer.

The prevailing hypothesis is that the hydrogen and oxygen concentrations at the catalyst layer-membrane layer interfaces are zero. However, the data presented in Figure 11 through Figure 18 showed that the bulk concentration of reactant at the catalyst layer-membrane layer interface is not zero. The aforementioned assumption ignores the fact that the reaction in PEM fuel cells occurs at the surface of the catalyst, and not in the bulk. The bulk concentration is defined as the concentration of reactant outside of the diffusion layer.
Figure 18: Cathode Oxygen Concentration (System Pressure = 5 bar).

When the model was initially constructed, a zero Dirichlet boundary condition for the concentration at the membrane-catalyst interface was used. However, the models with these Dirichlet boundary conditions gave unrealistic results. Table 5 shows the resulting current density given a zero Dirichlet boundary condition at the catalyst layer-membrane layer interface.

Table 5: Current Density Calculation Assuming Zero Interface Concentration

<table>
<thead>
<tr>
<th>Diffusivity (m²/s)</th>
<th>Inlet Concentration (moles/m³)</th>
<th>Interface Concentration (moles/m³)</th>
<th>Flux (moles/(m²-s))</th>
<th>Current Density (A/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00011</td>
<td>34.5102</td>
<td>0</td>
<td>76.1157</td>
<td>1468.8042</td>
</tr>
</tbody>
</table>
If the pressure within the gas channel is 101,325 Pascals, then the concentration at the gas channel-gas diffusion layer is 34.51 moles/m$^3$ of hydrogen. The diffusivity of hydrogen within the gas diffusion layer and catalyst layer is approximately $1.1028 \times 10^{-4}$ m$^2$/s (Ju & Wang, 2004). Using the aforementioned concentration data and the diffusivity cited in Ju & Wang (2004), the current density would be approximately 1468.8 A/cm$^2$, if the concentration at the interface were zero. Therefore, something else must be occurring. The something else is localized starvation of the active sites.

The results suggest that the reactant deficit experienced at high current densities is localized to the catalyst surface. Barbir (2005) refers to the catalyst surface as the active site (Barbir, 2005). The active site is where the reaction actually occurs. When the current density reaches the limiting current density, the active site is being starved of reactant. Specifically, reactant is supplied at the same rate at which the reactant is consumed. There is a mass transfer resistance, which is established around the active site, and, as the current density increase, the rate of mass transfer to the active site is insufficient to maintain the forward reaction.

This treatment attempts to explain that localized starvation of the active sites is the cause of the sudden drop in the voltage at the limiting current density. More specifically, a resistance is established around the active site and the time constant required for the migration of reactant to the active site is much less than the time constant associated with the reaction at the active site at higher current densities. Forment & Bischoff (1990) and Fogler (1992) discuss the
phenomenon of surface catalysis. The consumption of reactants (hydrogen or oxygen) at the catalyst active site interface, i.e. on the surface of the catalyst, has to be compensated for by transport from the bulk fluid (Forment & Bischoff, 1990).

The reaction occurs on the surface of the catalyst. Prior to reaching the limiting current density, the mass transfer step is much faster than the surface reaction; thus, the reactant concentration \( (C_A) \) at the surface is the same as the concentration \( (C_A) \) measured in the bulk. However, when the current density exceeds the limiting current density, the rate of mass transfer through the mass transfer diffusion layer surrounding the active site is much slower than the rate of reaction. Equation 260 is used to describe the flux of reactant \( (N_A) \) across the mass transfer diffusion layer.

\[
N_A = k_g (C_A - C_{Ai})
\]  
(260)

At the limiting current density, the rate of mass transfer equals the rate of reaction. The aforementioned equation relates the flux of species A \( (N_A) \) to the mass transfer coefficient \( (k_g) \) and the concentration \( (C_A) \) of species A within the bulk minus the concentration \( (C_{Ai}) \) of species A at the catalyst surface.

Therefore, the reactant gases cannot be supplied fast enough to allow the reaction to proceed at or above the limiting current density (Forment & Bischoff, 1990). At limiting current density, there is a localized reactant deficit around the active site, and the current density is prohibited from exceeding the limiting
current density, because the reactants cannot be supplied to the active site quickly enough (Barbir, 2005). Therefore, increasing catalyst dispersion and/or increasing catalyst surface within the catalyst layer might increase the limiting current density by a finite amount in micro PEM fuel cells.

Although the concentration is not zero at the membrane-catalyst layer interface, the current density is not allowed to increase without bound. One reason for the limitation on the current density is the balance between reaction kinetics and mass transport. The current density is not allowed to increase without bound, because of local kinetic and mass transport limitations. The dissociation of hydrogen gas into hydrogen ions and two electrons only occurs at specific active sites at the surface of the catalyst. Although the anode and cathode are typically depicted with defined layers, the reality is that both are a web of small channels, similar to capillaries. The gas channel is integrated within the gas diffusion layer, and the gas diffusion layer directs the reactant gases toward active sites.

Specifically, the reactant gases diffuse through the catalyst diffusion layer surrounding the catalyst at the same rate as the reactant gases are being consumed. When the flux of reactant gases equals the rate of reaction at the catalyst surface, the current density cannot increase. This is the limiting current density.

These active sites are special. In order for the forward reaction to occur, the reactant gas must be in contact with the platinum catalyst and the platinum catalyst must be in contact with the membrane (Barbir, 2005). It is this triple
point, which is essential. When the active sites are saturated, the current density cannot increase. The point of saturation of the active sites is the limiting current density. At the limiting current density, neither the bulk oxygen concentration nor the bulk hydrogen concentration is zero at the catalyst layer-membrane interface. The term bulk concentration means the concentration of reactant outside of the mass transfer boundary layer. The bulk concentration of reactants does not go to zero at the limiting current density.

Although the concentration change is small, the entire width of the system is 215 microns, and the catalyst layer is 5 microns thick. Once one acknowledges that the size of the model influences the residence time within the catalyst layer and, therefore, the concentration gradient, one is less concerned about this small change in concentration. The concentration gradient is not insignificant in these models, because of the size of the model.

The current is limited, because there are no free active sites. The inference from these data is that if the number of active sites can be increased then the limiting current density could be increased. However, because of the impact of size on voltage losses, as the number of active sites is increased the voltage losses will increase proportionally.

There are other reasons for the limitation on the current density. Specifically, the other losses associated with the system dynamics. The polarization curve (Figure 19) for the 1-D PEM fuel cell case is presented below for various pressures within the anode and cathode gas channels.
The fuel cell reaction occurs on the surface of the catalyst. Prior to reaching the limiting current density, the mass transfer step is much faster than the surface reaction. As long as the current density is greater than the limiting current density, the surface concentration will be something greater than zero. This treatment attempts to predict the concentration at the surface of the catalyst by using the bulk concentration and the boundary conditions.

At low current densities, the concentration will be very close to the bulk concentration of reactant; however, when the current density exceeds the limiting current density, the rate of mass transfer through the mass transfer diffusion layer surrounding the active site is much slower than the rate of reaction.

Figure 19: Polarization Curve PEM Fuel Cell (Membrane Thickness = 5 microns).
For this reason at the limiting current density, the reaction is prevented from exceeding the limiting current density. As shown in Equation 261, the flux \( N \) of reactant is a function of the current density.

\[
N_{H_2} = \frac{i}{nF} = j \tag{261}
\]

The flux of reactant across the diffusion layer is a function of the concentration difference between the bulk concentration \( (C_{H_2, \text{Bulk}}) \) and the catalyst surface concentration \( (C_{H_2, \text{Surface}}) \).

\[
N_{H_2} = k_g (C_{H_2, \text{Bulk}} - C_{H_2, \text{Surface}}) \tag{262}
\]

In heterogeneous catalysis, the reaction does not occur within the bulk; rather the reaction occurs at the surface of the catalyst, so it is the catalyst surface concentration that is important, not the bulk concentration. Equation 263 relates the mass flux to the source term.

\[
k_g (C_{H_2, \text{Bulk}} - C_{H_2, \text{Surface}}) = \frac{i}{nF} \tag{263}
\]

Equation 263 is rearranged to get the following functional relationship between the mass transfer coefficient \( (k_g) \) and the concentration in the bulk and at the surface as shown in Equation 264.

\[
k_g = \frac{i}{nF} \times \frac{1}{(C_{H_2, \text{Bulk}} - C_{H_2, \text{Surface}})} \tag{264}
\]
This model assumes that at the limiting current density ($i_L$) that the concentration of reactant at the catalyst surface is zero. The bulk concentration in this model is the average bulk concentration. Equation 265 shows the functional relationship between the limiting current density ($i_L$) and the mass transfer coefficient ($k_g$).

$$k_g(C_{H_2,Bulk}) = \frac{i_L}{nF} \tag{265}$$

Although the concentration at the catalyst surface for a PEM fuel cell has not been measured, the concentration must be zero. If the concentration were greater than zero, the system would be able to exceed the limiting current density.

This model uses two important boundary conditions. First, the catalyst surface concentration at $i = 0$ A/cm$^2$ is assumed to be the bulk concentration. Second, the surface concentration at the limiting current density is assumed to be zero. Although no studies document the surface concentration, if the concentration at the surface of the catalyst were greater than zero, then the system would not be limited. Using the value for the mass transfer coefficient calculated for the limiting current density case, the other surface concentrations were calculated. Figure 20 through Figure 27 show the predicted concentrations within the bulk and the predicted surface concentrations of reactant for several pressures. The concentrations are the concentrations at the catalyst layer-membrane layer interface.
Figure 20 is a graph of the concentration of hydrogen within the anode at the catalyst layer-membrane layer interface in the bulk and at the catalyst surface. The concentration of hydrogen within the bulk is the concentration from the 1 bar case simulation. The concentration at the surface of the catalyst is the concentration that was calculated using the derived mass transfer coefficients. The graph shows that the concentration of hydrogen within the bulk changes very little. However, the concentration at the catalyst surface changes significantly. At the limiting current density, the concentration at the surface of the catalyst is zero.

![Figure 20: Current Density vs. Anode Hydrogen Concentration at Catalyst Layer-Membrane Layer Interface (Pressure = 1 bar).](image)

Figure 21 is another graph of the hydrogen concentration within the bulk in the 1 bar case. This graph is presented to show that the concentration within the bulk is change. Figure 20 would give one the impression that the concentration
of hydrogen within the bulk is not change; however, Figure 21 clearly shows that the concentration of hydrogen is not constant.

Figure 22 is a graph of the concentration of hydrogen within the anode at the catalyst layer-membrane layer interface in the bulk and at the catalyst surface. The concentration of hydrogen within the bulk is the concentration from the 2 bar case simulation. The concentration at the surface of the catalyst is the concentration that was calculated using the derived mass transfer coefficients.

![Graph showing current density vs. anode hydrogen bulk concentration at the catalyst layer-membrane layer interface.](image)

Figure 21: Current Density vs. Anode Hydrogen Bulk Concentration at the Catalyst Layer-Membrane Layer Interface (Pressure = 1 bar).

Similar to the 1 bar simulation, the graph shows that the concentration of hydrogen within the bulk changes very little. As was described previously, as the concentration within the gas channel increases, the percentage change in concentration in the bulk of hydrogen is reduced. Again, the concentration at the
catalyst surface is predicted to change significantly. At the limiting current density, the concentration at the surface of the catalyst is zero.

Figure 23 is another graph of the hydrogen concentration within the bulk in the 2 bar simulation. Again, this graph is presented to show that the concentration within the bulk is change within increasing current density.
Figure 24 shows the hydrogen layer concentration within the bulk and the calculated concentration at the catalyst surface. Both concentrations are the concentrations at catalyst-layer membrane layer. Figure 24 is the 4 bar simulation.

Figure 25 is another graph of the hydrogen concentration within the bulk in the 4 bar simulation. Again, this graph is presented to show that the concentration within the bulk is change within increasing current density. Figure 26 shows that the concentration of hydrogen within the bulk at the catalyst layer-membrane layer are quadratic.

![Graph of Hydrogen Concentration](image)

Figure 24: Current Density vs. Anode Hydrogen Concentration at the Catalyst Layer-Membrane Layer Interface (Pressure = 4 bar).
Figure 25: Current Density vs. Anode Hydrogen Bulk Concentration at the Catalyst Layer-Membrane Layer Interface (Pressure = 4 bar).

Figure 26 shows the concentration within the bulk and at the catalyst surface. The concentration at the surface of the catalyst was calculated using the mass transfer coefficients, which were calculated previously.

Figure 26: Current Density vs. Anode Hydrogen Concentration at the Catalyst Layer-Membrane Layer Interface (Pressure = 5 bar).
Figure 27 is another graph of the hydrogen concentration within the bulk in the 5 bar simulation. Again, this graph is presented to show that the concentration within the bulk is change within increasing current density. Again, the change in bulk concentration at the catalyst layer-membrane layer interface is quadratic.

![Graph of Current Density vs. Anode Hydrogen Bulk Concentration at the Catalyst Layer-Membrane Layer Interface (Pressure = 5 bar)](#)

**Figure 27:** Current Density vs. Anode Hydrogen Bulk Concentration at the Catalyst Layer-Membrane Layer Interface (Pressure = 5 bar).

The mass transfer coefficients for each of the aforementioned pressure scenarios were plotted for both the anode and the cathode. Figure 28 and Figure 29 are plots of the estimated mass transfer coefficient ($K_g$) at different pressures. Figure 28 is the plot of the mass transfer coefficients for the anode side processes for different pressures. The graph shows that the mass transfer coefficients are inversely related to the pressure. The mass transfer coefficients
are computed using the limiting current density and the hydrogen concentration at the catalyst layer-membrane layer interface.

![Graph showing mass transfer coefficient vs. pressure](image)

Figure 28: Pressure vs. Anode Mass Transfer Coefficient.

Figure 29 is the plot of the mass transfer coefficients for the cathode side processes for different pressures. Similar to the anode side mass transfer coefficients, the graph shows that the mass transfer coefficients are inversely related to the pressure. The mass transfer coefficients are computed using the limiting current density and the oxygen concentration at the catalyst layer-membrane layer interface.

The data show that the mass transfer coefficients were inversely proportional to the gas channel pressure. Equation 266 and Equation 267 are the functional forms for the mass transfer coefficients and their dependence on gas channel pressure.
Figure 29: Pressure vs. Cathode Mass Transfer Coefficient.

\[
k_{g, \text{Anode}} = \frac{0.0031}{P_{\text{Anode}}} \quad (266)
\]

\[
k_{g, \text{Cathode}} = \frac{0.0015}{P_{\text{Cathode}}} \quad (267)
\]

The constant of proportionality is a function of the number of electrons presented in the balanced equation. The mass transfer coefficients vary with concentration, but it is likely that because of the size of the system that the mass transfer coefficients may be constant over the entire region.

The aforementioned data are significant for many reasons, but it is the link that is established between the reactant transport and the fuel cell overpotentials that is most significant. Although prior fuel cell models indirectly discuss the impact of concentration on activation losses and concentration losses, this treatment is the first to develop an explicit link between the fuel cell
overpotentials and the moment of reactants within the PEM fuel cell system. Specifically, this treatment identifies the link between the bulk concentration and the surface concentration. It is the surface concentration that is key to calculating the activation overpotential and the concentration overpotential. While it is intuitive that the Ohmic losses are directly related to the movement of the charged ions within PEM fuel cell systems, the relationship between uncharged ions and fuel cell overpotentials is typically ignored in computational models.

As previously stated, the output voltage of a real PEM fuel cell is reduced by the system overpotentials. This model makes this link. Bulk concentrations, which can be calculated with relative ease, can be linked via the flux equation to the concentration at the catalyst surface or active site, and it is the surface concentration that is the critical concentration in activation overpotential correlations, like the Butler-Volmer equation (Oldham & Myland, 1994). Specifically, at the limiting current density, it is the surface concentration that goes to zero, not the bulk concentration of reactant.

The results from the 1-D model were compared to the data from Vasileiadis, Brett, Vesovic, Kucervak, Fontes, and Brandon (2007) of the Imperial College of London. Vasileiadis et al. (2007) proposed a two-dimensional numerical model of a PEM fuel cell. The model was described as an extension of the pioneering work of Bernardi and Verbrugge (1991) (Vasileiadis et al., 2007). Bernardi and Verbrugge (1991) proposed a one-dimensional model of the PEM fuel cell; Vasileiadis et al. (2007) modeled the system in two-dimensions. The model assumed that the system was operated in a cross flow orientation.
Although the Vasileiadis et al. (2007) allude to the heterogeneity of the membrane, the Vasileiadis et al. model assumed that the membrane is homogeneous and the hydration of the membrane is constant (Vasileiadis et al., 2007). The model also assumes that the ionic current density across the membrane is constant for voltage potential. The data show that both models predict reactant concentration at the catalyst layer-membrane layer interface. In addition, the change in concentration for the two models is approximately the same order of magnitude. Figure 30 is a comparison of the Vasileiadis et al data and the 1-D model data.

Figure 30: Comparison of Vasileiadis et al. Model & 1-D Model Data.
Figure 31: Percentage Change of Vasileiadis et al. Model & 1-D Model.

Figure 31 shows the data from the Vasileiadis et al. (2007) article and 1-D model data. The figure shows that there is relatively good agreement between the two data sets. The overall conclusion is that there is good agreement between the Vasileiadis et al. (2007) data and 1-D model data.

2-D Computational Model

A 2-D model of the system was constructed. The Knudsen number (Kn) for the anode is 0.002, and the Kn equals 0.001 for the cathode. The system inlet pressure was 101,325 Pascals and the temperature was held constant at 353 K. The flow domain is solved with the gas channel for both the anode and the cathode gas channels. These data from the gas channel are used as the input to the gas diffusion layers, and are incorporated into the boundary conditions.
Figure 32 though Figure 39 show the hydrogen and oxygen concentrations for the anode and cathode gas diffusion layers and catalyst layers.

Figure 32 is a graph of the concentration of hydrogen within the gas diffusion layer in the two dimensional model (2-D). The inlet pressure for this case is 1 bar. Figure 32 shows the hydrogen concentration data within the gas diffusion layer for a current density of 1 $\text{A/cm}^2$. The pressure drop along the length of the gas channel was set at 5 Pascals from entrance of the gas channel to the exit of the gas channel. Similar to what was observed in the 1-D cases, the concentration within the gas diffusion layer is linear. However, in the 2-D cases, the concentration also changes in the direction of flow.

![Figure 32: Anode Gas Diffusion Layer Hydrogen Concentration ($i = 1.0 \text{ A/cm}^2$ & $\Delta P = 5 \text{ Pa}$).](image-url)
Figure 33 shows the concentration of hydrogen within the catalyst layer. Similar to what was observed in the 1-D cases, the concentration at the catalyst layer-membrane layer interface is not zero. Actually, the concentration at this interface is significantly above zero. The pressure drop across the gas channel was set at 5 Pascals, and the current density was 1 A/cm² in this case. Although a pressure drop of 5 Pascals across the gas channel was not selected for any particular reason, the velocities for the system were maintained within the Stokes flow regime.

Figure 33: Anode Catalyst Layer Hydrogen Concentration (i = 1.0 A/cm² & ΔP = 5 Pa).
Cathode Gas Diffusion Layer (microns)

Figure 34: Cathode Gas Diffusion Layer Oxygen Concentration (i = 1.0 A/cm$^2$ & ΔP = 5 Pa).

Figure 35 shows the concentration of oxygen gas within the catalyst layer. Similar to what was observed in the 1-D cases, the concentration at the catalyst layer-membrane layer interface is not zero. The pressure drop across the gas channel was set at 5 Pascals, and the current density was 1 A/cm$^2$ in this case. Again, 5 Pascals was not selected for any particular reason, but the flow was maintained within the Stokes flow regime.

Figure 36 shows the concentration of hydrogen in the 2-D case within the gas diffusion layer. The current density for this case was 1.5 A/cm$^2$ and the pressure drop across the gas channel was 25 Pascals. The gas channel inlet pressure was 1 bar. The pressure drop across the gas channel was increased to assess the impact of pressure drop on the system. As expected, the
concentration gradient was more pronounced at the higher pressure drop of 25 Pascals. However, many of the other trends were unchanged.

Figure 35: Cathode Catalyst Layer Oxygen Concentration ($i = 1.0 \text{ A/cm}^2 \& \Delta P = 5 \text{ Pa}$).

Figure 36: Anode Gas Diffusion Layer Hydrogen Concentration ($i = 1.5 \text{ A/cm}^2 \& \Delta P = 25 \text{ Pa}$).
Figure 37 shows the concentration of hydrogen in the 2-D case within the catalyst layer. The current density for this case was 1.5 A/cm\(^2\) and the pressure drop across the gas channel was 25 Pascals. The concentration changes were more dramatic in the direction of flow compared to the 5 Pascal case. However, similar to the 1-D cases, the concentration at the catalyst layer-membrane layer the concentration was not zero. The gas channel inlet pressure was 1 bar.

Figure 38 shows the oxygen concentration data within the gas diffusion layer for a current density of 1.5 A/cm\(^2\). The pressure drop along the length of the gas channel was set at 25 Pascals from entrance of the gas channel to the exit of the gas channel. Similar to observations in the 1-D cases, the concentration within the gas diffusion layer is linear. However, in the 2-D cases, the concentration also changes in the direction of flow. The gas channel inlet pressure was 1 bar.

![Graph showing hydrogen concentration in the anode catalyst layer](image)

**Figure 37:** Anode Catalyst Layer Hydrogen Concentration (i = 1.5 A/cm\(^2\) & ΔP = 25 Pa).
Figure 39 shows the concentration of oxygen gas within the catalyst layer. Similar to what was observed in the 1-D cases, the concentration at the catalyst layer-membrane layer interface is not zero. The pressure drop across the gas channel was set at 25 Pascals, and the current density was 1.5 A/cm$^2$ in this case. Because the pressure drop across the gas channel was higher, the changes in concentration Figure 39 are more dramatic than the changes in concentration for the 5 Pascal case. In addition to changing the pressure drop across the gas channel, the current density was also increased in this case to 1.5 A/cm$^2$. The inlet pressure was 1 bar.
Again, the models show that the concentration of the reactant gases hydrogen and oxygen at the membrane-catalyst layer interface is not zero. The concentration at the catalyst layer-membrane layer be non-zero is an important finding, because prior models had simulated fuel cells assuming that the concentration at the catalyst layer-membrane layer was zero.

The polarization curve (Figure 40) for the micro PEM fuel cell case is presented below for a system pressure of 101,325 Pascals within the anode and cathode gas channels.

The micro PEM fuel cell case was compared to the polarization curve (Figure 41) generated for PEM fuel cell with a membrane thickness of 250
microns. The polarization curve for this case is presented below. The data for each of the overpotentials was reviewed. The data suggest that the activation losses and concentration losses are not affected by the size of the fuel cell. However, the Ohmic losses, which are functions of the thickness of the fuel cell, are almost non-existent in microscale models.

Figure 40: Polarization Curve Micro PEM Fuel Cell (Membrane Thickness = 5 microns & Pressure = 101,325 Pascals).

Figure 41: Polarization Curve Micro PEM Fuel Cell (Membrane Thickness = 250 microns & Pressure = 101,325 Pascals).
A graph of the current density versus the Ohmic losses is presented for the micro PEM fuel cell case. The micro PEM fuel cell model was compared to data for a 250-micron membrane model. Figure 42 and Figure 43 are graphs that show the change in Ohmic losses for the 5-micron membrane fuel cell and for the 250-micron membrane fuel cell, respectively. The data show that the Ohmic losses in the micro PEM fuel cell case are approximately 50 times smaller than the 250-micron membrane case.

![Graph of current density versus Ohmic losses](image)

**Figure 42: Ohmic Losses Micro PEM Fuel Cell (Membrane Thickness = 5 microns).**

Although the Ohmic losses are reduced in the micro PEM fuel cell case, the benefit of size does not come without a price. As the thickness of the membrane is decreased, the migration of hydrogen across the polymer membrane is increased.
Using the aforementioned hydrogen concentration data, the flux of hydrogen crossing the polymer membrane was calculated for the micro PEM fuel cell case and another PEM fuel cell case. The hydrogen flux was calculated assuming that the major transport mechanism was diffusion. The diffusivity of hydrogen within the membrane is $2.59 \times 10^{-10} \text{ m}^2/\text{s}$ (Ju & Wang, 2004). The parasitic losses associated with hydrogen migration across the polymer membrane were calculated using the Fick’s Law. Equation 268 shows the functional relationship between flux of hydrogen gas across the membrane and the hydrogen concentration at the anode catalyst layer-member layer interface.

\[
N_{H_2} \mid_{\text{Membrane}} = D_{H_2} \frac{dC_{H_2}}{dx} \approx D_{H_2} \left( \frac{C_{H_2} \mid_{\text{Anode}}}{\Delta x} \right)
\]  

(268)
The concentration of hydrogen at the anode membrane-catalyst layer interface was taken from the simulation results. The concentration of hydrogen at the cathode membrane-catalyst layer interface was assumed to be zero. The data are presented in Figure 44, Figure 45, and Figure 46.

The data show that the size of the fuel cell has an impact on the performance of the fuel cell. Parasitic losses increase as the fuel cell gets smaller. As the graphs show, the flux of hydrogen across the membrane in the micro PEM fuel cell case, whose membrane thickness is 5 microns, is approximately 50 times larger than the hydrogen flux across the larger fuel cell, membrane thickness of 250 microns. Therefore, as expected, the parasitic losses will be much larger as the fuel cell gets smaller.

Figure 44: Parasitic Losses Hydrogen Flux across Membrane for Micro PEM Fuel Cells (Membrane Thickness = 5 microns).
Figure 45: Parasitic Voltage Losses Micro PEM Fuel Cells (Membrane Thickness = 5 microns).

Figure 46: Parasitic Losses Hydrogen Flux across the Membrane for PEM Fuel Cell (Membrane Thickness = 250 microns).
The data show that as the fuel cells get smaller the parasitic losses get larger, so although the Ohmic losses are much reduced in micro PEM fuel cell system, the parasitic losses must be included, because these losses can no longer be neglected for micro PEM fuel cell systems.
Fossils fuels are an extremely important energy source. The pitfalls of a fossil fuel dependent energy supply are many. The most obvious concerns are that fossil fuels are not renewable, and that burning these fuels releases billions of tons of pollutants into the air each year. Because fossil fuels, like oil, natural gas, and coal, are a non-renewable natural resource, the United States Congress commissioned the Department of Energy (DOE) to investigate other, more sustainable energy sources. One of DOE’s stated goals is to move the country away from a carbon-based economy to move the country toward a hydrogen-based economy and an economy, which is more dependent on renewable energy resources.

The belief is that novel renewable energy technologies will be required to address the world’s future energy requirements. Polymer Electrolyte Membrane (PEM) fuel cells have the potential to meet all of the world’s energy needs, while mitigating many of the disadvantages of fossil fuels. (Fauvarque, 2001). Consistent with the Hydrogen Research and Development Act, which directed the Department of Energy to fund technologies that would reduce the United States dependence on fossil fuels, PEM fuel cells are a novel way to transition from a carbon-based economy to a hydrogen-based economy. A key premise
revolves around looking at hydrogen as an energy storage device. Fundamentally, a PEM fuel cell is a method of extracting the energy stored within the covalent bonds of hydrogen gas molecules (Fauvarque, 2001).

A Polymer Electrolyte Membrane (PEM) fuel cell produces electrical energy via an electrochemical process. Specifically, oxygen (O$_2$) is combined electrochemically with hydrogen (H$_2$) in the presence of a catalyst to produce water, heat, and electrical energy. However, it is the polymer membrane, which separates the anode from the cathode, which distinguishes a PEM fuel cell from a battery.

Although there are many computational models that describe the behavior of Polymer Electrolyte Membrane (PEM) fuel cells, few model the dynamics within the non-continuum region near the solid surfaces of the fuel cell. The typical approach to PEM fuel cell models is to describe the dynamics within the fuel cell as a continuum. However, unlike macroscale processes, microscale and nanoscale fuel cells are not described by continuum mechanics. At the microscale and nanoscale, more specialized tools, which account for the increased surface forces and micro length scales, are needed to understand the dynamics of these micro-devices.

As PEM fuel cell systems become smaller, traditional assumptions, like the empirically derived no-slip condition, must be checked. If the flow is not within the continuum flow regime, other computational models may be necessary to correct for non-continuum dynamics at the boundaries. These data show that for microfluidics flows within the gas channel the model must abandon the empirical
no-slip condition at the gas channel-gas diffusion layer boundary. In addition, the computational data show that the concentration of hydrogen and oxygen gases at the gas channel-gas diffusion layer boundary within microfluidics system may be significantly different from the concentrations predicted by continuum flow models.

There were two main objectives of this study. The first object was to develop a functioning one-dimensional (1-D) computational model of a PEM fuel cell, which could be used to calculate both bulk and catalyst surface concentrations of the reactant gases. The second objective was to develop a functioning 2-D computational model of a microscale PEM fuel cell. This research was limited to Knudsen numbers (Kn) less than $10^{-1}$. The size in the 2-D case was selected to ensure that the flow within the gas channel of both the anode and the cathode was characterized as slip flow.

Table 6 shows the mean free path for each of the reactants and the equivalent Knudsen number (Kn) for a gas channel with a width of 50 microns.

Table 6: Reactant Gases, Mean Free Path, and Knudsen Number (II)

<table>
<thead>
<tr>
<th>Gas</th>
<th>Mean Free Path (microns)</th>
<th>Kn</th>
<th>Gas Channel Width (microns)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen</td>
<td>0.11</td>
<td>0.0022</td>
<td>50</td>
</tr>
<tr>
<td>Oxygen</td>
<td>0.06</td>
<td>0.0012</td>
<td>50</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>0.06</td>
<td>0.0012</td>
<td>50</td>
</tr>
</tbody>
</table>
The study looked at three research questions:

1. What is the effect of the physical geometry on the performance of the fuel cell?

2. Is there a limit to the size of fuel cells?

3. How do the microfluidic properties of the system and the phenomenon of slip flow impact the performance of PEM fuel cells?

Three hypotheses were developed. First, it was hypothesized that the size of the fuel cell would influence the performance of PEM fuel cells. Second, it was hypothesized that the Ohmic losses would be almost non-existent in microscale models. Therefore, higher current densities would be theoretically possible. Third, it was hypothesized that there would be a physical limitation on the minimum size of PEM fuel cells. The key would be determining the point at which the size of the fuel cell starts to affect its performance, i.e. the overpotentials start to become too large. Finally, it was hypothesized that the microfluidic properties would have little impact on the performance of the fuel cell.

A key result from the study was that the bulk concentration of reactants at the catalyst layer-membrane layer is not zero. One possible explanation is that in the micro PEM fuel cell case the residence time is sufficiently small to prevent the reaction to go to completion. The study suggests that the reactant deficit at the catalyst layer-membrane layer interface reported in prior studies at high current densities may be localized to the catalyst surface; however, the bulk concentration around the catalyst active site may not be zero.
PEM fuel cells are heterogeneous catalytic systems, and it is the concentration at the surface of the catalyst that is paramount, not the bulk concentration. This treatment attempts to explain that localized starvation of the active sites is the cause of the sudden drop in the voltage at the limiting current density. More specifically, a resistance is established around the active site and the time constant required for the migration of reactant to the active site is much less than the time constant associated with the reaction at the active site at higher current densities. The limitation on the current density is the balance point where the reaction kinetics equals the mass transport flux.

These active sites are special. In order for the forward reaction to occur, the reactant gas must be in contact with the platinum catalyst and the platinum catalyst must be in contact with the membrane. It is this triple point, which is essential. When the active sites are saturated, the current density cannot increase. The point of saturation of the active sites is the limiting current density. At the limiting current density, neither the bulk oxygen concentration nor the bulk hydrogen concentration is zero at the catalyst layer-membrane interface. The term bulk concentration means the concentration of reactant outside of the mass transfer boundary layer of the active sites. The bulk concentration of reactants does not go to zero at the limiting current density.

To address the first and second research question, the study turns to the losses associated with PEM fuel cells. A PEM fuel cell is a device that is capable of extracting the energy stored within the covalent bonds of hydrogen gas molecules. Although PEM fuel cell are far more efficient than conventional
engines. PEM fuel cells are still not 100% efficient. A typical PEM fuel cell has an efficiency of approximately 79% at 100°C (Larminie & Dicks, 2003).

Because fuel cells are the output voltage source of an electrical circuit, some amount of heat is lost to the environment. This loss of heat is an inefficiency or irreversibility. Within the fuel cell vernacular, scientists often use the term overpotentials, in lieu of the terms losses or irreversibilities. There are four major fuel cell irreversibilities: activation losses ($V_a$), Ohmic losses ($V_o$), parasitic losses ($V_p$), and concentration losses ($V_c$) (Larminie & Dicks, 2003). The fuel cell output ($E^\circ$) is a function of the open circuit voltage minus the losses.

$$E_{cell} = E^\circ - V_{act} - V_{ohm} - V_{conc} - V_p$$  \hspace{1cm} (269)

One of the stated goals of this research was to determine the impact of size of the PEM fuel cell on the performance of the fuel cell. Specifically, the study attempted to determine a lower limit on PEM fuel cell size. The models showed that the size of the size does affect the overall performance of the system. There are really two overpotentials that are functions of the size of a PEM fuel cell: parasitic losses and Ohmic losses.

Parasitic losses are typically not addressed in macroscale PEM fuel cell models, because these parasitic losses are negligible. However, these data suggest that parasitic losses cannot be ignored, as the fuel cell gets smaller. Specifically, as the fuel cells get smaller, the parasitic losses get larger. Parasitic losses increase as the membrane of the fuel cell gets thinner. As the data show, the flux of hydrogen across the membrane in the micro PEM fuel cell case is
approximately 50 times larger than the hydrogen flux across the larger fuel cell. Thus, the parasitic losses would be much larger as the fuel cell gets smaller. Therefore, there is likely a lower limit on the size of PEM fuel cells. Although the lower was not determined, the data suggest that as the fuel cell gets smaller the parasitic losses associated with crossover of hydrogen from the anode to the cathode will reach an intolerable level.

The Ohmic losses are also a function of the size of the system. The data suggested that as PEM fuel cell systems get smaller that the Ohmic losses become much smaller.

The data show that the size of the fuel cell has an impact on the performance of the fuel cell. However, although the Ohmic losses are much reduced in micro PEM fuel cell system, the parasitic losses increase, because these losses can no longer be neglected for micro PEM fuel cell systems. The model shows that the Ohmic losses are much reduced in the micro PEM fuel case compared to larger fuel cells. Because of the impact on the Ohmic and parasitic losses, this treatment concludes that the size of the fuel cell has an impact on the performance of the fuel cell.

The third research question was addressed by applying slip velocity boundary conditions at the gas channel-gas diffusion layer interface. The study concluded that, as PEM fuel cell systems become smaller, traditional assumptions, like the empirically derived no-slip condition, must be checked. If the flow is not within the continuum flow regime, other computational models may be necessary to correct for non-continuum dynamics at the boundaries. These
data show that for microfluidics flows within the gas channel the model must abandon the empirical no-slip condition at the gas channel-gas diffusion layer boundary.

Recommendations

The study examined the effects of size on the output and performance of micro PEM fuel cells. However, a limitation of this study that was not explicitly stated was that the gas channel walls were smooth surfaces. Real fuel cells are composed of a carbon fiber weave which makes up the gas diffusion layer. This carbon fiber weave protects the catalyst and the membrane. Because the gas channel is composed of this weave, prior models, which modeled the gas channel as a smooth surface, do not model the real geometry of the system.

The gas channel has a rough surface; therefore, it is recommended that a sine function be used to simulate the roughness of the gas channel. The gas channel roughness average (Ra) could be simulated using a sine function. A variable transformation would be required depending on the method used within the simulation. The variable transformation translates the sinusoidal physical domain (x, y) into a rectangular computational domain (\(\dot{x}, \dot{y}\)).

\[
\dot{x} = x \quad (270)
\]

\[
\dot{y} = A\left(\frac{y}{y_{Max}}\right)\sin(Bx + C) + y \quad (271)
\]
In the aforementioned equation, the variable A is the amplitude of the sine function. The variable B describes the period of the function. The variable C is the angle phase shift. Because the incorporation of the angle phase shift does not add to the computational model’s relevance, the angle phase shift has been omitted from the model. Therefore, for the purposes of this model, the variable C is equal to zero.

Given any function $\alpha(x, y)$, the derivative of $\alpha$ can be expressed as the partial derivative of $\alpha$ with respect to $x$ and $y$ (Currie, 1993):

$$\delta \alpha = \frac{\partial \alpha}{\partial x} \delta x + \frac{\partial \alpha}{\partial y} \delta y$$

(272)

Using the aforementioned definition of the derivative, the following differential expression is constructed for each of the computational domain variables.

$$dx = \frac{\partial x}{\partial x} dx + \frac{\partial x}{\partial y} dy$$

(273)

$$dy = \frac{\partial y}{\partial x} dx + \frac{\partial y}{\partial y} dy$$

(274)

Each of the partial derivatives is evaluated using the transformation equation.

$$\frac{\partial x}{\partial x} = 1$$

(275)

$$\frac{\partial x}{\partial y} = 0$$

(276)
\[ \frac{\partial y}{\partial x} = AB \left( \frac{y}{Y_{\text{Max}}} \right) \cos(Bx) \tag{277} \]

\[ \frac{\partial y}{\partial y} = A \left( \frac{1}{Y_{\text{Max}}} \right) \sin(Bx + C) + 1 \tag{278} \]

The aforementioned differential equations can be expressed as vector equation (Tannehill, Anderson, & Pletcher, 1997).

\[
\begin{bmatrix}
dx \\
dy
\end{bmatrix} = 
\begin{bmatrix}
\frac{\partial x}{\partial x} & \frac{\partial x}{\partial y} \\
\frac{\partial y}{\partial x} & \frac{\partial y}{\partial y}
\end{bmatrix}
\begin{bmatrix}
dx \\
dy
\end{bmatrix}
\tag{279}
\]

The Jacobian (J) is used to transform from the physical domain \((x, y)\) to the computational domain \((\hat{x}, \hat{y})\) (Tannehill, Anderson, & Pletcher, 1997).

\[ J = \begin{bmatrix}
1 & 0 \\
AB \cos(Bx) & 1
\end{bmatrix} \tag{280} \]

Therefore, to convert from the computational variables back to the physical variables, the following equation is used.

\[
\begin{bmatrix}
dx \\
dy
\end{bmatrix} = 
\begin{bmatrix}
\frac{\partial x}{\partial x} & \frac{\partial x}{\partial y} \\
\frac{\partial y}{\partial x} & \frac{\partial y}{\partial y}
\end{bmatrix}
\begin{bmatrix}
dx \\
dy
\end{bmatrix}
\tag{281} \]
Physically, the Jacobian (J) is a ratio of the area in the physical domain to the area in the computational domain. Substituting for the partial derivatives, the following form of the Jacobian (J) is obtained:

$$J = \begin{bmatrix} \frac{\partial x}{\partial x} & \frac{\partial x}{\partial y} \\ \frac{\partial y}{\partial x} & \frac{\partial y}{\partial y} \end{bmatrix}$$

(282)

Again, the variable C has been removed, because the variable C is zero. Using this transformation method, the vector form of the Navier-Stokes equations is transformed into the following equation (Tannehill, Anderson, & Pletcher, 1997):

$$\frac{\partial U}{\partial t} + \frac{\partial}{\partial x}(\frac{\partial E}{\partial x}) + \frac{\partial}{\partial y}(\frac{\partial E}{\partial y}) + \frac{\partial}{\partial x}(\frac{\partial E}{\partial y}) + \frac{\partial}{\partial y}(\frac{\partial E}{\partial y}) = H \tag{283}$$

Because x is only a function of x and is not a function of y, the partial derivative with respect to y is zero.

$$\frac{\partial U}{\partial t} + \frac{\partial E}{\partial x} + \Bigg[ AB \left( \frac{y}{y_{Max}} \right) \cos(Bx) \Bigg] \frac{\partial E}{\partial y} + \Bigg[ A \left( \frac{1}{y_{Max}} \right) \sin(Bx) + 1 \Bigg] \frac{\partial F}{\partial y} = H \tag{284}$$

The variable A is the amplitude and the variable A will be set to 0.1% of \(y_{Max}\). The variable B is the period factor, and is set to 500,000. The benefit of this model would be that the model would more closely simulate the real behavior at the gas channel-gas diffusion layer boundary.
Along with the aforementioned recommendation on the modeling of the roughness of the gas channel, it is recommended that future research investigate the possibility that the mass transfer across the polymer membrane maybe limiting the fuel cell’s output. Although it is believed that the residence time is not sufficient to get the bulk concentration at the catalyst layer-membrane layer to zero, it is possible that the flux across the polymer membrane may also be influencing the performance of the fuel cell.

The Future of PEM Fuel Cells

The potential for polymer electrolyte membrane (PEM) fuel cells to change the way humankind lives and works are limitless. The future of this technology may be the key to solving many problems that were previously thought to be unsolvable. As engineers and policy makers ponder the benefits of fuel cells, they might reflect upon the socio-economic and political benefits of this technology.

The polymer electrolyte membrane (PEM) fuel cells are a novel class of energy device, which hold limitless potential. These devices make it possible to transform previously resource-limited areas around the globe into self-sufficient localities. The key to this new technology is that PEM fuel cells can be used in combination with other renewable energy devices to transform our planet into a fossil fuel free engine of limitless energy.

The socio-economic benefits of PEM fuel cell devices are many. The planet Earth is over 75% water; however, most of this water is undrinkable. PEM
fuel cells have the potential to reduce the net cost of desalination, and these devices may one day transform harsh, arid environments into lush, green oases.

PEM fuel cells are important energy resources, which have the potential to balance humankind’s insatiable thirst for cheap energy with the need to find sources of energy that, reduce or eliminate the type and quantity of pollutants that enter our atmosphere each year. PEM fuel cells produce “green” energy. Unlike traditional hydrocarbon based energy sources, PEM fuel cells generate an abundance of energy without generating the deleterious pollutants and waste commonplace in other non-renewable energy devices, like coal-fired power plants or nuclear facilities.

The future of fuel cell research is building hybrid fuel cell devices. Researchers need to study how fuel cells can be combined with other renewable devices to produce energy more efficiently. As Shrestha and Ale (2008) explained, countries, like Nepal, with few natural resources could leverage the benefits of fuel cells in combination with other forms of readily available energy, like hydro-power, solar energy, or wind energy, to produce an almost limitless quantity of energy, which would transform these historically energy dependent countries into energy reservoirs (Shrestha & Ale, 2008). Nepal has few natural resources, but, during the rainy season, the abundance of water and hydropower from rivers and waterfalls could be transformed into hydrogen, which could potential transform a country, like Nepal, into a net energy producer.

There are other developing countries with similar weather patterns, as Nepal, which could also benefit from this technology. Haiti, the poorest country in
the western hemisphere, has a rainy season that deluges the country of Haiti
with water causing floods and mass starvation. If fuel cell technology were
employed in Haiti, potentially, the rain that is today a source of great misery could
be used in combination with fuel cells to power a rebirth of this poor country.

The final frontier is space. The key to space exploration is having plentiful
sources of oxygen, water, and energy. PEM fuel cells will one day propel
humankind into space. In 2008, NASA confirmed that water in the form of ice had
been discovered on Mars. The discovery of water was exciting. The presence of
water means that Mars may be capable of supporting human life. Water also
means that by using hybrid fuel cell devices in combination with solar energy
microenvironments could be established on Mars. Although the focus of this
research is the generation of energy from PEM fuel cells, PEM fuel cells, unlike
traditional hydrocarbon systems, can be run in reverse. Therefore, if energy is
inputted into a fuel cell circuit, water can be transformed into hydrogen and
oxygen gas. One day, the water found on Mars might one day be used in
combination with fuel cells to produce microenvironments on the Red Planet.

Humankind has only scratched the surface of the usefulness of PEM fuel
cell technology. Hopefully, fuel cells will revolutionize the planet. However, in
order to attain the perceived limitless potential of fuel cells, more research is
required.
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Appendix A

1-D Model Program
Although the aforementioned description of the mathematical models, boundary conditions, and initial conditions outline in general terms the overall methodology used to solve the computational domain, the details of the computation are in the programming. Because of the libraries available for a variety of mathematical equations and problems, FORTRAN was selected as the programming language of choice. However, the methodology, which will be outlined, is not specific to FORTRAN.

All programming was written in Microsoft Visual Studio 2005 and Intel® compiler 10.0.0.27 was used to compile and run the programs. The use of Microsoft Visual Studio 2005 helped with the debugging of the program, because Microsoft Visual Studio 2005 uses a color code for command words, and MS Visual Studio 2005 allows the programmer to quickly go to any line of code using a GOTO function integral to the platform. The Intel® compiler and MS Visual Studio are well integrated. However, if one wishes to run both on a personal computer, the installation of the programs onto the computer to be used must be performed in order. The Intel® compiler must be installed first prior to installing any portions of MS Visual Studio. If the order of installation is not followed, the compiler will not recognize MS Visual Studio.

Because solving programs of this magnitude requires several lines of code, the program was subdivided into subroutines. The subroutines served two purposes. First, the use of subroutines made the identification and correction of coding errors easier. Second, the subroutines were treated as discrete modules that could be used in later simulations. The modular nature of this program
increases the likelihood that future researchers will be able to use this program or portions of this program for future research with little, if any, modification to the program. The modularity of the subroutines will be apparent.

An original program was developed to solve the computational domain. The computational domain was divided into four groupings: the main program, the anode subroutine, the cathode subroutine, and the membrane subroutine.

For ease of coding and debugging, the main program calls subroutines to perform iterations and other calculations: these subroutines are used to perform the detailed calculations. Three of the subroutines used within the program were taken from FORTRAN subroutine libraries. These subroutines have a reference to their libraries in the program (Press, 1992).

The program starts with the initializing of the given information. The computational grid is defined. Specifically, program requests that the user input the number of rows (I) to specify the computational grid. Next, the maximum number of iterations is entered. The program requires that a maximum number of iterations be specified to eliminate the possibility of the program being stuck in an endless loop. Next, the boundary conditions are entered. The user is asked to specify the gas channel hydrogen pressure, the concentration of water in the gas channel, the concentration of water at the catalyst layer-membrane interface, the percent hydration of the polymer membrane, and the concentration of hydrogen at the catalyst-membrane interface.

During the debugging process, it was observed that several of the constants were changing variable within the subroutines. It is believed that the
names of these constants were too closely linked to names of variables used within the subroutine and in other locations, so these constants were changed to prevent confusion within the code. For example, the constant INDX (N) was changing values within the subroutine. Therefore, INDX (N) was changed to XINDX (N). This change resolved the issue. Similar observations were made throughout the program process.

Initially, the variables within the program were declared as REAL. However, because of the precision required for many of the calculations, all variables and constants were reclassified as DOUBLE PRECISION.
Anode Subroutine Flow Chart

Anode

Step 1 - Data Entry
1. Enter number of grids points.
2. Enter $C_{\text{hydrogen}}$ in Gas Channel (GC).
3. Enter $C_{\text{water}}$ in Gas Channel.
4. Enter Guess for $C_{\text{hydrogen}}$ at Gas Diffusion Layer (GDL) - Catalyst Layer (CL) interface.
5. Enter Guess for $C_{\text{water}}$ at GDL-CL interface.
6. Enter maximum number of iterations.

Loop

Step 2 - GDL Cathode
Main program calls subroutine GDLAND.
1. Solves continuity and species equations for the gas diffusion layer (GDL) for hydrogen and water.
2. Returns updated values for concentration of water and hydrogen in GDL.

Step 3 - CL Cathode
Main program calls Subroutine CLAND.
1. Solves continuity and species equations for the catalyst layer (CL) for hydrogen and water.
2. Returns updated values for concentration of water and hydrogen in CL.

Step 4 - Comparison
Main program calls subroutine COMPR.
1. Uses flux boundary condition (Neumann boundary condition) to specify concentration of hydrogen and water at the GDL-CL interface.
2. Iterates within subroutine until convergence criteria satisfied.

Step 5 - Comparison
Main program calls subroutine COMCL.
1. Uses constant flux boundary condition (Neumann boundary condition) to specify concentration of hydrogen and water at the CL-Membrane interface.
2. Iterates within subroutine until convergence criteria satisfied.

Step 6 - Update Values
Main program updates old values from previous iteration.

Step 7 - Converged?

No

Yes

Main Program
Cathode Subroutine Flow Chart

**Step 1 - Data Entry**
1. Enter number of grids points.
2. Enter $C_{\text{oxygen}}$ in Channel.
3. Enter $C_{\text{water}}$ in Channel.
4. Enter Guess for $C_{\text{oxygen}}$ at GDL-CL interface.
5. Enter Guess for $C_{\text{water}}$ at GDL-CL interface.
6. Enter maximum number of iterations.

**Loop**

**Step 2 - GDL Cathode**
Main program calls subroutine GDLCAT.

**Subroutine GDLAND**
1. Solves Continuity and Momentum for the gas diffusion layer (GDL) for oxygen and water.
2. Returns updated values for concentration of water and oxygen in GDL.

**Step 3 - CL Cathode**
Main program calls Subroutine CLCAT.

**Subroutine CLLAND**
1. Solves Continuity and Momentum for the catalyst layer (CL) for oxygen and water.
2. Returns updated values for concentration of water and oxygen in CL.

**Step 4 - Comparison**
Main program calls subroutine COMPR.

**Subroutine COMPR**
1. Uses constant flux boundary condition to specify concentration of oxygen and water at the GDL-CL interface.
2. Iterates within subroutine until convergence criteria satisfied.

**Step 5 - Comparison**
Main program calls subroutine COMCL.

**Subroutine COMCL**
1. Uses constant flux boundary condition to specify concentration of oxygen and water at the CL-Membrane interface.
2. Iterates within subroutine until convergence criteria satisfied.

**No**
Converged?

**Yes**
Main Program
Membrane Subroutine Flow Chart

Step 1 - Data Entry
1. Enter the number of grid points.
2. Enter the thickness of the membrane.
3. Enter the pressure differential between the cathode and the anode.
4. Enter the maximum number of iterations.
5. Subroutine receives hydrogen ion concentration from anode catalyst layer subroutine. The hydrogen ion will diffuse in one direction.
6. Subroutine receives water concentration from cathode catalyst layer subroutine and anode catalyst layer subroutine.

Loop

Step 2 - Water Transport
Subroutine calls subroutine, which calculates the diffusion of water across the membrane.

Subroutine calculates the net flux of water.
1. Electro-osmotic Drag - Hydrogen ions pull water molecules with it as it diffuses across the membrane from the anode to the cathode.
2. Pressure Differences - The difference in pressure between the anode and the cathode causes the water to move from the area of high pressure to the area of lower pressure.
3. Concentration Gradients - The concentration of water in the cathode is higher than the concentration in the anode, so water diffuses toward the anode.

Step 3 - Hydrogen Ion Transport
Subroutine calls subroutine, which calculates the diffusion of hydrogen ions (H\(^+\)) across the membrane.

Subroutine calculates the net flux of hydrogen ions.
1. Hydrogen ions move in one direction from the anode to the cathode.
2. The rate of diffusion of hydrogen ions is dependent upon the hydration rate of the polymer membrane.

Note: Diffusion is the only method of transport modeled.

Step 4 - Update Membrane Subroutine Info
Subroutine sends information back to both anode and cathode subroutines. The anode and cathode subroutine must recalculate the data to the point of convergence. After convergence, the updated information is received from the other subroutines.

Main Program
Appendix B

FORTRAN Program
1-D MODEL - ANODE-CATHODE

THE GAS DIFFUSION LAYER & CATALYST LAYER ARE MODELED.

MODEL-8

EXPLICIT MACCORMACK METHOD

ISOOTHERMAL MODEL

THIS SUBROUTINE CALCULATES THE PRIMITIVE VARIABLES AT A GIVEN POINT IN THE COMPUTATIONAL DOMAIN.

REFERENCE: COMPUTATIONAL FLUID MECHANICS AND HEAT TRANSFER SECOND EDITION

AUTHORS: JOHN C. TANNEHILL
          DALE A. ANDERSON
          RICHARD H. PLETCHER

PAGE: 625

THE DERIVATIVES APPEARING IN THE VISCOUS TERMS OF E, F, AND G MUST BE DIFFERENCED CORRECTLY IN ORDER TO MAINTAIN SECOND-ORDER ACCURACY. THIS IS ACCOMPLISHED IN THE FOLLOWING MANNER. THE X DERIVATIVE TERMS APPEARING IN E ARE DIFFERENCED IN THE OPPOSITE DIRECTION TO THAT USED FOR DE/DX, WHILE THE Y DERIVATIVES AND THE Z DERIVATIVES ARE APPROXIMATED WITH CENTRAL DIFFERENCES. LIKewise, THE Y DERIVATIVES TERMS APPEARING IN F AND THE Z DERIVATIVES TERMS APPEARING IN G ARE DIFFERENCED IN THE OPPOSITE DIRECTION TO THAT USED FOR DF/DY AND DG/DZ, RESPECTIVELY, WHILE THE CROSS-DERIVATIVES TERMS IN F AND G ARE APPROXIMATED WITH CENTRAL DIFFERENCES.

CH2OCL - CONCENTRATION OF WATER IN CATALYST LAYER

INTEGER PNT1, LOOP, LOOP1, I

DOUBLE PRECISION CH2(1:1000), DIFF, CH2MEM
DOUBLE PRECISION CH2O(1:1000)
DOUBLE PRECISION CH2OC(1:1000)
DOUBLE PRECISION CH21 (1:1000), DIFF2
DOUBLE PRECISION CH2O1(1:1000)
DOUBLE PRECISION CH23(1:1000)
DOUBLE PRECISION CH2O3(1:1000)
DOUBLE PRECISION CH2CL(1:1000), CH2OCL(1:1000)
DOUBLE PRECISION CH2GDL(1:1000), CHOGDL(1:1000)
DOUBLE PRECISION CO2C(1:1000), THCKCL
DOUBLE PRECISION CO2CLC(1:1000), CHOCLC(1:1000)
DOUBLE PRECISION DELTAT, DELTAX, OLDMAX, OLDMIN
DOUBLE PRECISION UVEL1, CH2IN, CH2MAX, CH2MIN
DOUBLE PRECISION XCH2IN, CH2MX, CH2MN
DOUBLE PRECISION OLDLMX, OLDLMN
DOUBLE PRECISION DNSTY1(1:1000)
DOUBLE PRECISION DNSTY2(1:1000)
DOUBLE PRECISION DNSTY3(1:1000)
DOUBLE PRECISION UVEC1(1:1000, 1:3)
DOUBLE PRECISION EWEC1(1:1000, 1:3)
PROGRAM MAC

\* LEXICON:
\* PNTI1 - NUMBER OF GRID POINTS
\* LOOP - NUMBER OF LOOPS
\* LOOP1 - NUMBER OF LOOPS
\* I, J, K ARE DUMMY VARIABLES THAT REPRESENT INTEGER COUNTERS.
\* CH2 - CONCENTRATION OF HYDROGEN
\* CH2O - CONCENTRATION OF WATER
\* CH2CL - CONCENTRATION OF HYDROGEN IN CATALYST LAYER

DOUBLE PRECISION PRESH2
DOUBLE PRECISION DH2H2O
DOUBLE PRECISION TX, DUMBX(1:1000)
DOUBLE PRECISION DMBX(1:1000)
DOUBLE PRECISION EX
DOUBLE PRECISION DE, GAMMA, MH2, MH2O
DOUBLE PRECISION THICK, RHODRY
DOUBLE PRECISION PRES02, CRRNTD, PERA
DOUBLE PRECISION CHOMAX, CHOMIN
DOUBLE PRECISION OLDMXH, OLDMNH
DOUBLE PRECISION CVCA, CVAN, NVMEM
DOUBLE PRECISION YVH20A, YVH20C
DOUBLE PRECISION CH2GUE(1:1000)
DOUBLE PRECISION CHOGUE(1:1000), CHOMX, CHOMN
DOUBLE PRECISION PERAGU

\* DOUBLE PRECISION UVCPS(1:1000, 1:3)
\* DOUBLE PRECISION UVCPS1(1:1000, 1:3)
\* DOUBLE PRECISION UVEC1N1(1:1000, 1:3)
\* DOUBLE PRECISION EVECN1(1:1000, 1:3)
\* DOUBLE PRECISION TEMP
\* DOUBLE PRECISION VS
\* DOUBLE PRECISION DELTAP
\* "HYDROGEN IN THE CHANNEL."
\* "THE PRESSURE IS IN PASCALS."
WRITE (*,*)

PRESH2 = 101325*2

WRITE (*,*) 'ENTER THE CONCENTRATION OF ',
+ 'WATER IN THE MEMBRANE. ',
+ 'THE WATER CONTENT OF THE MEMBRANE HAS ',
+ 'A VALUE BETWEEN 0 AND 14. '
WRITE (*,*)

GAMMA = 14

WRITE (*,*) 'ENTER THE CONCENTRATION OF ',
+ 'HYDROGEN AT THE INTERFACE. ',
+ 'THE HYDROGEN CONCENTRATION SHOULD BE ',
+ 'LESS THAN CONCENTRATION IN GAS CHANNEL. '
WRITE (*,*)

CH2(PNTI1) = PRESH2/(8.314*353.15)

WRITE (*,*) CH2(PNTI1)

CH2O(PNTI1) = 0.05*PRESH2/(8.314*353.15)

WRITE (*,*)
OPEN(UNIT1 = 55,
+ FILE =
+ '1D-AC-21-GTK5CTK05-P2ATM-071109-I0.25-V1.TXT',
+ STATUS = 'NEW')

* EXPPLICIT MACCORMACK METHOD

* NOTE: THE EXPPLICIT MACCORMACK METHOD REQUIRES THAT THE
* SYSTEM BE GIVEN AN INITIAL GUESS, AND THE PROGRAM
* WILL ITERATE TO THE FINAL STEADY STATE SOLUTION.

***X***********************************************************************
** STEP 1 - DATA ENTRY
 ***X***********************************************************************

WRITE (55,'(A)') 'ANODE DATA'
WRITE (',')
WRITE (',')'ENTER THE NUMBER OF POINTS',
+ 'IN I DIRECTION',
+ 'THE MAXIMUM NUMBER OF POINTS IS 1000.'
WRITE (',')
PNT11 = 21

WRITE (',')
WRITE (',')'ENTER THE NUMBER OF LOOPS',
+ 'TO BE EXECUTED',
+ 'THIS PARAMETER HAS NOT LIMIT.'
WRITE (',')
LOOP1 = 1000000

WRITE (',')
WRITE (',')'ENTER THE PRESSURE OF THE',
CH20(I) = CH20(PNT11)

11070 CONTINUE

DO 11075 I = 1, PNT11
CH2(I) = CH2(PNT11)
CH20(I) = CH20(PNT11)
11075 CONTINUE

DO 11102 K = 1, 500

11102 CONTINUE

CALL CLAND(LOOP1, PNT11,
+ CH2GUE, CHOGUE, CRRNTD,
+ CH2CL, CH2CL)

***X***********************************************************************
** STEP 7 - REPLACE OLD VALUES - GUESS
 ***X***********************************************************************

***X***********************************************************************
** STEP 8 - SETS INTERFACE HYDROGEN CONCENTRATION
 ***X***********************************************************************

CH2(PNT11) = CH2IN
* STEP 2 - GDL ANODE - SUBROUTINE

CALL GDLAND (CRRNTD, LOOP1, PNTI1, PRESH2, + GAMMA, CH2, CH2O, CH2GDL, CHOGDL)

* STEP 3 - COMPARISON - SUBROUTINE

CALL COMPRAG(CH2MAX, CH2MIN, PNTI1, + THCK, CH2GDL, CRRNTD, CH2IN, OLDMAX, + OLDMIN, PERA)

CH2MAX = OLDMAX
CH2MIN = OLDMIN
DUMBX(K) = CH2IN

* STEP 4 - REPLACE OLD VALUES

DO 110801 = 1, PNTI1
CH2(I) = CH2GDL(I)
CH2O(I) = CHOGDL(I)
11080 CONTINUE

* STEP 5 - CL ANODE GUESS - SUBROUTINE

CALL GDLCLA (CRRNTD, LOOP1, PNTI1, CH2(PNTI1), + GAMMA, CH21, CH2O1, CH2GUE, CHOGUE)

THCKCL = 0.00005
CALL CMPRAG(CH2MX, CH2MN, PNTI1, THCKCL, CH2GUE, CRRNTD, XCH2IN, OLDMAX, + OLDMIN, PERAGU)

CH2MX = OLDMAX
CH2MN = OLDMIN

* STEP 6 - COMPARISON - SUBROUTINE

DO 19010 I = 1, PNTI1
DO 19040 L = 1, 3

DO 19030 I = 1, PNTI2

DO 19040 L = 1, 3

CH21(PNTI1) = XCH2IN
DIFF = 0.0
DIFF = DUMBX(K) - DUMBX(K-5)
WRITE (,*)
WRITE (*,*) 'K =',K,'PERCENT GDL'.PERA,'PERCENT GUESS',PERAGU
WRITE (,*)
WRITE (*,*'APREAL(0.01))GOTO 11103

IF (ABS(DIFF) LT 0.001*DUMBX(K)) .AND. + (K.GT. 20) AND. (PERA LE. 0.01) + AND. (PERAGU LE. 0.01)) GOTO 11103

11102 CONTINUE
11103 CONTINUE

WRITE (55,*) CH2(I),',', CH2O(I)
WRITE (*,*) CH2(I),',', CH2O(I)
19010 CONTINUE

WRITE (55,*) CH2CL(I),',', CH2OCL(I)
WRITE (*,*) CH2CL(I),',', CH2OCL(I)
19030 CONTINUE

DMBX(K) = CH2IN

11105 CONTINUE

PRES02 = PRESH2

CALL CTHDE (CRRNTD, LOOP1, PNTI1, GAMMA, CH2, PRESH2,
+ PRES02, CO2C, CH2OC, CO2CLC, CHOCLC)

YVH20A = CH2OCL(PNTI1)/((CH2CL(PNTI1) + CH2OCL(PNTI1))

WRITE (*, *) 'MOLE FRACTION OF WATER (ANODE)', YVH20A

WRITE (*, *)

YVH20C = CHOCLC(PNTI1)/(C02CLC(PNTI1) + CHOCLC(PNTI1))

CALL MMBRNE (CRRNTD, YVH20A, YVH20C, PRESH2,
+ PRES02, CVCA, CVAN, NVMEM)

END

***x**************************************************************************

* PREDIC = PREDICTOR SUBROUTINE - FORWARD DIRECTION

**************************************************************************

SUBROUTINE PREDIC(PNTI2,
+ DT, DX,
+ UVEC, EVEC, EWC, HVEC, UVCP1S)

DOUBLE PRECISION DT, DX

INTEGER PNTI2

DOUBLE PRECISION UVEC(1:1000, 1:3)

DOUBLE PRECISION EVEC(1:1000, 1:3)

DOUBLE PRECISION EWC(1:1000, 1:3)

DOUBLE PRECISION UVCP1S(1:1000, 1:3)

DOUBLE PRECISION EE(1:1000, 1:3)

DOUBLE PRECISION HVEC(1:1000, 1:3)

DO 19120 L = 1, PNTI2

DO 19150 L = 1, 3

EE(I,L) = EVEC(I,L) - EWC(I,L)

19150 CONTINUE

19120 CONTINUE

**************************************************************************

* CORREC = CREDITOR SUBROUTINE - FORWARDS

**************************************************************************

SUBROUTINE CORREC(PNTI2,
+ DT, DX,
+ UVECP1, UVEC, EVEC, EVVC, HVEC, UVCP1)

DOUBLE PRECISION DT, DX

INTEGER PNTI2

DOUBLE PRECISION UVEC(1:1000, 1:3)

DOUBLE PRECISION EVEC(1:1000, 1:3)

DOUBLE PRECISION EVC(1:1000, 1:3)

DOUBLE PRECISION UVCP1(1:1000, 1:3)

DOUBLE PRECISION UVECP1(1:1000, 1:3)

DOUBLE PRECISION EE(1:1000, 1:3)

DOUBLE PRECISION HVEC(1:1000, 1:3)

DO 19120 I = 1, PNTI2

DO 19150 L = 1, 3

EE(I,L) = EVEC(I,L) - EVVC(I,L)

19150 CONTINUE

19120 CONTINUE

**************************************************************************

* DT/DX(EI,J,K - EI-1,J,K)

**************************************************************************
EE(I,L) = EVEC(I,L) - EWC(I,L)

DO 19150 CONTINUE
19150 CONTINUE

19120 CONTINUE

***x******************************************************************************
* - DT/DX*(EE(I+1,L) - EE(I,L)) + DT*HVEC(I,L)
***x******************************************************************************

DO 19010 I = 1, PNTI2-1
DO 19020 L = 1, 3
UVCP1S(I,L) = UVEC(I,L) + - DT/DX*(EE(I+1,L) - EE(I,L)) + DT*HVEC(I,L)
19020 CONTINUE
20010 CONTINUE

DO 20030 I = 1, PNTI2
DO 20040 L = 1, 3
UVCP1(I,L) = 0.5*(UVEC(I,L) + UVEC1(I,L) + -DT/DX*(EE(I,L)-EE(I-1,L)) + DT*HVEC(I,L))
20040 CONTINUE
20030 CONTINUE

RETURN
END

SUBROUTINE CRRECB(PNTI2,
+ DT, DX,
+ UVEC, EVEC, EWC, HVEC, UVCP1)
DOUBLE PRECISION DT, DX
INTEGER PNTI2
DOUBLE PRECISION UVEC(1:1000, 1:3)
DOUBLE PRECISION EVEC(1:1000, 1:3)

SUBROUTINE MATADD(PNTI3, MAT1, MAT2, MAT3)
INTEGER I, PNTI3
DOUBLE PRECISION MAT1(1:1000)
DOUBLE PRECISION MAT2(1:1000)
DOUBLE PRECISION MAT3(1:1000)
DO 16010 I = 1, PNTI3
MAT3(I) = MAT1(I) + MAT2(I)
16010 CONTINUE
RETURN
END

SUBROUTINE MTMULS (PNTI3,
DOUBLE PRECISION EVVC(1:1000, 1:3)
DOUBLE PRECISION UVEC(1:1000, 1:3)
DOUBLE PRECISION UVEC(1:1000, 1:3)
DOUBLE PRECISION EE(1:1000, 1:3)
DOUBLE PRECISION HVEC(1:1000, 1:3)

DO 19120 I = 1, PNTI2
  DO 19150 L = 1,3
    EE(I,L) = EVEC(I,L) - EWC(I,L)
  19150 CONTINUE
  19120 CONTINUE

***"X * ...........

* - DT/DX(EI+1,J,K) - EE(I,L) - EE(I,L) + DT*HVEC(I,L))

20010 CONTINUE

RETURN
END

SUBROUTINE UVEC(EX, CH2, CH20, PNTI2, DNSTY, UVCTR)

...-

VARIABLE DEFINITIONS:
* U = FILTRATION VELOCITY
* DENST = DENSITY

SCAL1, MAM, MAlii)
* MTMULS = MATRIX MULTIPLICATION BY A SCALAR - SUBROUTINE

INTEGER I, J, K, PNTI3, PNTJ3, PNTK3
DOUBLE PRECISION MAT1(1:1000, 1:3)
DOUBLE PRECISION MAT2(1:1000, 1:3)
DOUBLE PRECISION SCAL1

DO 17010 I = 1, PNTI3
  DO 17020 L = 1,3
    MAT2(I, L) = SCAL1 * MAT1(I, L)
  17020 CONTINUE

DOUBLE PRECISION U
DOUBLE PRECISION DNSTY(1:1000)
DOUBLE PRECISION CH2(1:1000)
DOUBLE PRECISION CH20(1:1000)
DOUBLE PRECISION E1VCTR(1:1000, 1:3)
DOUBLE PRECISION P
DOUBLE PRECISION R, TEMP

...-

SUBROUTINE UVEC(Ex, CH2, CH20, PNTI2, + DNSTY, UVCTR)
DOUBLE PRECISION DNSTY(1:1000)

DOUBLE PRECISION UVCTR(1:1000, 1:3)

DOUBLE PRECISION R, TEMP

DOUBLE PRECISION EX

* VARIABLE DEFINITIONS:
* DNSTY = DENSITY
* R = UNIVERSAL GAS CONSTANT
* CH2 = MOLAR CONCENTRATION OF HYDROGEN
* CH2O = MOLAR CONCENTRATION OF WATER
* EX = POROSITY
* UVCTR = SOLUTION VECTOR (ANSWER STORED HERE)

R = 8.314

TEMP = 353.15

DO 12010 I = 1, PNTI2
  UVCTR(I,1) = EX*DNSTY(I)
  UVCTR(I,2) = EX*CH2(I)
  UVCTR(I,3) = EX*CH2O(I)
12010 CONTINUE

RETURN

END

SUBROUTINE EVEC(CH2, CH20, PNTI3, U, DNSTY, EIVCTR)

DOUBLE PRECISION CH2O(1:1000)

DOUBLE PRECISION DNSTY(1:1000), GAMMA, OMEGA

R = 8.314

TEMP = 353.15

DO 13010 I = 1, PNTI3
  EIVCTR(I,1) = DNSTY(I)*U
  EIVCTR(I,2) = U*CH2(I)
  EIVCTR(I,3) = U*CH2O(I)
13010 CONTINUE

RETURN

END

SUBROUTINE EWEC(DE, CH2, CH20, PNTI3, DNSTY, DX, EWCTR)

INTEGER I, PNTI3

DOUBLE PRECISION DX, TEMP, DE

DOUBLE PRECISION CH2(1:1000)

* PVARN(1) = DENSITY
* PVARN(2) = CONCENTRATION OF HYDROGEN
* PVARN(3) = CONCENTRATION OF WATER

R = 8.314

MH2 = 2
DOUBLE PRECISION R

**X**..............................................
*
* VARIABLE DEFINITIONS:
*
* U = U VELOCITY
*
* DENST = DENSITY
*
* R = UNIVERSAL GAS CONSTANT
*
* DE = EFFECTIVE DIFFUSIVITY
*
* P = PRESSURE ASSUMING THAT THE GAS IS AN IDEAL GAS
*
* EVCTR = EI VECTOR
*
**X**..............................................

R = 8.314

TEMP = 353.15

DO 13010 I = 2, PNTI3

EWCTR(I,1) = 0.0

EWCTR(I,2) = DE*(CH2(I) - CH2(I-1))/DX

EWCTR(I,3) = DE*(CH20(I) - CH20(I-1))/DX

13010 CONTINUE

RETURN

END

**X**..............................................
*
* CALCULATES THE RESIDUALS.
***
**X**..............................................
*

SUBROUTINE FRESID(N, C, BK, XRXSID)

DOUBLE PRECISION XRXSID

DOUBLE PRECISION C(1:1000), BK(1:1000)

INTEGER I, N

XRXSID = 0.0

DO 700 I = 1, N

XRXSID = XRXSID + ABS(C(I) - BK(I))

700 CONTINUE

RETURN

END

**X**..............................................
*
* CALCULATES THE COMPARISON.
***
DOUBLE PRECISION K, GAMMA, EX

***X-------------------------------------------------------------------------------------
.
* THIS SUBROUTINE CALCULATES THE PRIMITIVE VARIABLES.  
***X-------------------------------------------------------------------------------------

***X-------------------------------------------------------------------------------------
.
* VARIABLE DEFINITIONS:
  DOUBLE PRECISION FLXGDL, FLXCL, DIFF1, DLTXCL
  DOUBLE PRECISION CO2GDL(1:1000), NEWMAX, NEWMIN
  DOUBLE PRECISION CO2CL(1:1000)
  DOUBLE PRECISION DELTAX, CO2MAX, CO2MIN, THICK
  INTEGER PNT11
  DOUBLE PRECISION CO2IN, ERRXR

WRITE ('', *)
WRITE ('', *) THICK =
DOUBLE PRECISION CH2O3(1:1000)
WRITE (*,*)
DOUBLE PRECISION DELTAT, DELTAX
DELTAX = THICK/(PNT11-1)
DLTXCL = THICK/(PNT11-1)/10
FLXGDL = (CO2GDL(PNT11) - CO2GDL(PNT11-1))/DELTAX
FLXCL = (CO2CL(2) - CO2CL(1))/DLTXCL
DIFF1 = FLXGDL-FLXCL
ERRXR = 0.25*FLXGDL
CO2IN = CO2GDL(PNT11)
IF (ABS(DIFF1) LT. ERRXR) THEN
  CO2IN = CO2GDL(PNT11)
ELSEIF (ABS(DIFF1) GE. ERRXR) THEN
  IF (FLXGDL .GT. FLXCL) THEN
    NEWMAX = CO2IN
    NEWMIN = CO2MIN
    CO2IN = (CO2MAX + CO2MIN)/2.0
  ELSE
    NEWMAX = CO2IN
    NEWMIN = CO2MIN
    CO2IN = (CO2MAX + CO2MIN)/2.0
  END IF
END IF

SUBROUTINE GDLAND(CRRNITD, LOOP1, PNT11, PRESH2, 
  + GAMMA, CH2, CH20, CH23, CH203)
  INTEGER I, PNT11, NUM8, LOOP, LOOP1
  INTEGER XRESX1
  DOUBLE PRECISION CH2(1:1000)
  DOUBLE PRECISION CH20(1:1000)
  DOUBLE PRECISION CH23(1:1000)
ELSEIF (FLXCL .GT. FLXGDL) THEN

NEWMAX = CO2MAX
NEWMIN = CO2IN
CO2IN = (CO2MAX + CO2MIN)/2.0

ENDIF

ENDIF

WRITE (55, *)
WRITE (55, *) 'VALUE OF INTERFACE', CO2IN
WRITE (55, *)
WRITE (*, *) 'VALUE OF INTERFACE ', CO2IN
RETURN
END

DOUBLE PRECISION UVEC1(1:1000, 1:3)
DOUBLE PRECISION EVEC1(1:1000, 1:3)
DOUBLE PRECISION EWEC1 = DIFFUSIVE PART OF E VECTOR
DOUBLE PRECISION UVEC1 = U VECTOR
DOUBLE PRECISION EVEC1 = E VECTOR
DOUBLE PRECISION THICK, RHODRY
EW= 1.1
DOUBLE PRECISION HVEC1(1:1000, 1:3)
DOUBLE PRECISION HVEC1N(1:1000, 1:3)
DOUBLE PRECISION CRRNTD

*> RHODRY IS THE DRY MEMBRANE DENSITY IN UNITS OF
*KILOGRAMS* PER METER CUBED.

* RHODRY = 1980

*> DH2H2O IS THE DIFFUSIVITY OF HYDROGEN AND WATER IN THE
* ANODE GAS CHANNEL IN UNITS OF METERS SQUARED PER
* SECOND.

* DH2H2O = 1.1028E-4

*> THE THICKNESS THICK IS THICKNESS OF GAS DIFFUSION
* LAYER

*> IN METERS.
* KHUUKY = KHUUKY IS THE DRY MEMBRANE DENSITY IN UNITS OF KILOGRAMS
* PER METER CUBED.

  THICK = 0.00005

* DH2H20 = DIFFUSIVITY OF HYDROGEN THROUGH WATER (BINARY)

  DELTAX = THICK/(PNTI1-1.0)

* THICK = THICKNESS OF GAS DIFFUSION LAYER

  DELTAX = SPATIAL STEP IN X DIRECTION

* DELTAT = TIME STEP

  DELTAX = SPATIAL STEP IN X DIRECTION

* VS = VS IS THE VISCOITY OF HYDROGEN IN PASCAL-SECONDS,

  DELTAT = DELTAX*0.0005

* DELTAP = CHANGE IN PRESSURE BETWEEN ANODE AND CATHODE

  DELTAP = 28.826 CURRENT

* EX = EX IS THE POROSITY AND IS DIMENSIONLESS.

  VS = 0.0000086

* TX = TORTUOSITY

  TX = 10

* DE = EFFECTIVE DIFFUSIVITY

  TX = THE EFFECTIVE DIFFUSIVITY.

* KPER = KPER IS PERMEABILITY OF ANODE/CATHODE GAS DIFFUSION

  LAYER. THE PERMEABILITY IS IN METERS SQUARED.

* R = UNIVERSAL GAS CONSTANT

  EX = 0.5

* MH2 = MOLECULAR WEIGHT OF HYDROGEN GAS

* MH20 = MOLECULAR WEIGHT OF WATER

* UVEL1 = FILTRATION VELOCITY IN X DIRECTION (CONSTANT)

* CH2( ) = CONCENTRATION OF HYDROGEN ARRAY

* CH20 ( ) = CONCENTRATION OF WATER ARRAY

* DNSTY1 ( ) = DENSITY ARRAY

* GAMMA = C/V

* PRESH2 = HYDROGEN PRESSURE IN GAS CHANNEL

* PNTI1 = LOCATION IN X DIRECTION (GRID POINT)

  CALL UVEC(EX, CH2, CH2O, PNTI1, DNSTY1, UVEC1)

  CALL EVEC(CH2, CH2O, PNTI1, UVEL1, DNSTY1, EVEC1)

  CALL ODDEVE(LOOP, NUM8)

  CALL EVVEC(DE, CH2, CH2O, PNTI1, DNSTY1, + DELTAX, EVEC1)

  IF (NUM8 .EQ. 1) THEN
\[ U = U_{H2} + \frac{U_{H20}}{X} \]

KPER is permeability of anode/cathode gas diffusion layer. The permeability is in meters squared.

**\( \text{KPER} = 1.12 \times 10^{-14} \)**

**\( \text{R} \) is the universal gas constant in J K^{-1} mol^{-1}.**

**\( \text{R} = 8.314 \)**

**\( \text{TEMP} \) is the temperature in Kelvin.**

**\( \text{TEMP} = 353.15 \)**

**\( \text{UVEL1} \) is the filtration velocity in meters/second.**

**\( \text{UVEL1} = \text{KPER} * \frac{\Delta 	ext{P}}{(\text{VS} \times \text{TTHICK})} \)**

**\( \text{MH2} \) is the molecular weight of hydrogen.**

**\( \text{MH2} = 2 \)**

**\( \text{MH20} \) is the molecular weight of water.**

**\( \text{MH20} = 18 \)**

**\( \text{DO 11071} \) I = 1, PNTI1**

\[
\begin{align*}
\text{HVEC1(I, 1)} & = 0.0 \\
\text{HVEC1(I, 2)} & = 0.0 \\
\text{HVEC1(I, 3)} & = 0.0 \\
\text{HVEC1(I, 4)} & = 0.0 \\
\text{HVEC1(I, 5)} & = 0.0 \\
\text{HVEC1(I, 6)} & = 0.0 \\
\text{HVEC1(I, 7)} & = 0.0 \\
\text{HVEC1(I, 8)} & = 0.0 \\
\text{HVEC1(I, 9)} & = 0.0 \\
\end{align*}
\]

**\( \text{11071 CONTINUE} \)**

**Extra Text:**

\[ \text{DO 11105} \] I = 1, PNTI1

* WRITE (65, *) CH2(I), CH20(I), DNSTY3(I)

**\( \text{ELSE IF} \) (NUM8 .EQ. 0) THEN**

**\( \text{CALL PRDCIB} \) (PNTI1, + DELTAT, DELTAX, + UVEC1, EVEC1, EVEC1, HVEC1, UVCP1S)**

**\( \text{ENDIF} \)**

**\( \text{CALL EVECB} \) (DE, CH2, CH20, PNTI1, DNSTY1, + DELTAX, EVEC1)**

**\( \text{ENDIF} \)**

**\( \text{CALL PRIM} \) (EX, PNTI1, UVCP1S, + DNSTY2, CH21, CH201)**

**\( \text{DO 11105} \) I = 1, PNTI1

* WRITE (65, *) CH2(I), CH20(I), DNSTY3(I)
DO 11200 LOOP = 1, LOOP1

CH2(1) = PRESH2/(R*TEMP)

CH20(1) = 0.05*PRESH2/(R*TEMP)

DNSTY1(1) = MH2*CH2(1) + MH20*CH20(1)

DNSTY1(PNTI1) = MH2*CH2(PNTI1)+ MH20*CH20(PNTI1)

CALL EWEC(DE, CH21, CH201, PNTI1, DNSTY2, + DELTAX, EWC1S)

ELSE IF (NUM8 .EQ. 0) THEN

CALL EWECB(DE, CH21, CH201, PNTI1, DNSTY2, + DELTAX, EVC1S)

ENDIF

STEP NO. 6 - CORRECTION

IF(NUM8.EQ.1)THEN

CALL CORREC(PNTI1, + DELTAT, DELTAX, + UVECN1, UVEC1, EVECN1, EVC1S, HVECN1, UVCP1)

ELSE IF (NUM8 .EQ. 0) THEN

CALL CRRECDB(PNTI1, + DELTAT, DELTAX, + UVECN1, UVEC1, EVECN1, EVC1S, HVECN1, UVCP1)

ENDIF

STEP NO. 7 - CALCULATE THE PRIMITIVE VARIABLE VALUES.

CALL PRIMI(EX, PNTI1, UVCP1, + DNSTY3, CH23, CH203)

CALL CNVRG (PNTI1, CH2, CH23, XRESX1)

DO 11100 I = 1, PNTI1

DNSTY1(I) = DNSTY3(I)

11105 CONTINUE

RETURN

END
CH2(I) = CH23(I)
CH20(I) = CH203(I)

11100 CONTINUE
IF ((XRESX1 GT PNTI1*0.90).AND. (LOOP GT 750000)) GOTO 11201
11200 CONTINUE
11201 CONTINUE
WRITE (55,*) 'LOOP = ', LOOP
RETURN
END

SUBROUTINE ODDEVE(PNTI3, NUM9)
INTEGER NUM5, NUM6, NUM7, NUM9
INTEGER PNTI3, NUM4
NUM5 = (-1)**(PNTI3)
IF (NUM5 .EQ. 1) THEN
NUM9 = 1
ELSE IF (NUM5 .EQ. -1) THEN
NUM9 = 0
ENDIF
RETURN
END

SUBROUTINE HVEC(DELTAT, CRRNTD, CH2, PNTI4, HVCTR)
INTEGER I, PNTI4
DOUBLE PRECISION CH2(1:1000)
DOUBLE PRECISION HVCTR(1:1000, 1:3)
DOUBLE PRECISION CRRNTD
DOUBLE PRECISION CRRNT

* EVEC = E VECTOR CALCULATOR SUBROUTINE
* VARIABLE DEFINITIONS:

* PREDIC = PREDICTOR SUBROUTINE - BACKWARD ITERATION
* VARIABLE DEFINITIONS:
SUBROUTINE HVEC(PNTI2, DT, DX, UVEC, EVEC, HVEC, UVCP1S)

DOUBLE PRECISION DT, DX
INTEGER PNTI2
DOUBLE PRECISION UVEC(1:1000, 1:3)
DOUBLE PRECISION EVEC(1:1000, 1:3)
DOUBLE PRECISION HVEC(1:1000, 1:3)
DOUBLE PRECISION EE(1:1000, 1:3)
DOUBLE PRECISION UVCP1S(1:1000, 1:3)

DO 19120 I = PNTI2, 1,-1
  DO 19150 L = 1,3
    EE(I,L) = EVEC(I,L) - EVEC(I,L)
  19150 CONTINUE
  19120 CONTINUE

CRRNT = CRRNTD*(100**2)

DO 13010 I = 1, PNTI4
  HVCTR(I,1) = 0.0
  HVCTR(I,2) = (CRRNTD/(2.0*96485))
  HVCTR(I,3) = 0.0
13010 CONTINUE

RETURN
END

SUBROUTINE COMCL(PNTI1, MXTRXN(1:1000), I, VLE, XGRID)

VLE = 0
DO 29010 1 = 1, XGRID
  IF (ABS((MXTRXN(I) - MXTRXO(I))) .LT. 0.001*MXTRXN(I)) THEN
    VLE = VLE + 1
  ELSE
    VLE = VLE + 0
  ENDIF
29010 CONTINUE

RETURN
END

* CALCULATES THE COMPARISON AND THE NEWTON-RAPHSON METHOD.

SUBROUTINE HVEC(PNTI2, DT, DX, UVEC, EVEC, HVEC, UVCP1S)

DOUBLE PRECISION DT, DX
INTEGER PNTI2
DOUBLE PRECISION UVEC(1:1000, 1:3)
DOUBLE PRECISION EVEC(1:1000, 1:3)
DOUBLE PRECISION HVEC(1:1000, 1:3)
DOUBLE PRECISION EE(1:1000, 1:3)
DOUBLE PRECISION UVCP1S(1:1000, 1:3)

DO 19120 I = PNTI2, 1,-1
  DO 19150 L = 1,3
    EE(I,L) = EVEC(I,L) - EVEC(I,L)
  19150 CONTINUE
  19120 CONTINUE

CRRNT = CRRNTD*(100**2)

DO 13010 I = 1, PNTI4
  HVCTR(I,1) = 0.0
  HVCTR(I,2) = (CRRNTD/(2.0*96485))
  HVCTR(I,3) = 0.0
13010 CONTINUE

RETURN
END

SUBROUTINE COMCL(PNTI1, MXTRXN(1:1000), I, VLE, XGRID)

VLE = 0
DO 29010 1 = 1, XGRID
  IF (ABS((MXTRXN(I) - MXTRXO(I))) .LT. 0.001*MXTRXN(I)) THEN
    VLE = VLE + 1
  ELSE
    VLE = VLE + 0
  ENDIF
29010 CONTINUE

RETURN
END
\[ DM_{\text{mem}} = \frac{Z_{\beta_0} - I_U}{1.1028 \times 10^{-4}} \]

\[ DE_{\text{H}_2O} = 1.1028 \times 10^{-4} \]

\[ \Delta = \frac{\text{THICK}}{\text{PNTI1}/10} \]

\[ D_{\text{LTXCL}} = \frac{\text{THICK}}{\text{PNTI1}/10} \]

\[ FL_{\text{MEM}} = DM_{\text{MEM}} \times (CH_{\text{MEM}})/DE_{\text{LTX}} \]

\[ FL_{\text{CL}} = DH_{\text{H}_2O} \times (CH_{\text{CL}(PNTI1)} \]

\[ + - CH_{\text{CL}(PNTI1-1)}/DL_{\text{TXCL}} \]

\[ \text{DIFF} = FL_{\text{MEM}} - FL_{\text{CL}} \]

\[ \text{ERRXR} = FL_{\text{MEM}} ^{0.05} \]

\[ \text{IF (ABS(DIFF) .LT. ERRXR) THEN} \]

\[ \text{CH}_{\text{MEM}} = \text{CH}_{\text{CL}(PNTI1)} \]

\[ \text{ELSEIF (ABS(DIFF) .GE. ERRXR) THEN} \]

\[ \text{IF (FLXMEM .GT. FLXCL) THEN} \]

\[ \text{CH}_{\text{MEM}} = \text{CH}_{\text{MEM}} ^{0.95} \]

\[ \text{ELSEIF (FLXCL .GT. FLXMEM) THEN} \]

\[ \text{CH}_{\text{MEM}} = \text{CH}_{\text{MEM}} ^{1.09} \]

\[ \text{ENDIF} \]

\[ \text{ENDIF} \]

\[ \text{WRITE (55, *)} \]

\[ \text{WRITE (55, *) \ 'VALUE OF CL-MEMBRANE INTERFACE',} \]

\[ \text{CH}_{\text{MEM}} \]

\[ \text{WRITE (55, *)} \]

\[ \text{WRITE (*, *) \ 'VALUE OF CL-MEMBRANE INTERFACE',} \]

\[ \text{CH}_{\text{MEM}} \]

\[ \text{WRITE (*, *)} \]

\[ \text{RETURN} \]

\[ \text{END} \]

---

* This subroutine checks the convergences (CNVRG).

---

* EVEC = E VECTOR CALCULATOR SUBROUTINE
SUBROUTINE CNVRG (XGRID, MXTRXO, MXTRXN, VLE)
DOUBLE PRECISION MXTRXO(1:1000)
DO 12010 I = 1, PNTI2
UVCTR(I,1) = EX*DNSTY(I)
UVCTR(I,2) = EX*C02(I)
UVCTR(I,3) = EX*CH2O(I)
12010 CONTINUE
RETURN
END

SUBROUTINE EVECO(C02, CH20, PNTI3,
+ U, DNSTY, EIVCTR)
EVEC = E VECTOR CALCULATOR SUBROUTINE
INTEGER I, PNTI3
DOUBLE PRECISION U
DOUBLE PRECISION DNSTY(1:1000)
DOUBLE PRECISION CO2(1:1000)
DOUBLE PRECISION CH2O(1:1000)
DOUBLE PRECISION EIVCTR(1:1000, 1:3)
DOUBLE PRECISION R
DOUBLE PRECISION TEMP

DO 13010 I = 2, PNTI3
EIVCTR(I,1) = 0.0
EIVCTR(I,2) = DE02*(C02(I) - C02(I-1))/DX
EIVCTR(I,3) = DEH2O*(CH2O(I) - CH2O(I-1))/DX
13010 CONTINUE
RETURN
END

SUBROUTINE PRIMIO(EX, PNTI2, NEWU,
* EIVCTR = EI VECTOR

* EIVCTR(I,1) = DNSTY(I)*U
* EIVCTR(I,2) = U*CO2(I)
* EIVCTR(I,3) = U*CH2O(I)

R = 8.314

TEMP = 353.15

DO 13010 I = 1, PNTI3
  EIVCTR(I,1) = DNSTY(I)*U
  EIVCTR(I,2) = U*CO2(I)
  EIVCTR(I,3) = U*CH2O(I)
13010 CONTINUE

DOUBLE PRECISION CH2O1(1:1000)
DOUBLE PRECISION CO21(1:1000)
DOUBLE PRECISION DENN1(1:1000)
DOUBLE PRECISION PVARN(1:1000, 1:3)
DOUBLE PRECISION R, GAMMA, EX

* THIS SUBROUTINE CALCULATES THE PRIMITIVE VARIABLES.

* VARIABLE DEFINITIONS:
* PVARN(1) = DENSITY
* PVARN(2) = CONCENTRATION OF OXYGEN
* PVARN(3) = CONCENTRATION OF WATER

R = 8.314
M02 = 32
MH20 = 18

DO 70010 I = 1, PNTI2
  EIVCTR(I,1) = DNSTY(I)*U
  EIVCTR(I,2) = U*CO2(I)
  EIVCTR(I,3) = U*CH2O(I)
70010 CONTINUE

DOUBLE PRECISION CH2O1(1:1000)
DOUBLE PRECISION CO21(1:1000)
DOUBLE PRECISION DENN1(1:1000)
DOUBLE PRECISION PVARN(1:1000, 1:3)
DOUBLE PRECISION R, GAMMA, EX

* THIS SUBROUTINE CALCULATES THE PRIMITIVE VARIABLES.

* VARIABLE DEFINITIONS:
* PVARN(1) = DENSITY
* PVARN(2) = CONCENTRATION OF OXYGEN
* PVARN(3) = CONCENTRATION OF WATER

R = 8.314
M02 = 32
MH20 = 18

DO 70010 I = 1, PNTI2
PVARN(I,3) = NEWU(I,3)/EX
PVARN(I,2) = NEWU(I,2)/EX
PVARN(I,1) = (PVARN(I,2)*MO2 + PVARN(I,3)*MH20)/EX

70010 CONTINUE
DO 70040 I = 1, PNTI2
  DENN1(I) = PVARN(I,1)
  C021(I) = PVARN(I,2)
  CH201(I) = PVARN(I,3)
70040 CONTINUE
RETURN

* CALCULATES THE COMPARISON.

SUBROUTINE XCMPRX(C02MAX, C02MIN, PNTI1, THICK, C02GDL, C02CL, C02IN, NEWMAX, NEWMIN)
DOUBLE PRECISION FLXGDL, FLXCL, DIFF1, DLTXCL
DOUBLE PRECISION CO2GDL(1:1000), NEWMAX, NEWMIN
DOUBLE PRECISION CO2CL(1:1000)
DOUBLE PRECISION UVEL3
DOUBLE PRECISION DNSTY3(1:1000)
DOUBLE PRECISION UVEC1(1:1000, 1:3)
DOUBLE PRECISION EVEC1(1:1000, 1:3)
DOUBLE PRECISION EWEC1(1:1000, 1:3)
DOUBLE PRECISION EWC1S(1:1000, 1:3)
DOUBLE PRECISION UVCP1S(1:1000, 1:3)
DOUBLE PRECISION UVCP1(1:1000, 1:3)
DOUBLE PRECISION UVECN1(1:1000, 1:3)
DOUBLE PRECISION EVECN1(1:1000, 1:3)
DOUBLE PRECISION TEMP
DOUBLE PRECISION VS
DOUBLE PRECISION KPER
DOUBLE PRECISION DELTAP
DOUBLE PRECISION PRES02, PRSH20

- AND (C02MAX .EQ. C02MIN)) THEN
  NEWMAX = CO2MAX
  NEWMIN = CO2MIN
  CO2IN = (CO2MAX)/2.0
  WRITE (*)
  WRITE (*) 'FLXGDL > FLXCL', C02IN
  WRITE (*) 'MAX =', NEWMAX, 'MIN', NEWMIN
  WRITE (*) 'EQUAL'
  WRITE (*)

ELSEIF ((FLXCL GT FLXGDL) .AND. (C02MAX .EQ. C02MIN)) THEN
  NEWMAX = C02IN
  NEWMIN = C02MIN
  CO2IN = (CO2MAX + CO2MIN)/2.0
  WRITE (*)
  WRITE (*) 'FLXGDL > FLXCL', C02IN
  WRITE (*) 'MAX =', NEWMAX, 'MIN', NEWMIN
  WRITE (*) 'EQUAL'
  WRITE (*)

ELSEIF ((FLXCL GT FLXGDL) .AND. (C02MAX .NE. C02MIN)) THEN
  NEWMAX = C02IN
  NEWMIN = C02MIN
  C02IN = (C02MAX + C02MIN)/2.0
  WRITE (*)
  WRITE (*) 'FLXCL > FLXGDL'
  WRITE (*) 'MAX =', NEWMAX, 'MIN', NEWMIN
  WRITE (*)

ELSEIF ((FLXCL GT FLXGDL) .AND. (C02MAX .EQ. C02MIN)) THEN
  NEWMAX = CO2MAX
  NEWMIN = CO2MIN
  CO2IN = (CO2MAX)/2.0
  WRITE (*)
  WRITE (*) 'FLXGDL > FLXCL', C02IN
  WRITE (*) 'MAX =', NEWMAX, 'MIN', NEWMIN
  WRITE (*) 'EQUAL'
  WRITE (*)

END
DOUBLE PRECISION UU2, UHidU

 ENDIF

 * WRITE (55, *)
 * WRITE (55, *) 'VALUE OF INTERFACE ', CO2IN
 * WRITE (55, *)

 * WRITE (' ', Datum)
 * WRITE (' ', Datum) 'VALUE OF INTERFACE ', CO2IN

 RETURN

 END

 DOUBLE PRECISION UO2, UH2O

 END

 *** X - GAS DIFFUSION LAYER SUBROUTINE

 SUBROUTINE GDLCTO(CRRNTD, LOOP1, PNTI1, PRESO2, PRSH20, GAMMA, C02, CH20, C023, CH203)

 INTEGER I, PNTI1, NUM8, LOOP, LOOP1
 INTEGER XRESX1
 DOUBLE PRECISION CO2(1:1000), CRRNTD
 DOUBLE PRECISION CH2O(1:1000)
 DOUBLE PRECISION CO21(1:1000)
 DOUBLE PRECISION CH2O1(1:1000)
 DOUBLE PRECISION CO23(1:1000)
 DOUBLE PRECISION CH2O3(1:1000)
 DOUBLE PRECISION DELTAT, DELTAX
 DOUBLE PRECISION UVEL1
 DOUBLE PRECISION DNSTY1(1:1000)
 DOUBLE PRECISION UVEL2
 DOUBLE PRECISION DNSTY2(1:1000)
 DOUBLE PRECISION DE02, DEH20

 DOUBLE PRECISION TX
 DOUBLE PRECISION EX
 DOUBLE PRECISION DE, GAMMA, MO2, MH20
 DOUBLE PRECISION THICK, RHODRY
 DOUBLE PRECISION HVEC1(1:1000, 1:3)
 DOUBLE PRECISION HVEC1(1:1000, 1:3)
 DOUBLE PRECISION HVEC1(1:1000, 1:3)

 DOUBLE PRECISION DE02, DEH20

 *** X - DELTAT = TIME STEP

 *** X - TX

 *** X - EX

 *** X - DE, GAMMA, MO2, MH20

 *** X - THICK, RHODRY

 *** X - HVEC1(1:1000, 1:3)

 *** X - HVEC1(1:1000, 1:3)

 *** X - HVEC1(1:1000, 1:3)

 *** X - DE02, DEH20

 ********* X - THICK = THICKNESS OF GAS DIFFUSION LAYER

 DH2O = 7.35E-4

 DH2O = 0.00005

 *** X - THICK IS THICKNESS OF GAS DIFFUSION LAYER

 THICK = 0.00005

 *** X - DELTAX IS THE CHANGE IN X IN METERS

 DELTAX = 0.00005

 *********
• DELTAX = SPATIAL STEP IN X DIRECTION
  
• VS = VS IS THE VISCOSITY OF OXYGEN IN PASCAL-SECONDS.
  
• DELTAP = CHANGE IN PRESSURE BETWEEN ANODE AND CATHODE
  
• EX = EX IS THE POROSITY AND IS DIMENSIONLESS.
  
• TX = TORTUOSITY
  
• DEO2 = EFFECTIVE DIFFUSIVITY OF OXYGEN
  
• DEH2O = EFFECTIVE DIFFUSIVITY OF WATER
  
• KPER = KPER IS PERMEABILITY OF ANODE/CATHODE GAS DIFFUSION
  
• LAYER. THE PERMEABILITY IS IN METERS SQUARED.
  
• R = UNIVERSAL GAS CONSTANT
  
• MO2 = MOLECULAR WEIGHT OF OXYGEN GAS
  
• MH2O = MOLECULAR WEIGHT OF WATER
  
• UVEL1 = FILTRATION VELOCITY IN X DIRECTION (CONSTANT)
  
• CO2I() = CONCENTRATION OF OXYGEN ARRAY
  
• CH2O() = CONCENTRATION OF WATER ARRAY
  
• DNSTY1() = DENSITY ARRAY
  
• GAMMA = Cp/Cv
  
• PRESO2 = PARTIAL PRESSURE OF OXYGEN IN GAS CHANNEL
  
• PRSH2O = PARTIAL PRESSURE OF WATER IN GAS CHANNEL
  
• PNTI1 = LOCATION IN X DIRECTION (GRID POINT)
  
• UVEC1 = U VECTOR
  
• EVEC1 = E VECTOR
  
• EVVEC1 = DIFFUSIVE PART OF E VECTOR
  
• EW = THE EQUIVALENT WEIGHT OF MEMBRANE IN UNITS OF KILOGRAMS PER MOLE.
  
• DELTAT IS THE CHANGE IN T IN SECONDS.

DELTAX = THICK((PNTI1-1.0))

DELTAP = 28.826*CURRENTD

DELTAT = DELTAX'0.0005

VS = 0.00002018

EX = 0.5

TX = 10

DEO2 = D02*EX/TX

DEH2O = DH2O*EX/TX

KPER = 1.12E-14

R = 8.314
\[ EW = 1.1 \]

* RHODRY IS THE DRY MEMBRANE DENSITY IN UNITS OF KILOGRAMS PER METER CUBED.

\[ RHODRY = 1980 \]

* DO2 AND DH2O ARE THE DIFFUSIVITIES OF OXYGEN AND WATER IN THE CATHODE GAS CHANNEL IN UNITS OF METERS SQUARED PER SECOND.

\[ D02 = 3.2348E-5 \]

\[ TEMP = 353.15 \]

* UVEL1 IS THE FILTRATION VELOCITY IN METERS/SECOND.

\[ UVEL1 = KPER \cdot DELTAP \cdot (VS \cdot THICK) \]

* MO2 IS THE MOLECULAR WEIGHT OF OXYGEN

\[ MO2 = 32 \]

* MH2O IS THE MOLECULAR WEIGHT OF WATER.

\[ MH2O = 18 \]

* THIS DO LOOP Initializes THE VALUES IN THE ARRAY.

\[ DO \ 11071 \ l = 1, PNT11 \]

\[ HVEC1(l,1) = 0.0 \]

\[ HVEC1(l,2) = 0.0 \]

\[ HVEC1(l,3) = 0.0 \]

\[ HVECN1(l,1) = 0.0 \]

\[ HVECN1(l,2) = 0.0 \]

* TEMP IS THE TEMPERATURE IN KELVIN.

IF (NUM8.EQ.1) THEN

CALL PREDIC(PNT11, + DELTAT, DELTAX, + UVEC1, EVEC1, HVEC1, UVCP1S)

ELSE IF (NUM8.EQ.0) THEN

CALL PRDICB(PNT11, + DELTAT, DELTAX, + UVEC1, EVEC1, HVEC1, UVCP1S)

ENDIF

* STEP NO. 3 - PREDICTION

* STEP NO. 4 - CALCULATE THE PRIMITIVE VARIABLES VALUES.

CALL PRIMIO(EX, PNT11, UVCP1S, + DNSTY2, CO21, CH201)

* STEP NO. 5 - CALCULATE THE VECTORS QUANTITIES.

CALL UVECO(EX, CO21, CH201, PNT11, + DNSTY2, + UVEC1)

CALL EVECO(CO21, CH201, PNT11, + UVEL1, DNSTY2, + EVECN1)
HVECN1(I,3) = 0.0

IF (NUM8 .EQ. 1) THEN
  CALL EVECO(DE02, DEH2O, CO21, CH2O1, PNTI1, + DNSTY2, DELTAX, EVC1S)
ELSE IF (NUM8 .EQ. 0) THEN
  CALL EVCSV0(DE02, DEH2O, CO21, CH2O1, PNTI1, + DNSTY2, DELTAX, EVC1S)
ENDIF

**X**---------------------------------------------------------------
* STEP NO. 6 - CORRECTION

**X**---------------------------------------------------------------
* CATALYST LAYER SUBROUTINE

SUBROUTINE CLCAT(CRRNTD, LOOP1, PNTI1, PRES02, PRSH20, + GAMMA, CO2XIN, CHOXIN, CO23, CH2O3)
INTEGER I, PNTI1, NM8, LOOP, LOOP1, J, XRESX1
DOUBLE PRECISION CO2XIN(1:1000)
DOUBLE PRECISION CHOXIN(1:1000)
DOUBLE PRECISION CO2(1:1000)
DOUBLE PRECISION CH2O(1:1000)
DOUBLE PRECISION CO21(1:1000)
DOUBLE PRECISION CH2O1(1:1000)
DOUBLE PRECISION CO23(1:1000)
DOUBLE PRECISION CH2O3(1:1000)
DOUBLE PRECISION DELTAT, DELTAX
DOUBLE PRECISION UVEL1, CRRNTD
DOUBLE PRECISION DNSTY1(1:1000)
DOUBLE PRECISION UVEL2
DOUBLE PRECISION DNSTY2(1:1000)
CALL HKIMIO(tX, H N I I 1 , UVCP1,

UUUtSLt P K t C I S l U N UVbL3

+ DNSTY3, C 0 2 3 , CH203)
DOUBLE PRECISION DNSTY3(1:1000)
CALL CNVRGO (PNTI1, C 0 2 , C 0 2 3 , XRESX1)
DOUBLE PRECISION UVEC1(1:1000, 1:3)
DO 111001 = 1.PNTI1
DOUBLE PRECISION EVEC1(1:1000, 1:3)
DNSTY1(I)=DNSTY3(I)
DOUBLE PRECISION EWEC1(1:1000, 1:3)
C02(I) = C023(I)
DOUBLE PRECISION EWC1S(1:1000, 1:3)
CH20(I) = CH203(I)
DOUBLE PRECISION UVCP1S(1:1000, 1:3)
11100

CONTINUE
DOUBLE PRECISION UVCP1(1:1000, 1:3)

IF((XRESX1 .GT. PNTI1*0.90).AND.
+

(LOOP .GT. 750000)) GOTO 11201

DOUBLE PRECISION UVECN1 (1:1000, 1:3)

11200

CONTINUE

DOUBLE PRECISION EVECN1(1:1000, 1:3)

11201

CONTINUE

DOUBLE PRECISION EWCN1(1:1000, 1:3)

WRITE (55,*)

DOUBLE PRECISION TEMP

WRITE (55,*)
WRITE (55,*) 'LOOP = ', LOOP

DOUBLE PRECISION VS

WRITE (55,*) 'GAS DIFFUSION LAYER'
WRITE (55,*)

DOUBLE PRECISION KPER

WRITE (*

DOUBLE PRECISION DELTAP

WRITE (*

*)
*)

WRITE (* *)'LOOP = ', LOOP

DOUBLE PRECISION PRES02, PRSH20

WRITE (*. *) 'GAS DIFFUSION LAYER'
WRITE (*

*)

DO 111051 = 1.PNTI1

WRITE (55,*) C023(l).\', CH203(I),',\ DNSTY3(I)

DOUBLE PRECISION D 0 2 , DH20

DOUBLE PRECISION DE02, DEH20

' PRES02 = OXYGEN PRESSURE IN GAS CHANNEL

WRITE (*,*) C023(l),\\ CH203(I),',', DNSTY3(I)
' PNTI1 = LOCATION IN X DIRECTION (GRID POINT)
11105

CONTINUE
' UVEC1 = U VECTOR
WRITE (55,*)
WRITE (*,*)

RETURN

END

'EVEC1 = E VECTOR

' E W E C 1 = DIFFUSIVE PART OF E VECTOR

<x..............

'"**X***********
DOUBLE PRECISION TX

"*»•"**•

....

' EW IS THE EQUIVALENT WEIGHT OF MEMBRANE IN UNITS OF
• KILOGRAMS PER MOLE.

DOUBLE PRECISION EX

.....x.....................................................


DOUBLE PRECISION GAMMA, MU2, MH2O

DOUBLE PRECISION THICK, RHODRY

DOUBLE PRECISION HVEC1(1:1000, 1:3)

DOUBLE PRECISION HVECN1(1:1000, 1:3)

* RHODRY IS THE DRY MEMBRANE DENSITY IN UNITS OF KILOGRAMS PER METER CUBED.

* STEP NO. 1 - INITIAL CONDITIONS AND BOUNDARY CONDITIONS

* LEXICON

* EW = EW IS THE EQUIVALENT WEIGHT OF MEMBRANE IN UNITS OF KILOGRAMS PER MOLE.

* RHODRY = RHODRY IS THE DRY MEMBRANE DENSITY IN UNITS OF KILOGRAMS PER METER CUBED.

* DO2 = DIFFUSIVITY OF OXYGEN

* DH2O = DIFFUSIVITY OF WATER

* THICK = THICKNESS OF GAS DIFFUSION LAYER

* DELTAX = CHANGE IN X IN METERS.

* DELTAT = TIME STEP

* DELTAX = SPATIAL STEP IN X DIRECTION

* VS = VS IS THE VISCOSITY OF OXYGEN IN PASCAL-SECONDS.

* DELTAP = CHANGE IN PRESSURE BETWEEN ANODE AND CATHODE

* EX = EX IS THE POROSITY AND IS DIMENSIONLESS.

* TX = TORTUOSITY

* DEO2 = EFFECTIVE DIFFUSIVITY OF OXYGEN

* DEH2O = EFFECTIVE DIFFUSIVITY OF WATER

* KPER = KPER IS PERMEABILITY OF ANODE/CATHODE GAS DIFFUSION

* LAYER, THE PERMEABILITY IS IN METERS SQUARED.

* RHODRY = 1980

* DO2 = 3.2348E-5

* DH2O = 7.35E-4

* THICK = 0.000005

DELTAX = THICK/(PNT11-1)

DELTAT = DELTAX*0.0005

DELTAT = DELTAP*0.0005

VS = 0.00002018

DELTAP = 28.826*CRRNTD

VS = 0.0002018

DELTAP = 28.826*CRRNTD

* EX IS THE POROSITY AND IS DIMENSIONLESS.
* \( K = \text{UNIVERSAL GAS CONSTANT} \)
* \( M_{O2} = \text{MOLECULAR WEIGHT OF OXYGEN GAS} \)
* \( M_{HO2} = \text{MOLECULAR WEIGHT OF WATER} \)
* \( UVEL1 = \text{FILTRATION VELOCITY IN X DIRECTION (CONSTANT)} \)
* \( CO2() = \text{CONCENTRATION OF OXYGEN ARRAY} \)
* \( CH2O() = \text{CONCENTRATION OF WATER ARRAY} \)
* \( DNSTY1() = \text{DENSITY ARRAY} \)
* \( \text{GAMMA = CP/CV} \)

\[ \text{EX} = 0.5 \]

\[ \text{TX} = 10 \]

\[ \text{DEO2} = D_{O2} \times \text{EXXTX} \]
\[ \text{DEH2O} = D_{H2O} \times \text{EXXTX} \]

\[ \text{KPER} = 1.12E-14 \]

\[ \text{R} = 8.314 \]

\[ \text{TEMP} = 353.15 \]

\[ \text{UVEL1} = \text{THE FILTRATION VELOCITY IN METERS/SECOND.} \]
UVEL1 = KPER*DELTAP/(VS*THICK)

* MO2 IS THE MOLECULAR WEIGHT OF WATER.

MO2 = 32

* MH2O IS THE MOLECULAR WEIGHT OF WATER

MH2O = 18

DO 1130 I = 1, PNT11
    CO2(I) = CO2XIN(I)
    CH2O(I) = CHOXIN(I)
 1130 CONTINUE

DO 1120 LOOP = 1, LOOP1
    CO2(1) = CO2XIN(1)
    CH2O(1) = CHOXIN(1)
 1120 CONTINUE

* THE PROGRAM ASSUMES THAT OXYGEN IS NOT DISSOLVED INTO THE

* STEP NO. 5 - CALCULATE THE VECTORS QUANTITIES.

CALL UVECO(EX, PNT11, UVCP1S,
+ DNSTY2, UVEC1, EVEC1, HVEC1, UVEL1, EVEL1, HVEL1)

CALL EVECO(DEO2, DEH2O, CO2, CH2O, PNT13,
+ DNSTY3, EVEC3, HVEC3)

ELSE IF (NM8.EQ.0) THEN
    CALL EVVCBO(DEO2, DEH2O, CO2, CH2O, PNT11,
+ DNSTY2, DELTA2, EVVC1S)

ENDIF

* STEP NO. 4 - CALCULATE THE PRIMITIVE VARIABLES VALUES.

CALL PRIMIO(EX, PNT11, UVCP1S,
+ DNSTY2, CO21, CH2O1)

* THE PROGRAM ASSUMES THAT OXYGEN IS NOT DISSOLVED INTO THE

* STEP NO. 5 - CALCULATE THE VECTORS QUANTITIES.

DO 1115 I = 1, PNT11
    WRITE (55,*) 'LOOP = ', LOOP
    WRITE (55,*) 'CATHODE CATALYST LAYER'
    CALL UVECO(EX, CO21, CH2O1, PNT11,
+ DNSTY2, UVEC1)
    CALL EVECO(CO21, CH2O1, PNT11,
+ UVEL1, DNSTY2, EVEC1)
    CALL HVECO(CRNTD, DELTAT, CO21, CH2O1,
+ PNT11, HVEC1)

SUBROUTINE EVVCBO(DEO2, DEH2O, CO2, CH2O, PNT13,
+ DNSTY, DX, EVVC1S)
CALL EVVC3I(UVE2, UVE20, CO21, CH2O1, PN11, + DNSTY2, DELTAX, EVVC1S)

ENDIF

******X**********************************************************************
* STEP NO. 6 - CORRECTION
*
******X**********************************************************************

IF (NM8 .EQ. 1) THEN
CALL CORREC(PNTI1, + DELTAT, DELTAX, + UVEC11, UVEC1, EVECN1, EVVC1S, HVEC11, UVCP1)
ELSE IF (NM8 .EQ. 0) THEN
CALL CRREC(PNTI1, + DELTAT, DELTAX, + UVEC11, UVEC1, EVECN1, EVVC1S, HVEC11, UVCP1)
ENDIF

******X**********************************************************************
* STEP NO. 7 - CALCULATE THE PRIMITIVE VARIABLE VALUES.
*
******X**********************************************************************

CALL PRIMO(EX, PNTI1, UVCP1, + DNSTY3, CO23, CH2O3)
CALL CNVRGO (PNTI1, CO2, CO23, XRESX1)
DO 1110 I = 1, PNTI1
  DNSTY1(I) = DNSTY3(I)
  CO2(I) = CO23(I)
  CH2O(I) = CH2O3(I)
1110 CONTINUE

IF ((XRESX1 .GT. PNTI1*0.90) .AND. + (LOOP .GT. 75000)) GOTO 1121
R = 8.314
TEMP = 353.15

INTEGER I, PNTI3
DOUBLE PRECISION DX, TEMP, DE02, DEH20
DOUBLE PRECISION CO2(1:1000)
DOUBLE PRECISION CH2O(1:1000)
DOUBLE PRECISION DNSTY(1:1000), GAMMA, OMEGA
DOUBLE PRECISION EWCTR(1:1000, 1:3)
DOUBLE PRECISION R

VARIABLE DEFINITIONS:
U = U VELOCITY
DENST = DENSITY
R = UNIVERSAL GAS CONSTANT
DE = EFFECTIVE DIFFUSIVITY
P = PRESSURE ASSUMING THAT THE GAS IS AN IDEAL GAS
EIVCTR = EI VECTOR

SUBROUTINE COMCLC(PNTI1, + THICK, CO2CL, CO2MEM)
DOUBLE PRECISION FLXMEM, FLXCL, DIFF1, DLTXCL
DOUBLE PRECISION CO2CL(1:1000)
DOUBLE PRECISION DELTAX, ERRXR
INTEGER PNTI1
DOUBLE PRECISION DMEM, D02H20, CO2MEM
DMEM = 2.59E-10
D02H20 = 1.1028E-4
DELTAX = THICK/PNTI1/10
DLTXCL = THICK/PNTI1/10
FLXMEM = DMEM*(CO2MEM)/DELTAX
**EVECTR(I,1) = 0.0**

**EVECTR(I,2) = DOE2*(CO2(I+1) - CO2(I))/DX**

**EVECTR(I,3) = DEH2O*(CH2O(I+1) - CH2O(I))/DX**

**DO 13010 CONTINUE**

**RETURN**

**END**

**INTEGER I, PNTI4**

**DOUBLE PRECISION CO2(1:1000)**

**DOUBLE PRECISION CH2O(1:1000)**

**DOUBLE PRECISION HVCTR(1:1000, 1:3)**

**DOUBLE PRECISION CRRNT**

**DOUBLE PRECISION CRRNTD**

**DOUBLE PRECISION HVCTR**

**DOUBLE PRECISION CRRNTD**

**SUBROUTINE HVECO(CRRNTD, DELTAT, CO2, CH2O, PNTI4, HVCTR)**

**INTEGER I, PNTI4**

**DOUBLE PRECISION CO2(1:1000)**

**DOUBLE PRECISION CH2O(1:1000)**

**DOUBLE PRECISION HVCTR(1:1000, 1:3)**

**DOUBLE PRECISION CRRNT**

**DOUBLE PRECISION CRRNTD**

**DOUBLE PRECISION HVCTR**

**DO 130101 = 1, PNTI4**

**HVCTR(I,1) = 0.0**

**HVCTR(I,2) = -1.0*(CRRNT/(4.0*96485))**

**FLXCL = D02H20*(C02CL(PNTI1) + -C02CL(PNTI1-1))/DLTXCL**

**DIFF1 = FLXMEM-FLXCL**

**ERRXR = FLXMEM*0.05**

**C02MEM = CO2CL(PNTI1)**

**IF (ABS(DIFF1) LT. ERRXR) THEN**

**ELSEIF (ABS(DIFF1) GE. ERRXR) THEN**

**IF (FLXMEM > FLXCL) THEN**

**C02MEM = CO2MEM*0.95**

**ELSEIF (FLXCL > FLXMEM) THEN**

**C02MEM = CO2MEMM.09**

**ENDIF**

**ENDIF**

**WRITE (55, *) VALUE OF CL-MEMBRANE INTERFACE',**

**WRITE (55, *) VALUE OF CL-MEMBRANE INTERFACE',**

**WRITE (*, *) VALUE OF CL-MEMBRANE INTERFACE',**

**WRITE (*, *) VALUE OF CL-MEMBRANE INTERFACE',**

**RETURN**

**END**

**SUBROUTINE CNVRGO (XGRID, MXTRXO, MXTRXN, VLE)**

**CO2IN = CO2GDL(PNTI1)**

**ELSEIF (ABS(DIFF1) GE. ERRXR) THEN**

**IF (FLXGDL GT. FLXCL) THEN**

**OLDMAX = CH2MAX**
HVC I K(l,3) = 1.1^{(\text{UHNN}1/(2.0^{*3485}))}

CONTINUE

RETURN

END

* CALCULATES THE COMPARISON AND THE NEWTON-RAPHSON METHOD.

DOUBLE PRECISION MXTRXO(1:1000)
DOUBLE PRECISION MXTRXN(1:1000)
INTEGER I, VLE, XGRID
VLE = 0
DO 29010 I = 1, XGRID
  IF (ABS(MXTRXN(I) - MXTRXO(I)) < 0.001*MXTRXN(I)) THEN
    VLE = VLE + 1
  ELSE
    VLE = VLE + 0
  ENDIF
29010 CONTINUE

RETURN

END

* CALCULATES THE COMPARISON AND THE NEWTON-RAPHSON METHOD.

DOUBLE PRECISION FLXGDL, FLXCL, DIFF1, DLTXCL
DOUBLE PRECISION CO2GDL(1:1000), OLDMAX, OLDMIN
DOUBLE PRECISION CO2CL(1:1000)

SUBROUTINE CTHDE(CRRNTD, LOOP1, PNTI1, GAMMA, CH2, PRESH2, PRES02, C02, CH20, CO2CL, CH2OCL)

* LEXICON:
* PNTI1 - NUMBER OF GRID POINTS
* LOOP - NUMBER OF LOOPS
* LOOP1 - NUMBER OF LOOPS
* I, J, K ARE DUMMY VARIABLES THAT REPRESENT INTEGER COUNTERS.
* CO2 - CONCENTRATION OF OXYGEN
* CH2O - CONCENTRATION OF WATER
* CO2CL - CONCENTRATION OF OXYGEN IN CATALYST LAYER
* CH2OCL - CONCENTRATION OF WATER IN CATALYST LAYER

RETURN

END
DOUBLE PRECISION DELTAX, CO2MAX, CO2MIN, THICK

INTEGER PNTI1

DOUBLE PRECISION CO2IN, ERRXR

WRITE (*)
WRITE (*) 'THICK = ', THICK
WRITE (*)

DELTAX = THICK/PNTI1
DLTXCL = THICK/PNTI1/10

FLXGDL = (CO2GDL(PNTI1) - CO2GDL(PNTI1-1))/DELTAX
FLXCL = (CO2CL(2) - CO2CL(1))/DLTXCL

DIFF1 = FLXGDL - FLXCL
ERRXR = 0.05*FLXGDL
C020LD = CO2GDL(PNTI1)
C02IN = CO2GDL(PNTI1)

IF (ABS(DIFF1) .LT. ERRXR) THEN

DOUBLE PRECISION CH2O1(1:1000)
DOUBLE PRECISION CO23(1:1000)
DOUBLE PRECISION CH2O3(1:1000)
DOUBLE PRECISION CO2CL(1:1000), CH2OCL(1:1000)
DOUBLE PRECISION CO2GDL(1:1000), CHOGDL(1:1000)
DOUBLE PRECISION DELTAT, DELTAX, OLDMAX, OLDMIN
DOUBLE PRECISION UVEL1, C02IN, C02MAX, C02MIN
DOUBLE PRECISION XHOMAX, XHOMIN, CH2OIN
DOUBLE PRECISION HLDMAX, HLDMIN
DOUBLE PRECISION HUMBX(1:1000)
DOUBLE PRECISION DNSTY1(1:1000)
DOUBLE PRECISION CH2(1:1000)
DOUBLE PRECISION CHOMEM
DOUBLE PRECISION CH2O(1:1000)
DOUBLE PRECISION CH2OA(1:1000)
DOUBLE PRECISION CO21(1:1000), DIFF2
DOUBLE PRECISION CH2O2(1:1000), CHOGUE(1:1000)
DOUBLE PRECISION THCKCL, XCO2IN, OLDMX, CO2MX

* EXPLICIT MACCORMACK METHOD
* NOTE: THE EXPLICIT MACCORMACK METHOD REQUIRES THAT THE
* SYSTEM BE GIVEN AN INITIAL GUESS, AND THE PROGRAM
* WILL ITERATE TO THE FINAL STEADY STATE SOLUTION.

***

STEP 1 - DATA ENTRY

WRITE (5,*) 'CATHODE DATA'
WRITE (5,*)
WRITE (5,*) 'ENTER THE PARTIAL PRESSURE OF THE OXYGEN IN THE CHANNEL. THE PRESSURE IS IN PASCALS.'
WRITE (5,*) PRESO2
WRITE (5,*)
WRITE (5,*) 'ENTER THE PARTIAL PRESSURE OF THE WATER IN THE CHANNEL. THE PRESSURE IS IN PASCALS.'
WRITE (5,*)
PRSH20 = PRESO2*0.05
WRITE (5,*)
WRITE (5,*) 'ENTER THE CONCENTRATION OF OXYGEN AT THE INTERFACE. THE OXYGEN CONCENTRATION SHOULD BE LESS THAN CONCENTRATION IN GAS CHANNEL.'
DOUBLE PRECISION UVEL3

DOUBLE PRECISION DNSTY3(1:1000)

DOUBLE PRECISION UVEC1(1:1000, 1:3)

DOUBLE PRECISION EVEC1(1:1000, 1:3)

DOUBLE PRECISION EWEC1(1:1000, 1:3)

DOUBLE PRECISION UVCP1S(1:1000, 1:3)

DOUBLE PRECISION UVCP1(1:1000, 1:3)

DOUBLE PRECISION UVECN1(1:1000, 1:3)

DOUBLE PRECISION EVECN1(1:1000, 1:3)

DOUBLE PRECISION EWCN1(1:1000, 1:3)

DOUBLE PRECISION TEMP

DOUBLE PRECISION VS

DOUBLE PRECISION KPER

DOUBLE PRECISION DELTAP

DOUBLE PRECISION PRES02, PRSH20

DOUBLE PRECISION D02H20

DOUBLE PRECISION TX, DUMBX(1:1000)

DOUBLE PRECISION EX, PRESH2

DOUBLE PRECISION DE, GAMMA, MO2, MH2O

DOUBLE PRECISION THICK, RHODRY

DOUBLE PRECISION OLDXP, OLDMNP, PERC

DOUBLE PRECISION PRESIN

CH2O(PNTI1) = PRSH2O/(8.314*353)

WRITE (*,*) 

WRITE (*,*) 'ENTER THE CONCENTRATION OF ', 

WRITE (*,*) 'WATER AT THE INTERFACE.'.

WRITE (*,*) 'THE WATER CONCENTRATION SHOULD BE ',

WRITE (*,*) 'LESS THAN CONCENTRATION IN MEMBRANE.'

WRITE (*,*)

WRITE (*,*) CH2O(PNTI1)

WRITE (*,*)

THICK = 0.00005

WRITE (V)'STEP V

C02(PNTI1) = PRES02/(8.314*353)

PRSH20 = PRESO2*0.05

CALL GDLCYC(CRRNTD, LOOP1, PNTI1, C02(PNTI1),

CH2O(PNTI1), GAMMA, C021, CH2O1, C02GUE, CHOGUE)

THCKCL = 0.000005

CALL CMPRCG(C02MX, C02MN, PNTI1,

THCKCL, C02GUE, CRRNTD, XC02IN, OLDMX,

OLDMN, PERCGU)

DO11085 I = 1, PNTI1

C021(I) = C02GUE(I)

DO 11085

CO221(I) = CO2GUE(I)
CO2MX = CO2(PNTI1)

CO2MN = 0.0

XHOMX = CH2O(PNTI1)

XHOMN = 0.0

DO 11070 I = 1, PNTI1
    CO2(I) = CO2(PNTI1)
    CH2O(I) = CH2O(PNTI1)
  11070 CONTINUE

CO2MN = 0.0

11085 CONTINUE

DO 11075 I = 1, PNTI1
    CO2(I) = CO2(PNTI1)
    CH2O(I) = CH2O(PNTI1)
  11075 CONTINUE

DO 11102 K = 1, 500

11102 CONTINUE

11103 CONTINUE

ELSEIF (FLXA .GT. FLXC) THEN
    NEWMAX = C02MAX
    NEWMIN = C02IN
    C02IN = (C02MAX + C02MIN)/2.0
    WRITE (*,*) THIS IS THE FLXA > FLXC, C02IN
    WRITE (*,*)'MAXIMUM =',NEWMAX,'MINIMUM =',NEWMIN
ENDIF
\[ C_{O_2}(I) = C_{O_2}GDL(I) \]

\[ CH_{2O}(I) = CH_{2O}GDL(I) \]

11080 CONTINUE
END

****x******************************************************************************
* CALCULATES THE COMPARISON.
****x******************************************************************************

SUBROUTINE COMPRE(C02MAX, C02MIN, PNTI1, THICK, C02GDL, CH2GDL, C02IN, NEWMAX, NEWMIN)
DOUBLE PRECISION FLXA, FLXC, DIFF1, DLTXCL
DOUBLE PRECISION CO2GDL(1:1000), NEWMAX, NEWMIN
DOUBLE PRECISION DELTAX, C02MAX, C02MIN
INTEGER PNTI1
DOUBLE PRECISION CH2GDL(1:1000), THICK
DOUBLE PRECISION C02IN, ERRXR, D02, DH2H20
D02 = 3.2348E-5
DH2H20 = 1.1028E-4
WRITE (*,*) 'THIS IS THE THICKNESS.', THICK
DELTAX = THICK/(PNTI1-1)
WRITE (*,*) 'THIS IS DELTA X.', DELTAX
FLXC = ABS(D02*
+ (C02GDL(PNT11) - C02GDL(PNT11 -1))
+ /DELTAX)
WRITE ('*',*) 'FLUX OF CATHODE', FLXC
FLXA = ABS(0.5*DH2H2O*
+ (CH2GDL(PNTI1) - CH2GDL(PNTI1-1))
+ /DELTAX)
WRITE ('*',*) 'FLUX OF ANODE', FLXA
DIFF1 = ABS(FLXC-FLXA)
WRITE (55, *) 'VALUE OF INTERFACE ', C02IN
RETURN
END
ERRXR = 0.1*FLXC

CO2IN = CO2GDL(1)*(8.314*353.15)

IF (ABS(DIFF1) .LT. ERRXR) THEN
  C02IN = CO2GDL(1)*(8.314*353.15)
ELSEIF (ABS(DIFF1) .GE. ERRXR) THEN
  IF (FLXC .GT. FLXA) THEN
    NEWMAX = C02IN
    NEWMIN = C02MIN
    C02IN = (C02MAX + CO2MIN/2.0
    WRITE (*) 'THIS IS THE FLXC > FLXA', C02IN
    WRITE (*) 'MAXIMUM =',NEWMAX,'MINIMUM =',NEWMIN
  ENDIF
ENDIF

DOUBLE PRECISION EVEC1(1:1000, 1:3)
BOX DOUBLE PRECISION EWEC1(1:1000, 1:3)
DOUBLE PRECISION EWC1S(1:1000, 1:3)
DOUBLE PRECISION UVCP1S(1:1000, 1:3)
DOUBLE PRECISION UVCP1(1:1000, 1:3)
DOUBLE PRECISION UVECN1(1:1000, 1:3)
DOUBLE PRECISION EVECN1(1:1000, 1:3)
DOUBLE PRECISION EWCN1(1:1000, 1:3)
DOUBLE PRECISION TEMP, CRRNTD
DOUBLE PRECISION VS
DOUBLE PRECISION KPER
DOUBLE PRECISION DELTAP
DOUBLE PRECISION PRESH2
DOUBLE PRECISION DH2H2O
DOUBLE PRECISION TX
DOUBLE PRECISION EX
DOUBLE PRECISION DE, GAMMA, MH2, MH20

TX = TORTUOSITY
DE = EFFECTIVE DIFFUSIVITY
KPER = KPER IS PERMEABILITY OF ANODE/CATHODE GAS DIFFUSION
LAYER. THE PERMEABILITY IS IN METERS SQUARED.
R = UNIVERSAL GAS CONSTANT
MH2 = MOLECULAR WEIGHT OF HYDROGEN GAS
MH20 = MOLECULAR WEIGHT OF WATER
UVEL1 = FILTRATION VELOCITY IN X DIRECTION (CONSTANT)
MAXIMUM =,NEWMAX,MINIMUM =,NEWMIN
CH2( ) = CONCENTRATION OF HYDROGEN ARRAY
CH2O ( ) = CONCENTRATION OF WATER ARRAY
DNSTY1 ( ) = DENSITY ARRAY
GAMMA = CP/CV
PRESH2 = HYDROGEN PRESSURE IN GAS CHANNEL
PNTI1 = LOCATION IN X DIRECTION (GRID POINT)
UVEC1 = U VECTOR
EVEC1 = E VECTOR
EVEC1 = DIFFUSIVE PART OF E VECTOR

EW = 1.1

RHODRY IS THE DRY MEMBRANE DENSITY IN UNITS OF KILOGRAMS PER METER CUBED.
DOUBLE PRECISION THICK, RHODRY

DOUBLE PRECISION HVEC1(1:1000, 1:3)

DOUBLE PRECISION HVECN1(1:1000, 1:3)

******x=============================================**

* STEP NO. 1 - INITIAL CONDITIONS AND BOUNDARY CONDITIONS

**

* THE THICKNESS THICK OF CATALYST LAYER IS IN METERS.

******x=============================================**

**

* DH2H2O = DIFFUSIVITY OF HYDROGEN AND WATER IN THE
* ANODE GAS CHANNEL IN UNITS OF METERS SQUARED PER
* SECOND.

******x=============================================**

**

* THE PRESSURE DELTAP IS IN PASCALS.

******x=============================================**

**
DELTAP = 28.826*CRRTND

* EX IS THE POROSITY AND IS DIMENSIONLESS.

EX = 0.5

* TX IS THE TORTUOSITY AND IS DIMENSIONLESS.

TX = 10

* DE IS THE EFFECTIVE DIFFUSIVITY.

DE = DH2H2O*EX/TX

* KPER IS PERMEABILITY OF ANODE/CATHODE GAS DIFFUSION LAYER. THE PERMEABILITY IS IN METERS SQUARED.

KPER = 1.12E-14

* R IS THE UNIVERSAL GAS CONSTANT IN JK-1-MOL-1.

R = 8.314

* TEMP IS THE TEMPERATURE IN KELVIN.

TEMP = 353.15

* UVEL1 IS THE FILTRATION VELOCITY IN METERS/SECOND.

UVEL1 = KPER*DELTAP/(VS*THICK)

* MH2 IS THE MOLECULAR WEIGHT OF HYDROGEN.

MH2 = 2

CALL UVEC(EX, CH2, CH2O, PNTI1, DNSTY1, UVEC1)

CALL EVEC(CH2, CH2O, PNTI1, UVEL1, DNSTY1, EVEC1)

CALL HVVEC(DELTAT, CRRTND, CH2, PNTI1, HVEC1)

CALL ODDEVE(LOOP, NM8)

IF (NM8 .EQ. 1) THEN

CALL EVVEC(DE, CH2, CH2O, PNTI1, DNSTY1, DELTAX, EVEC1)

ELSE IF (NM8 .EQ. 0) THEN

CALL EVVECB(DE, CH2, CH2O, PNTI1, DNSTY1, DELTAX, EVEC1)

ENDIF

KPER = 1.12E-14

IF (NM8 .EQ. 1) THEN

CALL PREDIC(PNTI1, DELTAT, DELTAX, UVEC1, EVEC1, EWEC1, UVCP1S)

R = 8.314

ELSE IF (NM8 .EQ. 0) THEN

CALL PRDICB(PNTI1, DELTAT, DELTAX, UVEC1, EVEC1, EWEC1, HVEC1, UVCP1S)

DO 1110 I = 1, PNTI1

DNSTY1(I) = DNSTY3(I)

CH2(I) = CH23(I)

CH2O(I) = CH2O3(I)

1110 CONTINUE

IF ((XRESX1 GT. PNTI1*0.90).AND. (LOOP .GT. 1000000)) GOTO 1121

MH2 = 2

1120 CONTINUE

1121 CONTINUE
* MH2O IS THE MOLECULAR WEIGHT OF WATER.  

ENDIF  

* STEP NO. 4 - CALCULATE THE PRIMITIVE VARIABLES VALUES.  

CALL PRIMI(EX, PNTI1, UVCP1S, + DNSTY2, CH21, CH201)  

* STEP NO. 5 - CALCULATE THE VECTORS QUANTITIES.  

CALL UVEC(EX, CH21, CH201, PNTI1, + DNSTY2, + UVEC1N1)  

CALL EVEC(CH21, CH201, PNTI1, + UVEL1, DNSTY2, + EVECN1)  

CALL HVEC(DELTAT, CRRNTD, CH21, PNTI1, HVECN1)  

IF (NM8 .EQ. 1) THEN  

CALL EVVEC(DE, CH21, CH201, PNTI1, DNSTY2, + DELTAX, EVECN1S)  

ELSE IF (NM8 .EQ. 0) THEN  

CALL EVVECCB(DE, CH21, CH201, PNTI1, DNSTY2, + DELTAX, EVECN1S)  

ENDIF  

* STEP NO. 6 - CORRECTION  

IF (NM8 .EQ. 1) THEN  

CALL CORREC(PNTI1, + DELTAT, DELTAX, + UVEC1N1, UVEC1, EVECN1, EVVC1S, HVEC1N1, UVCP1)  

WRITE (55,*)  

WRITE (55,*) 'LOOP = ', LOOP  

WRITE (55,*) 'ANODE CATALYST LAYER'  

WRITE (55,*) 'ANODE CATALYST LAYER'  

WRITE (*,*), LOOP  

WRITE (*,*) '************'  

SUBROUTINE COMPRC(CO2MAX, CO2MIN, PNTI1, + THICK, CO2GDL, CRRNTX, CO2IN, NEWMAX, NEWMIN, + PRCNT)  

DOUBLE PRECISION FLXGDL, FLXCL, DIFF1, DLTXCL  

DOUBLE PRECISION CO2GDL(1:1000), NEWMAX, NEWMIN  

DOUBLE PRECISION CRRNTX  

DOUBLE PRECISION DELTAX, CO2MAX, CO2MIN  

INTEGER PNTI1, K  

DOUBLE PRECISION CO2IN, ERRXR, THICK, PRCNT  

WRITE (*,*) '************'  

WRITE (*,*) '************'  

DELTAX = THICK/(PNTI1-1.0)
ELSE IF (NM5 .LT. U) THEN

CALL CRREC8(PNT1, 
+ DELTAT, DELTAX, 
+ UVEC1, UVEC1, EVEC1, EVEC1S, HVEC1, UVCP1)

ENDIF

***X******************************************************************************
* STEP NO. 7 - CALCULATE THE PRIMITIVE VARIABLE VALUES.                     *
* ***************************************************************************

CALL PRIMI(EX, PNT1, UVCP1, 
+ DNSTY3, CH23, CH203)

CALL CNVRG (PNT1, CH2, CH23, XRESX1)
WRITE (*,*)
WRITE (*,*) 'DELTA X = ', DELTAX
WRITE (*,*)

FCON = 96485.0
DF = 3.2348E-5
FLXGDL = 0.0
FLXCL = -4.0/(100)**2*FCON*DF*
+ (CO2GDL(PNTI1) - CO2GDL(PNTI1-1))/DELTAX

FLXCL = CRRNTX
WRITE ('**')
WRITE ('**') 'COMPARISON'
WRITE ('**') 'FLXGDL =',FLXGDL,'FLXCL = ',FLXCL
WRITE ('**')
DIFF1 = FLXGDL-FLXCL

PRCNT = 0.0
PRCNT = ABS(DIFF1)/FLXCL
WRITE ('**')
WRITE ('**') 'PERCENT DEVIATION = ', PRCNT
WRITE ('**')
ERRXR = 0.1*FLXGDL
CO2IN = CO2GDL(PNTI1)

IF (PRCNT .LE. 0.01) THEN

CO2IN = CO2IN'0.99995''(CRRNTX)
WRITE ('**') '3 CATHODE'
ELSEIF (FLXGDL .GT. FLXCL) AND. 
+ (PRCNT .GT. 0.5)) THEN

NEWMAX = CO2IN
NEWMIN = CO2MIN

CO2IN = CO2IN'1.0005''(CRRNTX)
WRITE ('**') '4 CATHODE'
ELSEIF (FLXCL .GT. FLXGDL) AND. 
+ (PRCNT .GT. 0.5)) THEN

NEWMAX = CO2IN
NEWMIN = CO2IN

CO2IN = CO2IN'0.99975''(CRRNTX)
WRITE ('**') '5 CATHODE'
ELSEIF (FLXGDL .GT. FLXCL) .AND. 
+ (PRCNT GT. 0.2)) THEN

NEWMAX = CO2IN
NEWMIN = CO2MIN

CO2IN = CO2IN'1.00001''(CRRNTX)
WRITE ('**') '6 CATHODE'
ELSEIF (FLXCL .GT. FLXGDL) .AND. 
+ (PRCNT .GT. 0.2)) THEN

NEWMAX = CO2IN
NEWMIN = CO2IN

CO2IN = CO2IN'0.99999''(CRRNTX)
WRITE ('**') '7 CATHODE'
ELSEIF (FLXGDL .GT. FLXCL) .AND. 
+ (PRCNT .GT. 0.1)) THEN

NEWMAX = CO2IN

CO2IN = CO2IN'0.9999995''(CRRNTX)
WRITE ('**') '8 CATHODE'
ELSEIF (FLXCL .GT. FLXGDL) .AND. 
+ (PRCNT .GT. 0.1)) THEN

NEWMAX = CO2IN
CLCIN = CO2GDL(PNTI1)
WRITE (*,*)
WRITE (*,*) 'INTERFACE VALUE DID NOT CHANGE.'
WRITE (*,*)
ELSEIF (PRCNT GT 0.01) THEN
WRITE (*,*) '0 CATHODE'
IF (FLXGDL LT 0.0) THEN
CO2IN = CO2IN*0.9995**(CRRNTX)
WRITE (*,*) '1 CATHODE'
ELSEIF ((FLXGDL GT FLXCL) AND (PRCNT GT 1.0)) THEN
NEWMAX = CO2IN
NEWMIN = CO2MIN
CO2IN = CO2IN*1.0005**(CRRNTX)
WRITE (*,*) '2 CATHODE'
ELSEIF ((FLXCL GT FLXGDL) AND (PRCNT LT 0.1)) THEN
NEWMAX = CO2IN
NEWMIN = CO2MIN
CO2IN = CO2IN*0.99995**(CRRNTX)
WRITE (*,*) '10 ANODE'
ELSEIF ((FLXCL GT FLXGDL) AND (PRCNT GT 0.1)) THEN
NEWMAX = CO2MAX
NEWMIN = CO2IN
CO2IN = CO2IN*0.999995**(CRRNTX)
ELSEIF (FLXCL GT FLXGDL) THEN
NEWMAX = CO2MAX
NEWMIN = CO2IN
FLXGDL = -2.0/((100)**2)*FCON*DF*(CO2GDL(PNTI1) - CO2GDL(PNTI1-1))/DELTAX
FLXCL = CRRNTX
WRITE (*,*) 'COMPARISON'
WRITE (*,*) 'FLXGDL =', FLXGDL, 'FLXCL =', FLXCL
WRITE (*,*)
DIFF1 = FLXGDL-FLXCL
PRCNT = 0.0
PRCNT = ABS(DIFF1)/FLXCL
WRITE (*,*) ' PERCENT DEVIATION = ', PRCNT
WRITE (*,*)
ERRXR = 0.1*FLXGDL
WRITE (*,*)
ELSEIF (FLXCL GT FLXGDL) THEN
NEWMAX = CO2MAX
NEWMIN = CO2IN
CO2IN = CO2IN*0.999995**(CRRNTX)
ELSEIF (FLXCL GT FLXGDL) THEN
NEWMAX = CO2IN
NEWMIN = CO2IN
CO2IN = CO2IN*0.999995**(CRRNTX)
WRITE (*,*)
WRITE (*,*)
**SUBROUTINE COMPRA(C02MAX, C02MIN, PNT11, THICK, CO2GDL, CRRNTX, C02IN, NEWMAX, NEWMIN, PRCNT)**

DOUBLE PRECISION FLXGDL, FLXCL, DIFF1, DLTXCL

DOUBLE PRECISION CO2GDL(1:1000), NEWMAX, NEWMIN

DOUBLE PRECISION CRRNTX

DOUBLE PRECISION DELTAX, C02MAX, C02MIN

INTEGER PNT11, K

DOUBLE PRECISION CO2IN, ERRXR, THICK, PRCNT

* WRITE (*, *)
  * WRITE (' ', 'THICK = ', THICK
  * WRITE (', ')

DELTAX = THICK/(PNT11-1.0)

* WRITE (' ', 'DELTA X = ', DELTAX
  * WRITE (', ')
  * WRITE (', ')

ELSEIF (FLXGDL .GT. FLXCL) AND. (PRCNT.GT. 0.5)) THEN

  NEWMAX = C02MAX
  NEWMIN = C02IN
  CO2IN = CO2IN*0.9995**(CRRNTX)

  WRITE (', ')
  WRITE (', ')
  WRITE (', ')

RETURN

END
NEWMAX = CO2IN

NEWMIN = CO2MIN

CO2IN = CO2IN*1.0007**(CRRNTX)

* WRITE (*,*) '4'

ELSEIF ((FLXCL GT. FLXGDL) AND. (PRCNT .GT. 0.5)) THEN

NEWMAX = CO2MAX

NEWMIN = CO2IN

CO2IN = CO2IN*0.99977**(CRRNTX)

WRITE (*,*) '5'

ELSEIF ((FLXGDL .GT. FLXCL) AND. (PRCNT .GT. 0.2)) THEN

NEWMAX = CO2IN

NEWMIN = C02MIN

DOUBLE PRECISION NVMEM, CRRNT

DOUBLE PRECISION CVCA, CVAN, FRDY

DOUBLE PRECISION THICK

DOUBLE PRECISION AM, AAN, ACA, RHODRY, MMDRY

C02IN = CO2IN*1.00017**(CRRNTX)

* LEXICON:

* REFERENCE -

* (PUKRUSHPAN, STEFANOPOULO, & PENG, 2004, PP. 53 - 56)

* X

ELSEIF (FLXGDL GT. FLXCL) AND. (PRCNT LT. 0.2)) THEN

NEWMAX = CO2IN

NEWMIN = CO2MIN

CO2IN = CO2IN*0.99999**(CRRNTX)

WRITE (55,*)

ELSEIF ((FLXCL GT. FLXGDL) AND. (PRCNT .GT. 0.5)) THEN

NEWMAX = CO2IN

NEWMIN = CO2MIN

CO2IN = CO2IN*1.00017**(CRRNTX)

* ACA = THE WATER (CATHODE) ACTIVITY AND IT IS
ELSEIF ((FLXCL .GT. FLXGDL) .AND. 
+ (PRCNT .LT. 0.2)) THEN

NEWMAX = CO2MAX

NEWMIN = CO2IN

CO2IN = CO2IN*0.999995**(CRRNTX)

* VARIABLE ARE IN UNITS OF METERS, NOT CENTIMETERS.
*
****X****************************

* RHODRY = IS THE MEMBRANE DRY DENSITY IN KG/M3.
* REFERENCE -
* (PUKRUSHAN, STEFANOPOULOU, & PENG, 2004, P. 58)
****X****************************

RHODRY = 0.002*(100**3)

****X****************************

* MMDRY = IS THE MEMBRANE DRY EQUIVALENT WEIGHT IN KG/MOLE.
* REFERENCE -
* (PUKRUSHAN, STEFANOPOULOU, & PENG, 2004, P. 58)
****X****************************

MMDRY = 1.1

****X****************************

* THICK = IS THE THICKNESS OF THE MEMBRANE IN METERS.
****X****************************

THICK = 0.000005

****X****************************

* FRDY = FARADAY'S CONSTANT
****X****************************

FRDY = 96485

****X****************************

* TFC = FUEL CELL TEMPERATURE IN KELVIN
****X****************************

TFC = 353.15

****X****************************

* PVAPOR = THE VAPOR PRESSURE IN PASCALS AT 353 K

VARIABLE ARE IN UNITS OF METERS, NOT CENTIMETERS.

ACAYH2OC*PCA/PVAPOR

WRITE (*, *)
WRITE (*, *) 'ACTIVITY OF WATER (CATHODE)', ACA
WRITE (*, *)
WRITE (55, *)
WRITE (55, *) 'ACTIVITY OF WATER (CATHODE)', ACA
WRITE (55, *)

AM = (AAN + ACA)/2.0

WRITE (*, *)
WRITE (*, *) 'ACTIVITY OF WATER (MEAN)', AM
WRITE (*, *)
WRITE (55, *)
WRITE (55, *) 'ACTIVITY OF WATER (MEAN)', AM
WRITE (55, *)

LMBDAA = 0.043+17.81*AAN-39.85*AAN**2 + 36.0*AAN**3
ELSEIF ((AAN .GT. 1.0) .AND. (AAN .LE. 3.0)) THEN

LMBDAA = 14+ 1.4*(AAN-1)
ENDIF

END IF
PVAPOR = 47360

* AAN = THE WATER (ANODE) ACTIVITY AND IT IS DIMENSIONLESS.

```
WRITE (*,*)
WRITE (*,*) 'MOLE FRACTION OF WATER (ANODE)', YVH2O
WRITE (*,*) 'PRESSURE OF HYDROGEN', PAN
WRITE (*,*)

WRITE (55,*)
WRITE (55,*) 'MOLE FRACTION OF WATER (ANODE)', YVH2O
WRITE (55,*) 'PRESSURE OF HYDROGEN', PAN
```

AAN = YVH2O*PAN/PVAPOR

```
WRITE (*,*) 'ACTIVITY OF WATER (ANODE)', AAN
WRITE (*,*)
WRITE (55,*)
WRITE (55,*) 'ACTIVITY OF WATER (ANODE)', AAN
```

AAN = YVH2O*PAN/PVAPOR

```
WRITE (55,*)
WRITE (55,*) 'LAMBDA(CATHODE)', LMBDAC
```

```
ELSEIF ((ACA .GT. 1.0) AND. (ACA .LE. 3.0)) THEN
LMBDAC = 14 + 1.4*(ACA-1)
ENDIF
```

```
WRITE (*,*)
WRITE (*,*) 'ELECTRO-OSMOTIC DRAG COEFFICIENT, ND
```

ND = (0.0029*LAMBDA**2 + 0.05*LAMBDA)

```
WRITE (*,*)
WRITE (*,*) 'CONCENTRATION (CATHODE)', CVCA
WRITE (*,*)
WRITE (55,*)
WRITE (55,*) 'CONCENTRATION (CATHODE)', CVCA
```

```
ELSEIF ((AM .GT. 0.0) AND. (AM .LE. 1.0)) THEN
LAMBDA = 0.043+17.81*AM-39.85*AM**2 + 36.0*AM**3
ENDIF
```

```
WRITE (*,*)
WRITE (*,*) 'LAMBDA(MEAN)', LAMBDA
WRITE (*,*)
WRITE (55,*)
WRITE (55,*) 'LAMBDA(MEAN)', LAMBDA
```

```
ENDIF
```

```
WRITE (*,*)
WRITE (*,*) 'CONCENTRATION (ANODE)', CVAN
WRITE (*,*)
WRITE (55,*)
WRITE (55,*) 'CONCENTRATION (ANODE)', CVAN
```

```
CVAN = RHODRY/MMDRY*LMBDAA
```

```
IF ((AM .GT. 0.0) AND. (AM .LE. 1.0)) THEN
LAMBDA = 0.043+17.81*AM-39.85*AM**2 + 36.0*AM**3
ELSEIF ((AM .GT. 1.0) AND. (AM .LE. 3.0)) THEN
LAMBDA = 14 + 1.4*(AM-1)
ENDIF
```

```
CVCA = RHODRY/MMDRY*LMBDAC
```

```
ELSEIF ((ACA .GT. 1.0) AND. (ACA .LE. 3.0)) THEN
LMBDAC = 14 + 1.4*(ACA-1)
ENDIF
```
* THIS BLOCK OUTPUTS THE $\Delta Y$, WHICH IS A DIFFUSIVITY.

```fortran
IF (LAMBDA .LT. 2.0) THEN
  DY = 1E-6
ELSEIF (LAMBDA .GE. 2.0) AND (LAMBDA .LE. 3.0) THEN
  DY = 1E-6*(1.0+2*(LAMBDA-2.0))
ELSEIF (LAMBDA .GT. 3.0) AND (LAMBDA .LT. 4.5) THEN
  DY = 1E-6*(3.0-1.67*(LAMBDA-3.0))
ELSEIF (LAMBDA .GE. 4.5) THEN
  DY = 1.25E-6
ENDIF
```

```fortran
WRITE (*,*)
WRITE (Y), DIFFUSIVITY(MEAN), I, DY
WRITE (*,*) WATER FLUX THROUGH THE MEMBRANE IS: NVMEM
WRITE (55,*)
WRITE (55,*) 'DIFFUSIVITY (WATER)', DW
```

```fortran
* DW = THE WATER A DIFFUSIVITY.
```

```fortran
DW = (DY * EXP(2416/(1/303 - 1/TFC)))/(100**2)
WRITE (55,*)
WRITE (55,*) 'INTERFACE VALUE AFTER EQN2', CH20IN
```

```fortran
* NVMEM = FLUX OF WATER WITHIN THE MEMBRANE.
```

```fortran
NVMEM = ND*((CRRNT*100**2)/FRDY) + DW'(CVCA - CVAN)/THICK
WRITE (*,*) WATER FLUX THROUGH THE MEMBRANE IS: NVMEM
WRITE (55,*) WATER FLUX THROUGH THE MEMBRANE IS: NVMEM
RETURN
END
```

```fortran
* CALCULATES THE COMPARISON.
```

```fortran
SUBROUTINE COMPRH(CHOMAX, CHOMIN, PNTI1, THICK, CHOGDL, CH20CL, CH20IN, NEWMAX, NEWMIN)
DOUBLE PRECISION FLXGDL, FLXCL, DIFF1, DLTXCL
DOUBLE PRECISION CHOGDL(1:1000), NEWMAX, NEWMIN
DOUBLE PRECISION CH2OCL(1:1000)
DOUBLE PRECISION DELTAX, CHOMAX, CHOMIN, THICK
INTEGER PNTI1
DOUBLE PRECISION CH20IN, ERRXR
```

```fortran
* VALUES OF INTERFACE (WATER - ANODE), CH20IN
```

```fortran
ENDIF
```

```fortran
* CALCULATES THE COMPARISON.
```

```fortran
ENDF
WRITE (*, *) 'THICK =', THICK

DELTAX = THICK/(PNTI1-1)

DLTXCL = THICK/(PNTI1-1)/10

FLXGDL = (CHOGDL(PNTI1) - CHOGDL(PNTI1-1))/DELTAX

WRITE (*, *) 'ANODE GAS DIFFUSION LAYER FLUX (WATER)', FLXGDL

FLXCL = (CH2OCL(2) - CH2OCL(1))/DLTXCL

WRITE (*, *) 'ANODE CATALYST LAYER FLUX (WATER)', FLXCL

DIFF1 = FLXGDL - FLXCL

ERRXR = 0.25*FLXGDL

CH2OIN = CHOGDL(PNTI1)

WRITE (*, *) 'INTERFACE VALUE BEFORE IF BLOCK', CH2OIN

IF (ABS(DIFF1).LT. ERRXR) THEN
  CH2OIN = CHOGDL(PNTM)
  WRITE (*, *) 'STEP C1', CH2OIN
ELSEIF (ABS(DIFF1).GE. ERRXR) THEN
  IF (FLXGDL .GT. FLXCL) THEN
    NEWMAX = CH2OIN
    NEWMIN = CHOMIN
    WRITE (*, *) 'INTERFACE VALUE BEFORE EQN1', CH2OIN
    NEWMAX = (CHOMAX + CHOMIN)/2.0
    WRITE (*, *) 'STEP C1', NEWMAX
    CALL SUBKUUI1N (CHOMAX, CHUMIN, PNTI1, THICK, CHOGDL, CH2OCL, CH2OIN, NEWMAX, NEWMIN)
    NEWMIN = CH2OIN
    WRITE (*, *) 'STEP C1', NEWMIN
    IF (ABS(DIFF1).LT. ERRXR) THEN
      CH2OIN = CHOGDL(PNTM)
      WRITE (*, *) 'STEP C1', CH2OIN
    ELSEIF (FLXCL .GT. FLXGDL) THEN
      NEWMAX = CHOMAX
      NEWMIN = CH2OIN
      WRITE (*, *) 'STEP C1', NEWMAX
      CALL SUBKUUIIN (CHOMAX, CHUMIN, PNTI1, THICK, CHOGDL, CH2OCL, CH2OIN, NEWMAX, NEWMIN)
      NEWMIN = CH2OIN
      WRITE (*, *) 'STEP C1', NEWMIN
  ELSEIF (FLXGDL .LT. FLXCL) THEN
    NEWMAX = CH2OIN
    NEWMIN = CHOMIN
    WRITE (*, *) 'STEP C1', NEWMAX
    CALL SUBKUUIIN (CHOMAX, CHUMIN, PNTI1, THICK, CHOGDL, CH2OCL, CH2OIN, NEWMAX, NEWMIN)
    NEWMIN = CH2OIN
    WRITE (*, *) 'STEP C1', NEWMIN
  ELSEIF (FLXGDL .EQ. FLXCL) THEN
    NEWMAX = CHOMAX
    NEWMIN = CH2OIN
    WRITE (*, *) 'STEP C1', NEWMAX
    CALL SUBKUUIIN (CHOMAX, CHUMIN, PNTI1, THICK, CHOGDL, CH2OCL, CH2OIN, NEWMAX, NEWMIN)
    NEWMIN = CH2OIN
    WRITE (*, *) 'STEP C1', NEWMIN
  END IF
ELSEIF (FLXCL .LT. FLXGDL) THEN
  NEWMAX = CHOMAX
  NEWMIN = CH2OIN
  WRITE (*, *) 'STEP C1', NEWMAX
  CALL SUBKUUIIN (CHOMAX, CHUMIN, PNTI1, THICK, CHOGDL, CH2OCL, CH2OIN, NEWMAX, NEWMIN)
  NEWMIN = CH2OIN
  WRITE (*, *) 'STEP C1', NEWMIN
ELSEIF (FLXGDL .GT. FLXCL) THEN
  NEWMAX = CH2OIN
  NEWMIN = CHOMIN
  WRITE (*, *) 'STEP C1', NEWMAX
  CALL SUBKUUIIN (CHOMAX, CHUMIN, PNTI1, THICK, CHOGDL, CH2OCL, CH2OIN, NEWMAX, NEWMIN)
  NEWMIN = CH2OIN
  WRITE (*, *) 'STEP C1', NEWMIN
END IF

DOUBLE PRECISION FLXGDL, FLXCL, DIFF1, DLTXCL
DOUBLE PRECISION CHOGDL(1:1000), CHOMAX, CHOMIN, PNTI1
DOUBLE PRECISION CH2OCL(1:1000), NEWMAX, NEWMIN
DOUBLE PRECISION DELTAX, CHOMAX, CHOMIN, THICK
DOUBLE PRECISION CH2OIN, ERRXR
WRITE (*,*) 'INTERFACE VALUE BEFORE EQN 2', CH2OIN
CH2OIN = (CHOMAX + CHOMIN)/2.0
WRITE (*,*) CHOGDL(PNTH)
ELSEIF (ABS(DIFFI) .GE. ERRXR) THEN
IF (FLXGDL .GT. FLXCL) THEN
NEWMAX = CH2OIN
NEWMIN = CHOMIN
WRITE (*,*) 'MAX', CHOMAX, 'MIN', CHOMIN
WRITE (*,*) 'STEP C3'
WRITE (Y) CH2OIN
ELSEIF (FLXCL .GT. FLXGDL) THEN
NEWMAX = CHOMAX
NEWMIN = CH2OIN
CH2OIN = (CHOMAX + CHOMIN)/2.0
WRITE (*,*) 'STEP C4'
WRITE (*,*) CH2OIN
ENDIF
WRITE (55, *) 'VALUE OF INTERFACE', CH2OIN
WRITE (55, *) 'STEP C3'
WRITE (*,*) CH2OIN
ELSEIF (FLXCL .GT. FLXGDL) THEN
NEWMAX = CHOMAX
NEWMIN = CH2OIN
CH2OIN = (CHOMAX + CHOMIN)/2.0
WRITE (*,*) 'STEP C4'
WRITE (*,*) CH2OIN
ENDIF
ENDIF
WRITE (55, *)
WRITE (55, *) 'VALUE OF INTERFACE ', CH2OIN
WRITE (55, *)
WRITE (*, *)
WRITE (*, *) 'VALUE OF INTERFACE ', CH2OIN
WRITE)*,*
RETURN
END

DOUBLE PRECISION DNSTY2(1:1000)
DOUBLE PRECISION UVEL3
DOUBLE PRECISION UVEL2
DOUBLE PRECISION DNSTY3(1:1000)
DOUBLE PRECISION UVEC1(1:1000, 1:3)
DOUBLE PRECISION EVEC1(1:1000, 1:3)
DOUBLE PRECISION EVVC1S(1:1000, 1:3)
DOUBLE PRECISION UVEC1N(1:1000, 1:3)
DOUBLE PRECISION EVCN1(1:1000, 1:3)
DOUBLE PRECISION TEMP
DOUBLE PRECISION VS
DOUBLE PRECISION KPER
DOUBLE PRECISION DELTAP
DOUBLE PRECISION PRESH2
DOUBLE PRECISION TX
DOUBLE PRECISION EX
DOUBLE PRECISION DE, GAMMA, MH2, MH2O
DOUBLE PRECISION THICK, RHODRY
DOUBLE PRECISION HVEC1(1:1000, 1:3)
DOUBLE PRECISION HVECN1(1:1000, 1:3)
DOUBLE PRECISION CRRNTD
SUBROUTINE GDLCLA(CURRENTD, LOOP1, PNT11, PRESH2, GAMMA, CH2, CH2O, CH23, CH2O3)

INTEGER I, PNT11, NUM8, LOOPX, LOOP1
INTEGER XRESX1

DOUBLE PRECISION CH2(1:1000)
DOUBLE PRECISION CH2O(1:1000)
DOUBLE PRECISION CH21(1:1000)
DOUBLE PRECISION CH2O1(1:1000)
DOUBLE PRECISION CH23(1:1000)
DOUBLE PRECISION CH2O3(1:1000)

* EW = EW IS THE EQUIVALENT WEIGHT OF MEMBRANE IN UNITS OF KILOGRAMS PER MOLE.

* RHODRY = RHODRY IS THE DRY MEMBRANE DENSITY IN UNITS OF KILOGRAMS PER METER CUBED.

* DH2H2O = THE DIFFUSIVITY OF HYDROGEN AND WATER IN THE ANODE GAS CHANNEL IN UNITS OF METERS SQUARED PER SECOND.

* THE THICKNESS THICK IS THICKNESS OF GAS DIFFUSION LAYER IN METERS.

* DELTAX IS THE CHANGE IN X IN METERS.

* DELTAT IS THE CHANGE IN T IN SECONDS.

* VS IS THE VISCOSITY OF HYDROGEN IN PASCAL-SECONDS.

* DELTAP = CHANGE IN PRESSURE BETWEEN ANODE AND CATHODE.

* EX = EX IS THE POROSITY AND IS DIMENSIONLESS.

* TX = TORTUOSITY.

* DE = EFFECTIVE DIFFUSIVITY.

* KPER = KPER IS PERMEABILITY OF ANODE/CATHODE GAS DIFFUSION LAYER. THE PERMEABILITY IS IN METERS SQUARED.

THICK = 0.000005

DELTAX = THICK/(PNT11-1.0)

DELTAT = DELTAX*0.0005

VS = 0.0000086

DELTAPE = 28.826*CRRNTD

EX = 0.5
* K = UNIVERSAL GAS CONSTANT
* MH2 = MOLECULAR WEIGHT OF HYDROGEN GAS
* MH2O = MOLECULAR WEIGHT OF WATER
* UVEL1 = FILTRATION VELOCITY IN X DIRECTION (CONSTANT)
* CH2() = CONCENTRATION OF HYDROGEN ARRAY
* CH2O () = CONCENTRATION OF WATER ARRAY
* DNSTY1 () = DENSITY ARRAY
* GAMMA = CP/CV
* PRESH2 = HYDROGEN PRESSURE IN GAS CHANNEL
* PNTI1 = LOCATION IN X DIRECTION (GRID POINT)
* UVEC1 = U VECTOR
* EVEC1 = E VECTOR
* EVEC1 = DIFFUSIVE PART OF E VECTOR

DE = DH2H2O*EX/ TX

R = 8.314

RHODRY = 1980

UVEL1 = KPER*DELTA P/(VS*THICK)
* MH2 IS THE MOLECULAR WEIGHT OF HYDROGEN.
MH2 = 2

* MH20 IS THE MOLECULAR WEIGHT OF WATER.
MH20 = 18

DO 11071 I = 1, PNTI1
HVEC(I,1) = 0.0
HVEC(I,2) = 0.0
HVEC(I,3) = 0.0
HVECN(I,1) = 0.0
HVECN(I,2) = 0.0
HVECN(I,3) = 0.0
11071 CONTINUE

DO 11200 LOOPX = 1, LOOP1
CH2(1) = PRESH2
CH2O(1) = 0.05*PRESH2
DNSTY1(1) = MH2*CH2(1) + MH20*CH20(1)
DNSTY1(PNTI1) = MH2*CH2(PNTI1) + MH20*CH20(PNTI1)

CALL PRIMI(EX, PNTI1, UVCP1S, DNSTY2, CH21, CH201)
CALL UVEC(EX, CH2, CH2O, PNTI1, DNSTY1, UVEC1)
CALL EVEC(CH2, CH2O, PNTI1, UVEL1, DNSTY1, EVECN1)
CALL ODDEVE(LOOP, NUM8)
IF (NUM8.EQ. 1) THEN
CALL EWEC(DE, CH2, CH2O, PNTI1, DNSTY1, DELTAX, EWEC1S)
CALL PRIMI(EX, PNTI1, UVCP1S, DNSTY2, CH21, CH201)
CALL UVEC(EX, CH2, CH2O, PNTI1, DNSTY1, UVEC1)
CALL EVEC(CH2, CH2O, PNTI1, UVEL1, DNSTY1, EVECN1)
IF (NUM8.EQ. 1) THEN
CALL EWEC(DE, CH2, CH2O, PNTI1, DNSTY1, DELTAX, EWEC1S)
ELSE IF (NUM8 .EQ. 0) THEN
DOUBLE PRECISION FLXGDL, FLXCL, DIFF1, DLTXCL
DOUBLE PRECISION CO2GDL(1:1000), NEWMAX, NEWMIN
DOUBLE PRECISION CRRNTX
DOUBLE PRECISION DELTAX, CO2MAX, CO2MIN
INTEGER PNTI1, K
DOUBLE PRECISION CO2IN, ERRXR, THICK, FRCNT
ELSE IF (NUM8 .EQ. 0) THEN
  CALL EVVECB(DE, CH2, CH2O, PNTI1, DNSTY1, DELTAX, EVVEC1)
  CALL CRRECBI(PNTI1, DELTAT, DELTAX, UVECN1, UVEC1, EVECN1, HVECN1, UVCP1)
ENDIF

***X***********************************************************************************
* STEP NO. 7 - CALCULATE THE PRIMITIVE VARIABLE VALUES.                             *
***X***********************************************************************************

CALL PRIMI(EX, PNTI1, UVCP1, DNSTY3, CH23, CH203)
CALL CNVRG (PNTI1, CH2, CH23, XRESX1)
DO 11100 I = 1, PNTI1
  DNSTY1(i) = DNSTY3(i)
  CH2(i) = CH23(i)
  CH2O(i) = CH203(i)
11100 CONTINUE

IF ((XRESX1 .GT. PNTI1*0.90) .AND. (LOOP .GT. 750000)) GOTO 11201

11200 CONTINUE

ERRXR = 0.1*FLXGDL
C02IN = C02GDL(PNTI1)
IF (PRCNT .LE. 0.01) THEN
  WRITE (55,"(55,*)'INTERFACE VALUE DID NOT CHANGE.'")
  WRITE (55,"(55,*)'CATALYST LAYER - GUESS'")
  WRITE (55,"(55,*)'CATALYST LAYER - GUESS'")
  WRITE (55,"(55,*)'CATALYST LAYER - GUESS'")
  DO 11105 I = 1, PNTI1
    WRITE (55,"(55,*)'")
    WRITE (55,"(55,*)'")
    WRITE (55,"(55,*)'")
 11105 CONTINUE
END IF
ELSEIF (PRCNT .GT. 0.01) THEN
  WRITE (55,"(55,*)'0'")
  DO 11105 I = 1, PNTI1
    WRITE (55,"(55,*)'")
    WRITE (55,"(55,*)'")
    WRITE (55,"(55,*)'")
 11105 CONTINUE
END IF

**FCON = 96485.0
DF = 0.00011028
FLXGDL = 0.0
FLXGDL = -2.0((100)**2)*FCON*DF*
(C02GDL(PNTI1) - C02GDL(PNTI1-1))/DELTAX
FLXCL = CRRNTX

WRITE (55,"(55,*)'COMPARISON'")
WRITE (55,"(55,*)'FLXGDL =',FLXGDL,'FLXCL =',FLXCL")
DIFF1 = FLXGDL-FLXCL
PRCNT = 0.0
11100 CONTINUE

IF (PRCNT .LE. 0.01) THEN
  WRITE (55,"(55,*)'PERCENT DEVIATION = ',PRCNT")
END IF
ELSEIF (PRCNT .GT. 0.01) THEN
  WRITE (55,"(55,*)'0'")
  DO 11105 I = 1, PNTI1
    WRITE (55,"(55,*)'")
    WRITE (55,"(55,*)'")
    WRITE (55,"(55,*)'")
 11105 CONTINUE
END IF

ERRXR = 0.1*FLXGDL
C02IN = C02GDL(PNTI1)
IF (PRCNT .LE. 0.01) THEN
  WRITE (55,"(55,*)'INTERFACE VALUE DID NOT CHANGE.'")
  WRITE (55,"(55,*)'CATALYST LAYER - GUESS'")
  WRITE (55,"(55,*)'CATALYST LAYER - GUESS'")
  WRITE (55,"(55,*)'CATALYST LAYER - GUESS'")
  DO 11105 I = 1, PNTI1
    WRITE (55,"(55,*)'")
    WRITE (55,"(55,*)'")
    WRITE (55,"(55,*)'")
 11105 CONTINUE
ENDIF
ELSEIF (PRCNT .GT. 0.01) THEN
  WRITE (55,"(55,*)'0'")
  DO 11105 I = 1, PNTI1
    WRITE (55,"(55,*)'")
    WRITE (55,"(55,*)'")
    WRITE (55,"(55,*)'")
 11105 CONTINUE
ENDIF

IF (FLXGDL .LT. 0.0) THEN


WRITE (55,*)
WRITE (*,*)
RETURN
END

CO2IN = CO2IN*1.00005**(CRRNTX)

WRITE (55,*)
WRITE (*,*)
RETURN
END

NEWMAX = C02IN
NEWMIN = C02MIN
CO2IN = CO2IN*0.9999995**(CRRNTX)

WRITE (55,*)
WRITE (*,*)
RETURN
END

NEWMAX = C02IN
NEWMIN = C02MIN
CO2IN = CO2IN*1.000007**(CRRNTX)

WRITE (55,*)
WRITE (*,*)
RETURN
END

NEWMAX = C02IN
NEWMIN = C02MIN
CO2IN = CO2IN*0.999995**(CRRNTX)

WRITE (55,*)
WRITE (*,*)
RETURN
END

NEWMAX = C02IN
NEWMIN = C02MIN
CO2IN = CO2IN*1.000007**(CRRNTX)

GAS DIFFUSION LAYER SUBROUTINE - GUESS

SUBROUTINE GDLCTC(CRRNTD, LOOP1, PNTI1, PRES02, + PRSH20, GAMMA, CO2, CH2O, CO23, CH2O3)
WRITE (*)'4'

ELSEIF ((FLXCL .GT. FLXGDL) AND. (PRCNT .GT. 0.5)) THEN
  NEWMAX = CO2MAX
  NEWMIN = CO2IN
  CO2IN = CO2IN*0.9999977**(CRRNTX)
  WRITE (*)'5'

ELSEIF ((FLXGDL .GT. FLXCL) AND. (PRCNT .GT. 0.2)) THEN
  NEWMAX = C02IN
  NEWMIN = C02MIN
  C02IN = CO2IN*1.0000017**(CRRNTX)
  WRITE (*)'6'

ELSEIF ((FLXCL .GT. FLXGDL) AND. (PRCNT .GT. 0.2)) THEN
  NEWMAX = C02MAX
  NEWMIN = C02IN
  C02IN = CO2IN*0.9999999**(CRRNTX)

DOUBLE PRECISION DNSTY1(1:1000)
DOUBLE PRECISION UVEL1
DOUBLE PRECISION DNSTY2(1:1000)
DOUBLE PRECISION UVEL2
DOUBLE PRECISION DNSTY3(1:1000)
DOUBLE PRECISION UVEL3
DOUBLE PRECISION DNSTY3(1:1000)
DOUBLE PRECISION UVEC1(1:1000, 1:3)
DOUBLE PRECISION EVEC1(1:1000, 1:3)
DOUBLE PRECISION EWEC1(1:1000, 1:3)
DOUBLE PRECISION EWC1S(1:1000, 1:3)

INTEGER I, MN111, NUMBi, LOOP, LOOP1

INTEGER XRESX1

DOUBLE PRECISION CO2(1:1000), CRRTD
DOUBLE PRECISION CH2O(1:1000)
DOUBLE PRECISION CO21(1:1000)
DOUBLE PRECISION CH2O1(1:1000)
DOUBLE PRECISION CO23(1:1000)
DOUBLE PRECISION CH2O3(1:1000)
DOUBLE PRECISION DELTAT, DELTAX
DOUBLE PRECISION UVEL1

* DO2 = DIFFUSIVITY OF OXYGEN

* DH2O = DIFFUSIVITY OF WATER

* THICK = THICKNESS OF GAS DIFFUSION LAYER

* DELTAT = TIME STEP

* DELTAX = SPATIAL STEP IN X DIRECTION

* VS = VS IS THE VISCOSITY OF OXYGEN IN PASCAL-SECONDS.

* DELTAP = CHANGE IN PRESSURE BETWEEN ANODE AND CATHODE

* EX = EX IS THE POROSITY AND IS DIMENSIONLESS.

* TX = TORTUOSITY

* DEO2 = EFFECTIVE DIFFUSIVITY OF OXYGEN

* DEH2O = EFFECTIVE DIFFUSIVITY OF WATER

* KPER = KPER IS PERMEABILITY OF ANODE/CATHODE GAS DIFFUSION

* LAYER. THE PERMEABILITY IS IN METERS SQUARED.

* R = UNIVERSAL GAS CONSTANT

* MO2 = MOLECULAR WEIGHT OF OXYGEN GAS

* MH2O = MOLECULAR WEIGHT OF WATER
DOUBLE PRECISION UVCP1S(1:1000, 1:3)
DOUBLE PRECISION UVCP1(1:1000, 1:3)
DOUBLE PRECISION UVEC1(1:1000, 1:3)
DOUBLE PRECISION EVECN1(1:1000, 1:3)
DOUBLE PRECISION EWCN1(1:1000, 1:3)
DOUBLE PRECISION TEMP
DOUBLE PRECISION VS
DOUBLE PRECISION KPER
DOUBLE PRECISION DELTAP
DOUBLE PRECISION PRES02, PRSH20
DOUBLE PRECISION D02, DH20
DOUBLE PRECISION TX
DOUBLE PRECISION EX
DOUBLE PRECISION DE, GAMMA, M02, MH20
DOUBLE PRECISION THICK, RHODRY

DOUBLE PRECISION HVEC1(1:1000, 1:3)
DOUBLE PRECISION HVECN1(1:1000, 1:3)

EW = 1.1

RHODRY = 1980

R = 8.314

TEMP = 353.15

UVEL1 = FILTRATION VELOCITY IN X DIRECTION (CONSTANT)

* CO2() = CONCENTRATION OF OXYGEN ARRAY

* CH2O() = CONCENTRATION OF WATER ARRAY

* DNSTY1() = DENSITY ARRAY

* GAMMA = CP/CV

* PRES02 = PARTIAL PRESSURE OF OXYGEN IN GAS CHANNEL

* PRSH20 = PARTIAL PRESSURE OF WATER IN GAS CHANNEL

* PNTI1 = LOCATION IN X DIRECTION (GRID POINT)

* UVEC1 = U VECTOR

* EVECN1 = E VECTOR

* EWECN1 = DIFFUSIVE PART OF E VECTOR

* EW IS THE EQUIVALENT WEIGHT OF MEMBRANE IN UNITS OF KILOGRAMS PER MOLE.

* RHODRY IS THE DRY MEMBRANE DENSITY IN UNITS OF KILOGRAMS PER METER CUBED.

* TEMP IS THE TEMPERATURE IN KELVIN.

* UVEL1 IS THE FILTRATION VELOCITY IN METERS/SECOND.

UVEL1 = KPER*DELTAP/(VS*THICK)
**DO2 AND DH20 ARE THE DIFFUSIVITIES OF OXYGEN AND WATER IN THE CATHODE GAS CHANNEL IN UNITS OF METERS SQUARED PER SECOND.**

\[
D_{O2} = 3.2348 \times 10^{-5} \\
D_{H2O} = 7.35 \times 10^{-4}
\]

**THE THICKNESS THICK IS THICKNESS OF GAS DIFFUSION LAYER IN METERS.**

\[
THICK = 0.00005
\]

**DELTA X IS THE change in x in METERS.**

\[
DELTA X = \frac{THICK}{PNTI1-1.0}
\]

**DELTA T IS THE CHANGE IN T IN SECONDS.**

\[
DELTA T = DELTA X \times 0.0005
\]

**VS IS THE VISCOSITY OF OXYGEN IN PASCAL-SECONDS.**

\[
VS = 0.00002018
\]

**THE PRESSURE DELTAP IS IN PASCALS.**

\[
DELTA P = 28.826^\text{CRRNTD}
\]

**EX IS THE POROSITY AND IS DIMENSIONLESS.**

\[
EX = 0.5
\]

**TX IS THE TORTUOSITY AND IS DIMENSIONLESS.**

**MUZ IS THE MOLECULAR WEIGHT OF OXYGEN.**

\[
MO2 = 32
\]

**MH2O IS THE MOLECULAR WEIGHT OF WATER.**

\[
MH2O = 18
\]

**THIS DO LOOP Initializes THE VALUES IN THE ARRAY.**

\[
DO 11071 I = 1, PNTI1 \\
HVEC1(I,1) = 0.0 \\
HVEC1(I,2) = 0.0 \\
HVEC1(I,3) = 0.0 \\
HVECN1(I,1) = 0.0 \\
HVECN1(I,2) = 0.0 \\
HVECN1(I,3) = 0.0
\]

11071 CONTINUE

**THIS DO LOOP ITERATES TO FIND A SOLUTION.**

\[
DO 11200 LOOP = 1, LOOP1 \\
C02(1) = PRES02 \\
CH2O(1) = PRSH2O \\
DNSTY1(1) = MO2*C02(1) + MH2O*CH2O(1) \\
DNSTY1(PNTI1) = MO2*C02(PNTI1) + MH2O*CH2O(PNTI1)
\]

**STEP NO. 2 - CALCULATE THE VECTORS QUANTITIES.**

**CALL UVECO(EX, C02, CH2O, PNTI1, DNSTY1, UVEC1)**

**CALL EVECO(C02, CH2O, PNTI1, UVEL1, DNSTY1, EVEC1)**
**DE IS THE EFFECTIVE DIFFUSIVITIES OF OXYGEN AND WATER.**

\[ \text{DEO}_2 = \text{DO}_2 \cdot \text{EX} / \text{TX} \]
\[ \text{DEH}_2O = \text{DH}_2O \cdot \text{EX} / \text{TX} \]

**STEP NO. 6 - CORRECTION**

\[ \text{DE}_02 = \text{DO}_2 \cdot \text{EX} / \text{TX} \]
\[ \text{DEH}_20 = \text{DH}_2O \cdot \text{EX} / \text{TX} \]

**KPER IS PERMEABILITY OF CATHODE/CATHODE GAS DIFFUSION LAYER. THE PERMEABILITY IS IN METERS SQUARED.**

\[ \text{KPER} = 1.12E-14 \]

**STEP NO. 7 - CALCULATE THE PRIMITIVE VARIABLE VALUES.**

CALL ODDEVE(LOOP, NUM8)

\[ \begin{align*}
\text{CALL EVVECO} & (\text{DEO}_2, \text{DEH}_2O, \text{CO}_2, \text{CH}_2O, \text{PNTI}_1, \text{DNSTY}_1, \\
& \text{DELTA}_1, \text{EVVEC}_1) \\
\text{ELSE IF (NUM8 .EQ. 0) THEN} \\
\text{CALL EVVCCB} & (\text{DEO}_2, \text{DEH}_2O, \text{CO}_2, \text{CH}_2O, \text{PNTI}_1, \text{DNSTY}_1, \\
& \text{DELTA}_1, \text{EVVEC}_1) \\
\text{ENDIF}
\end{align*} \]

**STEP NO. 3 - PREDICTION**

\[ \begin{align*}
\text{DO} & \text{ 11100} \\
\text{I} & = 1, \text{PNTI}_1 \\
\text{DNSTY}_1(I) & = \text{DNSTY}_3(I) \\
\text{CO}_2(I) & = \text{CO}_23(I) \\
\text{CH}_2O(I) & = \text{CH}_2O3(I) \\
\text{IF (NUM8 .EQ. 1) THEN} \\
\text{CALL PREDIC} & (\text{PNTI}_1, \\
& \text{DELTA}_1, \text{DELTA}_1, \\
& \text{UVEC}_1, \text{EVVEC}_1, \text{HVEC}_1, \text{UVCP1S}) \\
\text{ELSE IF (NUM8 .EQ. 0) THEN} \\
\text{CALL PREDICB} & (\text{PNTI}_1, \\
& \text{DELTA}_1, \text{DELTA}_1, \\
& \text{UVEC}_1, \text{EVVEC}_1, \text{HVEC}_1, \text{UVCP1S}) \\
\text{ENDIF}
\end{align*} \]

**ENDIF**

\[ \begin{align*}
\text{WRITE} & (55, *) \\
\text{WRITE} & (55, *) 'CATALYST LAYER (CATHODE) - GUESS' \\
\text{WRITE} & (55, *)
\end{align*} \]
STEP NO. 4 - CALCULATE THE PRIMITIVE VARIABLES VALUES.

CALL PRIMIO(EX, PNTI1, UVCPI1S,
+ DNSTY2, CO21, CH2O1)

STEP NO. 5 - CALCULATE THE VECTORS QUANTITIES.

CALL UVECO(EX, CO21, CH2O1, PNTI1,
+ DNSTY2,
+ UVECN1)

CALL EVECO(CO21, CH2O1, PNTI1,
+ UVEL1, DNSTY2,
+ EVECN1)

IF (NUM8 .EQ. 1) THEN
CALL EWECO(DE02, DEH2O, CO21, CH2O1, PNTI1,
+ DNSTY2, DELTAX, EWEC1S)
ELSEIF (NUM8 .EQ. 0) THEN
CALL EWCB0(DE02, DEH2O, CO21, CH2O1, PNTI1,
+ DNSTY2, DELTAX, EWCB1S)
ENDIF
RETURN
END

SUBROUTINE CMPRCG(C02MAX, C02MIN, PNTI1,
+ THICK, CO2GDL, CRRNTX, CO2IN, NEWMAX, NEWMIN,
+ PRCNT)
DOUBLE PRECISION FLXGDL, FLXCL, DIFF1, DLTXCL
DOUBLE PRECISION CO2GDL(1:1000), NEWMAX, NEWMIN
DOUBLE PRECISION CRRNTX
DOUBLE PRECISION DELTAX, CO2MAX, CO2MIN
INTEGER PNTI1, K
DOUBLE PRECISION CO2IN, ERRXR, THICK, PRCNT

WRITE (*,*) '0 CATHODE'
IF (FLXGDL .LT. 0.0) THEN
C02IN = CO2IN*0.999999
ELSEIF ((FLXCL .GT. FLXGDL) AND
+ (PRCNT.GT. 1.0)) THEN
NEWMAX = C02IN
NEWMIN = C02MIN
C02IN = C02IN*1.000005
ELSEIF ((FLXGDL .GT. FLXCL) .AND.
+ (PRCNT.GT. 0.5)) THEN
NEWMAX = C02IN
NEWMIN = C02MIN
ENDIF

WRITE (*,*) '1 CATHODE'
WRITE (*,*) '2 CATHODE'
ELSEIF ((FLXGDL .GT. FLXCL) .AND.
+ (PRCNT .GT. 0.5)) THEN
NEWMAX = CO2IN
NEWMIN = CO2MIN
CO2IN = CO2IN*1.000005
WRITE (*,*) '3 CATHODE'
ELSEIF (FLXCL .GT. FLXGDL) AND.
+ (PRCNT .GT. 1.0)) THEN
NEWMAX = CO2MAX
NEWMIN = CO2IN
CO2IN = CO2IN*0.999999
WRITE (*,*) '4 CATHODE'
ELSEIF (FLXGDL .LT. 0.0) THEN
NEWMAX = CO2IN
NEWMIN = CO2MIN
C02IN = C02IN*1.000005
ENDIF
RETURN
END
WRITE (*,*)
WRITE (*,*)'THICK = ', THICK
WRITE (*,*)
DELTAX = THICK/(PNTI1-1.0)
WRITE (*,*)
WRITE (*,*)'DELTA X = ', DELTAX
WRITE (*,*)
FCON = 96485.0
DF = 3.2348E-5
FLXGDL = 0.0
FLXGDL = -4.0/((100)**2)*FCON*DF*
+ (CO2GDL(PNT11) - CO2GDL(PNTI1-1))/DELTAX
FLXCL = CRRNTX
WRITE (*,*)'COMPARISON'
WRITE (*,*)'FLXGDL =', FLXGDL, 'FLXCL =', FLXCL
WRITE (*,*)
DIFF1 = FLXGDL-FLXCL
PRCNT = 0.0
PRCNT = ABS(DIFF1)/FLXCL
WRITE (*,*)'PERCENT DEVIATION = ', PRCNT
WRITE (*,*)
ERRXR = 0.1*FLXGDL
CO2IN = CO2GDL(PNT11)
IF (PRCNT .LE. 0.01) THEN
CO2IN = CO2GDL(PNT11)
WRITE (*,*)'INTERFACE VALUE DID NOT CHANGE.'
WRITE (*,*)
ELSEIF (PRCNT .GT. 0.01) THEN
CO2IN = CO2IN*0.9999999
WRITE (*,*)'7 CATHODE'
ELSEIF (FLXGDL .GT. FLXCL) AND. + (PRCNT .GT. 0.1)) THEN
NEWMAX = CO2IN
NEWMIN = CO2IN
CO2IN = CO2IN*0.9999999
WRITE (*,*)'5 CATHODE'
ELSEIF (FLXCL .GT. FLXGDL) AND. + (PRCNT .GT. 0.1)) THEN
NEWMAX = CO2IN
NEWMIN = CO2IN
CO2IN = CO2IN*1.0000001
WRITE (*,*)'6 CATHODE'
ELSEIF (FLXCL .GT. FLXGDL) AND. + (PRCNT .GT. 0.1)) THEN
NEWMAX = CO2IN
NEWMIN = CO2IN
CO2IN = CO2IN*1.0000002
WRITE (*,*)'4 CATHODE'
ELSEIF (FLXCL .GT. FLXGDL) AND. + (PRCNT .GT. 0.5)) THEN
NEWMAX = CO2MAX
NEWMIN = CO2IN
CO2IN = CO2IN*0.9999975
WRITE (*,*)'5 CATHODE'
ELSEIF (FLXGDL .GT. FLXCL) AND. + (PRCNT .GT. 0.2)) THEN
NEWMAX = CO2IN
NEWMIN = CO2MIN
CO2IN = CO2IN*1.0000001
WRITE (*,*)'6 CATHODE'
ELSEIF (FLXCL .GT. FLXGDL) AND. + (PRCNT .GT. 0.2)) THEN
NEWMAX = CO2IN
NEWMIN = CO2IN
CO2IN = CO2IN*0.9999999
WRITE (*,*)'7 CATHODE'
ELSEIF (FLXGDL .GT. FLXCL) AND. + (PRCNT .GT. 0.01) THEN
NEWMAX = CO2IN
NEWMIN = CO2IN
CO2IN = CO2IN*0.9999999
NEWMIN = CO2MIN
CO2IN = CO2IN^1.0000005
WRITE (",", '9 CATHODE'
ELSEIF ((FLXCL .GT. FLXGDL) .AND.
+ (PRCNT .GT. 0.1)) THEN
NEWMAX = CO2MAX
NEWMIN = CO2IN
CO2IN = CO2IN^0.9999995
WRITE (",", '9 CATHODE'
ELSEIF ((FLXGDL .GT. FLXCL) .AND.
+ (PRCNT .LE. 0.1)) THEN
NEWMAX = CO2IN
NEWMIN = CO2MIN
CO2IN = CO2IN^1.0000005
WRITE (",", '10 ANODE'
ELSEIF ((FLXCL .GT. FLXGDL) .AND.
+ (PRCNT .LE. 0.1)) THEN
NEWMAX = CO2MAX
NEWMIN = CO2IN
CO2IN = CO2IN^0.999999215
WRITE (",", '11 ANODE'
ENDIF
ENDIF
WRITE (55, *)
WRITE (55, )'VALUE OF INTERFACE ', CO2IN
WRITE (55, *)
WRITE (', ')
WRITE (', ')
WRITE ('VALUE OF INTERFACE ', CO2IN
WRITE (', ')
RETURN
END