Mathematical and Computational Modeling of Polymer Exchange Membrane Fuel Cells

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in Mechanical Engineering

by

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We recommend that the thesis prepared under our supervision by

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Abstract

In this thesis a comprehensive review of fuel cell modeling has been given and based on the review, a general mathematical fuel cell model has been developed in order to understand the physical phenomena governing the fuel cell behavior and in order to contribute to the efforts investigating the optimum performance at different operating conditions as well as with different physical parameters. The steady state, isothermal model presented here accounts for the combined effects of mass and species transfer, momentum conservation, electrical current distribution through the gas channels, the electrodes and the membrane, and the electrochemical kinetics of the reactions in the anode and cathode catalyst layers. One of the important features of the model is that it proposes a simpler modified pseudo-homogeneous/agglomerate catalyst layer model which takes the advantage of the simplicity of pseudo-homogenous modeling while taking into account the effects of the agglomerates in the catalyst layer by using experimental geometric parameters published. The computation of the general mathematical model can be accomplished in 3D, 2D and 1D with the proper assumptions. Mainly, there are two computational domains considered in this thesis. The first modeling domain is a 2D Membrane Electrode Assembly (MEA) model including the modified agglomerate/pseudo-homogeneous catalyst layer modeling with consistent treatment of water transport in the MEA while the second domain presents a 3D model with different flow filed designs: straight, stepped and tapered. COMSOL Multiphysics along with Batteries and Fuel Cell Module have been used for 2D & 3D model computations while ANSYS FLUENT PEMFC Module has been used for only 3D two-phase computation. Both models have been validated with experimental data. With 2D MEA model, the effects of temperature and water content of the membrane as well as the equivalent weight of the membrane on the performance have been addressed. 3D COMSOL simulation results showed that the fuel
performance can be improved by using flow field designs alleviating the reactant depletion along the channels and supplying more uniform reactant distribution. Stepped flow field was found to show better performance when compared to straight and tapered ones. ANSYS FLUENT model is evaluated in terms of predicting the two phase flow in the fuel cell components. It is proposed that it is not capable of predicting the entire fuel cell polarization due to the lack of agglomerate catalyst layer modeling and well-established two-phase flow modeling. Along with the comprehensive modeling efforts, also an analytical model has been computed by using MathCAD and it is found that this simpler model is able to predict the performance in a general trend according to the experimental data obtained for a new novel membrane. Therefore, it can be used for robust prediction of the cell performance at different operating conditions such as temperature and pressure, and the electrochemical properties such as the catalyst loading, the exchange current density and the diffusion coefficients of the reactants. In addition to the modeling efforts, this thesis also presents a very comprehensive literature review on the models developed in the literature so far, the modeling efforts in fuel cell sandwich including membrane, catalyst layer and gas diffusion layer and fuel cell model properties. Moreover, a summary of possible directions of research in fuel cell analysis and computational modeling has been presented.
To My Family,
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List of Symbols

a Water activity

$a_c$ Catalyst specific area, m$^2$

$\text{ave}$ Average value

$A$ Area, m$^2$

$A_0$ Catalyst surface area per unit mass of catalyst particle, m$^2$/kg

$A_v$ Specific reaction surface area per volume of CL and dependent on the platinum loading

$b$ Swelling coefficient of membrane

$C$ Molar concentration, mol/m$^3$

$C_{Ox}$ Surface concentration of the reacting species oxidized, mol/m$^3$

$C_{Rd}$ Surface concentration of the reacting species reduced, mol/m$^3$

$D$ Diffusivity, m$^2$/s

$E$ Electrode potential, V

$E_c$ Activation energy, J/mol

$E_r$ Reversible cell potential, V

$E_{W}$ Equivalent weight of membrane, kg/mol

$F$ Faraday’s constant, C/mol

$h$ Planck’s constant, J.s

$H$ Henry’s constant

$i$ Current density, A/m$^2$

$i_0$ Exchange current density, A/m$^2$

$j$ Reactant flux, mol/s.m$^2$

$J(s)$ Leverett J-function

$k$ Reaction rate coefficient
\( k_B \)  Boltzmann constant, J/K
\( k_b \)  Backward reaction (oxidation) rate coefficient
\( k_f \)  Forward reaction (reduction) rate coefficient
\( k_K \)  Kozeny constant
\( k_p \)  Hydraulic permeability of the membrane, m\(^2\)
\( K \)  Absolute permeability, m\(^2\)
\( K_{rk} \)  Relative permeability of phase k
\( L_c \)  Catalyst loading, m\(^2\)/kg
\( m_{P\nu} \)  Platinum loading, kg/m\(^2\)
\( M \)  Molecular weight, kg/mol
\( n \)  Number of electrons transferred
\( N \)  Number of agglomerates per unit volume, 1/m\(^3\)
\( N \)  Molar flux, mol/m\(^2\)
\( P \)  Pressure, Pa
\( P_C \)  Capillary pressure, Pa
\( P_{sat} \)  Saturation pressure, Pa
\( r \)  Radius, m
\( R \)  Universal gas constant, J/mol.K
\( s \)  Liquid saturation
\( s_{im} \)  Inmobile saturation
\( S \)  Reduced water saturation
\( S_x \)  Source term for x
\( t \)  Thickness of layer, m
\( T \)  Temperature, K
TS  Tafel slope, V/decade
u  Velocity vector, m/s
v  Velocity, m/s
V  Volume, m³
V_{cell}  Cell voltage, V
V_{OC}  Open cell voltage, V
W  Width, m
x  x-coordinate
y  y-coordinate
z  Charge number

Greek
\( \alpha \)  Transfer coefficient
\( \beta \)  Symmetry factor
\( \gamma \)  Pressure coefficient
\( \delta_{\text{avg}} \)  Average thickness of ionomer around agglomerates, m
\( \varepsilon \)  Porosity
\( \varepsilon_0 \)  Bulk porosity
\( \eta \)  Surface overpotential, V
\( \eta_{\text{drag}} \)  Electro-osmotic drag coefficient
\( \theta_c \)  Contact angle, degrees
\( \lambda \)  Water content
\( \lambda_k \)  Relative mobility of phase k
\( \mu \)  Viscosity, kg.m/s²
\( \nu \)  Kinematic viscosity, m²/s
\[ \xi \quad \text{Stoichiometric ratio} \]

\[ \rho \quad \text{Density, kg/m}^3 \]

\[ \rho_{m}^{dry} \quad \text{Dry density of membrane, kg/m}^3 \]

\[ \sigma \quad \text{Surface tension, N/m} \]

\[ \sigma_m \quad \text{Membrane conductivity, S/m} \]

\[ \Phi_e \quad \text{Electric potential of electrolyte phase, V} \]

\[ \Phi_s \quad \text{Electric potential of solid phase, V} \]

\[ \chi \quad \text{Mole fraction} \]

\[ \Delta G \quad \text{Gibbs free energy, J} \]

**Subscripts and Subscripts**

a \quad \text{Anode}

agg \quad \text{Agglomerate}

c \quad \text{Cathode}

C \quad \text{Carbon}

cc \quad \text{Current Collector}

ch \quad \text{Channel}

CL \quad \text{Catalyst layer}

eff \quad \text{Effective value}

G,g \quad \text{Gas, gas phase}

GDL \quad \text{Gas diffusion layer}

in \quad \text{Inlet}

L,l \quad \text{Liquid, liquid phase}

k \quad \text{species}

m \quad \text{Membrane}
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>ms</td>
<td>Mass</td>
</tr>
<tr>
<td>O</td>
<td>Reference state</td>
</tr>
<tr>
<td>PM</td>
<td>Porous medium</td>
</tr>
<tr>
<td>Pt</td>
<td>Platinum</td>
</tr>
<tr>
<td>r</td>
<td>Reactant</td>
</tr>
<tr>
<td>ref</td>
<td>Reference state</td>
</tr>
<tr>
<td>rds</td>
<td>Rate determining step</td>
</tr>
<tr>
<td>s</td>
<td>Solid</td>
</tr>
<tr>
<td>u</td>
<td>Momentum</td>
</tr>
<tr>
<td>w</td>
<td>Water</td>
</tr>
<tr>
<td>φ</td>
<td>Charge/current</td>
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1. INTRODUCTION

1.1. Introduction

Industrial Revolution which employs heat engines utilizing combustion of fossil fuels was one of the milestones of the human history. However, the major usage of fossil fuels has caused severe environmental pollution by emitting the greenhouse gases such as carbon dioxide, methane, nitrous oxide, ozone, etc. and concluded global warming that threatens the life on Earth. As the effect of climate change is getting worse, the aim to reduce greenhouse gas emissions drives the research and development for cleaner, more efficient energy technologies and alternative energy sources in order to minimize the pollutant emissions. In addition to the health and environmental concerns, the depletion of the limited fossil fuels increases the need for newer energy technologies employed with renewable energy sources for the sustainability.

Many of today's industries, policy makers, entrepreneurs, technology developers and scientists are investing considerable resources in searching and implementing alternative technologies to carry and convert energy. One of these potential energy technologies is the fuel cell. Fuel cells were invented 164 years ago by lawyer and scientist William Grove, firstly demonstrated in in 1939 by him, and then used in the early U.S. space program effectively. Although the fuel cell concept has been around for many years, they have only recently become economically competitive with traditional power systems due to technological advances over the last couple of decades.

Their superiorities concerning the health and environmental problems (less pollution comparatively with the same energy output) and high efficiency make them as one of the most promising and potential energy technologies of today. As fuel cell technology matures and further research advances are made in order to improve the performance and cost, fuel cells are expected to be more employed for
stationary, transportation applications and in small portable electronic devices such as laptops and cell phones.

This chapter gives a general overview of fuel cell technology with an emphasis on polymer electrolyte membrane fuel cells (PEMFCs) and meanwhile discusses the motivation for the study, research and development of fuel cells. An overview of fuel cell analysis, modeling and simulation are also provided while in the last section the thesis objectives are addressed.

1.2. Basics of Fuel Cells

A fuel cell is an electrochemical converter which continuously and directly derives electrical energy from the chemical energy of reactants that are fuel and oxidant. In Figure 1.1[1], the basic working principle of a fuel cell can be seen.

![Figure 1.1. Schematic showing a basic fuel cell[1].](image)

Actually, it is a device for power generation similar to batteries and heat engines. However, there are differences making fuel cell advantageous over batteries and heat engines. A fuel cell can work forever as soon as the reactants are supplied but a battery has a limited lifetime. Moreover, the efficiency of a
fuel cell is not limited by Carnot efficiency like in a heat engine. Further information will be given in the next section.

A fuel cell is simply composed of three major components, similar to a chemical battery: a fuel electrode (anode), an oxidant electrode (cathode) and an electrolyte squeezed between them. The electrodes are porous and electrically conductive and typically made of carbon cloth which is supported with catalyst particles at the interface with the electrolyte creating a catalyst layer where the reactions occur. The fuel is and the oxidized fuel or protons travel through

(i) The **anode** is the electrode where the fuel is split into the protons and electrons or in other words, the fuel is oxidized and electrons are released to travel through the external circuit. The reactions occur in the presence of a catalyst, typically Pt (although mixtures such as Pt/Ru may be used if there are carbon-containing species in the anode feed). Dissolved reactant gases must be available adjacent to the catalyst surface.

(ii) The **membrane**, separating the anode and cathode, is a thin layer of a special polymer. The protons pass through the membrane from the anode to the cathode, with the membrane serving as the “electrolyte” of the electrochemical cell. The electrolyte is supposed to be impermeable to gases and allows only protons to pass through whereas electrons are forced to transfer through an external circuit.

(iii) The **cathode** is the electrode where the electrons returning from the external circuit and protons passing through the membrane from anode side arrive at the cathode catalyst layer and react with the oxidant (mostly oxygen) by producing byproducts such as water. In other words, oxidant is reduced with the electrons coming from the external circuit. The direction of electric current in the external circuit is from the anode to the cathode and the direction of protonic current is again from the anode to the cathode side in the electrolyte membrane.
Fuel cells can be classified in many different ways but the common one is based on the electrolyte used. If a fuel cell contains the electrolyte as:

- An alkaline solution which is normally KOH in water, then it is referred to as an alkaline fuel cell (AFC): They have a wide range of operating temperature. High concentrated electrolyte (85%) is used for high temperature operation (250 °C) whereas for lower temperature operation (<120 °C), less concentrated solution (35-50 %) is used. Electro catalysts such as Ni, Ag, metal oxide and noble metals can be used. Alkaline fuel cells have been used in the space program (Apollo and Space Shuttle) since 1960s [2].

- Phosphoric acid, then it is called a phosphoric acid fuel cell (PAFC): It operates typically at temperatures between 150 and 220 °C. Platinum is the electro catalyst used in both anode and cathode. They are mostly used for stationary electricity generation.

- A molten carbonate salt, then it is referred to as a molten carbonate fuel cell (MCFC): The electrolyte is composed of carbonates of alkali metals such as Li, Na, K. They operate at high temperatures (600-700 °C) where noble catalysts are generally not required. They are promising for stationary power generation.

- A solid oxide ion-conducting ceramic, then it is called solid oxide fuel cell (SOFC): Operating temperature is between 800 and 1000 °C where oxygen ions provides the ionic conduction. These fuel cells have been used for portable power and auxiliary power in automobiles but offer promising technology for stationary power generation like MCFCs [2].

- A solid proton-conducting (or proton exchange) polymer membrane, then it is referred to as the proton exchange (polymer electrolyte) membrane fuel cell (PEMFC): The electrolyte is proton conductive polymer membrane such as perfluorosulfonated acid polymer. They operate typically at temperatures between 60 and 80 °C. The catalyst is typically platinum and
sometimes Pt-Ru mixtures are used in order to decrease the amount of CO in fuel (i.e., when the fuel is hydrocarbon like methanol).

The PEMFCs using hydrogen as the fuel is the focus of this thesis.

### 1.3. Hydrogen PEMFC

In a PEMFC which uses hydrogen as the fuel, the anode oxidation reaction, the cathode reduction reaction, and the overall reaction as a redox process are given in the following:

#### Half Reaction at the cathode:

\[
H_2 \rightarrow 2H^+ + 2e^- \tag{1.1}
\]

#### Half Reaction at the cathode:

\[
O_2 + 4e^- \rightarrow 2O_2^{2-} \tag{1.2}
\]

#### Overall:

\[
2H^+ + O_2^{2-} \rightarrow H_2O + \text{heat} \tag{1.3}
\]

The basic principle of operation of hydrogen PEMFC can be seen in Figure 1.2[3].

![Figure 1.2. Schematic of a hydrogen/air fuel cell[3].](image)

During the electrochemical reactions occurring at the anode and cathode, heat is also generated and is accepted as a byproduct called waste heat. Even if this waste heat is an unwanted byproduct since the temperature of the fuel cell is controlled to be uniform in the cell; this waste heat can be used to reform fuels, provide heat, and drive engines used for operating pumps or reformers in fuel cell systems.
1.4. Motivation for PEMFCs

The concept of PEMFCs has been well established since early 1960s, and they are successfully commercialized for many applications, such as electrical power sources in space crafts and submarines [4]. PEMFCs have attracted clean energy producers due to their high energy efficiency, low emission, low operation temperature and low noise; and in the last decades, they have been regarded as prominent and promising energy-conversion technology for mobile, stationary, and portable power applications, especially for the electrical vehicles and portable electrical devices in addition to residential applications.

Fuel cells have been developed and demonstrated in diverse power requiring applications. These applications include automobiles, scooters and bicycles, golf carts, utility vehicles, distributed power generation, backup power for facilities including hospitals, schools, portable power for laptops and cell phones, space, airplanes, locomotives, boats, underwater vehicles.

Fuel cells have many characteristics that make them a viable alternative to conventional energy conversion systems:

Efficiency: The main advantage of the fuel cells over heat engines is that they are not limited by Carnot efficiency. Secondly, while a heat engine driven generator converts chemical energy of reactants into electrical energy by multiple steps in several different devices, in fuel cells, the energy released from the inter-atomic bonds of the reactants is converted directly into usable electrical energy which increases the energy efficiency dramatically. Therefore, there is no need for gases to be heated to create explosive reactants and no moving parts similar to pistons and crankshafts to be built.

A comparison of fuel cell systems versus other energy conversion systems is shown in Figure 1.3[5].
Figure 1.3 demonstrates that the exergy or Second Law efficiency of fuel cell systems compares favorably to all other energy conversion systems using hydrocarbons for fuel. In fact, fuel cell systems have the highest overall average efficiency of all systems except hydroelectric plants. The clear boxes above each efficiency column indicate the theoretical improvements that are predicted for each system. Figure 1.3 also indicates fuel cell systems can be used to generate power over a large range of power requirements. These higher efficiencies allow for a better use of natural resources such as hydrocarbons.

**Low emissions:** As the world becomes more industrialized, a second key advantage of fuel cells, lower emissions, becomes essential for controlling global pollution. When pure hydrogen is used directly as a fuel, only water is created and no pollutant is rejected. The processing of hydrocarbon fuels into hydrogen can result in small amount of NOx, SOx, CO, and an amount of CO2 significantly lower when
compared, for example, to classical internal combustion engines[7]. In addition, CO concentrations are below 10 ppm and unreacted hydrocarbons are recirculated in the system[6].

**Scalability:** Fuel cells can be configured to suit a wide range of sizes for applications, ranging from a few watts to megawatts and they also are easily scaled, allowing them to be used for small applications such as the power source for a personal computer as well as large applications like vehicles or large stationary power plants[6].

**Fuel flexibility:** Fuel cells can be operated using commonly available fuels in addition to hydrogen discussed in this thesis such as natural gas, methanol, and various complex hydrocarbons.

**Reliability and low maintenance:** As mentioned before, in fuel cells, the energy released from the inter-atomic bonds of the reactants is converted directly into usable electrical energy which increases the energy efficiency dramatically. Therefore, there is no need for gases to be heated to create explosive reactants and no moving parts similar to pistons and crankshafts to be built. The absence of moving parts reduces the maintenance requirements. Furthermore such systems operate much more quietly, resulting in less noise pollution. On the other hand, when compared to batteries, the lifetime of a fuel cell is unlimited as long as the reactants are supplied whereas a battery can produce electric energy output depending on the amount of the reactants stored onboard or for the rechargeable kinds, depending on the charge they can hold[2].

**Cogeneration capability:** The use of fuel cells in stationary residential power applications allow electricity to be created where it is consumed, making the home to become less susceptible to power interruptions due to power grid failures and inclement weather[6]. Moreover, the heat resulted by the fuel cell’s exothermic chemical and electrochemical reactions can be harnessed and used to supplement home and hot water heating which make fuel cells more economically feasible.
**Less corrosion:** Because no liquid electrolyte is employed, corrosion problems in the polymer electrolyte fuel cell are reduced and cell construction is simplified[2, 8].

### 1.5. Main Fuel Cell Performance Issues

The electrochemical reactions occurring at the anode and the cathode are named as half-cell reactions. Each half reaction has its own electric potential which is simply the reaction energy per unit electrical charge. In the fuel cell operation, the anode has a lower electric potential and the cathode has a higher electric potential, and the electric potential difference between them is called the cell potential.

In practice, a fuel cell always has energy losses, demonstrated in terms of electric potential losses. These losses may decrease cell potential to about 0.7-0.8 V at practical current densities[2]. Voltage loss in a fuel cell is called overvoltage and mostly overpotential or polarization. Therefore, the curve representing this decreasing cell potential versus current density (current per unit surface area) is called as **polarization curve**. The performance of a fuel cell is examined by the relationship between the cell voltage and current density which gives polarization curve and the power curve corresponding to this polarization curve. The lower the polarizations, the higher power produced by the cell and the better performance obtained. A general polarization is given in Figure 1.4[9].

There are different kinds of voltage losses in a fuel cell caused by many irreversibilities due to kinetics of electrochemical reactions, internal electrical and ionic resistance, difficulties in getting the reactants to reaction sites, internal(stray) currents and crossover of reactants[9, 10]. These factors are grouped mainly in three polarization types which are activation, ohmic and concentration, respectively missing the last one.
Figure 1.4. A typical polarization curve showing different types of losses dominant in low, medium and high current density regions[9].

Activation polarization is due to the energy need to get the electrochemical reaction going, which is called activation energy by the chemists and it is associated with sluggish electrode kinetics[9, 10]. Therefore, in order to predict the activation loss in the cell voltage, typically, chemical kinetic parameters that determine the rates of reaction at the anode and cathode, involving a reaction rate parameter, the exchange current density, a function of the concentration of reactant in the electrolyte are used[11]. Oxygen reduction reaction at the cathode is much slower than the oxidation reaction at the anode so requires much higher overpotential compared to anode polarization. This polarization is higher at lower current densities since the activation energy is much higher at the beginning of the operation.
Ohmic polarization occurs due to resistance of the flow of hydrated H+ ions through the membrane electrolyte and resistance to the flow of electrons through the electrically conductive fuel cell components, briefly internal electrical and ionic resistance. These losses are expressed by Ohm’s Law, so they are linearly dependent on current density. Total internal resistance includes ionic, electronic and contact resistance[9, 11].

Concentration polarization is related to the difficulties in diffusion of the reactants to the reaction sites. When a reactant is rapidly consumed at the electrode by the electrochemical reaction, a concentration gradient is established which is directly related to the electrochemical reaction potential. The reactant concentration at the catalyst depends on current density since the current is formed as the reactant is consumed. When the reactant is consumed faster than it reach the active surface where the reaction occur, in other words, when the rate of consumption exceeds the diffusion rate of reactant; the surface concentration reaches zero finally. Since there is no reactant at the catalyst surface, fuel cell cannot produce current, which result in a sharp drop in cell potential at the highest possible current density as seen in Figure 1.4[9].

In addition to the activation, ohmic and concentration losses, there are also crossover losses and internal currents which decrease the cell potential, especially when the cell is at open circuit potential (no current) or when it operates at very low current densities. This is due to the fact that although the electrolyte is not electrically conductive and practically impermeable to reactant gases, some amount of hydrogen will diffuse from anode to cathode (fuel crossover) due to very high concentration of hydrogen in the start-up of fuel cell, and some electrons find a “shortcut” through the membrane (internal currents)[9]. However, this phenomenon is taken into consideration by using the open circuit voltage as the initial voltage (around 1.0V) instead of reversible cell voltage, 1.229 V [9, 12, 13].
Since the performance of a fuel cell depends on these polarizations, there is a major effort in the research and development (R&D) of fuel cell technology in reducing these polarization losses. The effective approaches to achieve this include\cite{2, 14}:

- Developing sufficiently utilized active catalysts to enhance the rate of electrochemical reactions in order to decrease the activation and concentration polarization,
- Engineering of cell components in order to decrease mainly ohmic losses by reducing the total resistance,
- Improving the diffusion of reactants and products as well as ions in order to decrease the concentration losses.

Overall fuel cell system performance is dependent on many parameters which strongly interact with each other. Limiting the investigation to the fuel cell itself and not the surrounding fuel processing and power conditioning sub-systems, focus is placed on the operation of a single fuel cell. The main performance issues needed to ensure efficient fuel cell operation are expressed as following.

**Reactant distribution:** In order to achieve high efficiency and higher power density, fuel cells must maintain a high current density distributed uniformly across the cell active area. Uniform reactant distribution at the interface between the gas channels and the electrodes is essential to ensure uniform current densities. Without homogeneous distribution of reactants, “dead zones may occur within the cell and this will increase the losses due to concentration polarization\cite{6, 7}.

**Water management:** Membrane transport properties are highly water dependent, and thus too little water causes the membrane to dry out and lose conductivity. In order to have functional proton conductivity in the membrane, the membrane must be hydrated with water. It is also necessary to avoid damage to the membrane structure and to prevent localized hot spots \cite{6, 7}. The reactants flow both at the anode and cathode sides are usually humidified to help ensure membrane hydration. In addition, at
the cathode, water is produced in liquid phase during the electrochemical reaction, providing another source for membrane hydration. Therefore, the sources of water in a fuel cell include the water vapor which is transported by the reactants flow both at the anode and cathode sides and water produced in liquid phase during the electrochemical reaction at the cathode. Water is transported through the membrane by convection due to a pressure gradient between electrodes, by diffusion due to a water concentration gradient, and by a drag force imposed on the water molecules by positively charged protons moving through the membrane from anode side to cathode side. When combined together, the action of these phenomena can result in an uneven water distribution in the membrane. For example, at high current densities, the anode side may dry out even if the cathode side remains hydrated. On the other hand, if an excess of water is present, this water could result in blocking the pores that allow reactant transport, and affecting the reaction rate, which is known as flooding. Flooding is a phenomenon which increases both the concentration and activation losses. In most applications, the concentration of water is higher on the cathode side than the anode side due to water transport through the membrane and the production of the water at cathode; and flooding if it occurs, occurs on the cathode side. The excess water must be removed from the cathode pores to prevent flooding. Due to the reasons explained above, water management in PEMFCs is critically important for the design of materials and operating conditions to produce sufficient liquid water to fully hydrate the membrane without flooding.

**Catalyst layer transport properties and utilization rate:** It is important to effectively utilize the catalyst layer because of the high costs of catalyst materials. In order to ensure the best utilization of the catalyst layer, the reactants need to be transported at a uniform rate to the reaction site at the surface of the agglomerates of Teflon® and platinum particles[15]. Reactant transport occurs within the pores separating these agglomerates, while proton transport occurs in the polymer phase. The transport of
reactants becomes a limiting factor if too much resistance is offered to diffusion of species in the pores. This can occur at high current densities, or in the case of flooding due to excess liquid water.

**Heat management:** Many material properties that govern the performance of the fuel cell are temperature dependent. The exothermic reaction taking place inside the PEMFC, their reversibility due to cathode over potential and the ohmic losses in the membrane and electrodes are the main heat sources during the operation. It is important to remove the heat from the system to avoid local temperature spikes occur within the cell, to maintain liquid water in the membrane and prevent the possible deformation of the cell components especially the membrane material. Therefore, homogenized temperature distribution is desired over the cell to keep away from thermal stresses, and local hot spots[16]. The membrane material and fuels used dictate the temperature range the cell must operate. For Nafion®, using gaseous fuels this range is 80-100°C.

Another major engineering challenge to the fuel cell development and practical applications is the low electrical potential of a single cell output. It is required to combine many cells in series in order to have feasible voltages for an application. This is accomplished by the so-called cell stacking which is defined as “the technique of electric connection between individual cells[2].”

Presently, bipolar arrangement is preferred by placing an electrically conducting bipolar plate separating each cell so that the cathode of one cell is in electrical contact with the anode of the next cell. The reactant supply to each cell is accomplished by the flow channels machined on the bipolar plate. The design of fuel cell stacks has a major impact on the performance and cost of the fuel cell systems[2]; but in this work, only design of a single cell is taken into consideration.

Over the last couple of decades, significant improvements have been achieved in PEMFC technology, including improved MEA preparation techniques, the incorporation of new materials of membrane and electrodes, lowered platinum catalyst loading, more uniform distribution of reactants by developing
different flow channel patterns. However, further improvements of the PEMFC in terms of performance and cost are necessary for fuel cell systems to become more competitive in the market place.

1.6. Background Needed for Fuel Cell Analysis, Research & Design (R&D) & Fuel Cell Modeling

The science and the technology of fuel cells involve many branches and disciplines of science and engineering, including but not limited to the following:

- Thermodynamics,
- Electrochemistry,
- Chemistry and chemical engineering,
- Fluid mechanics,
- Heat and mass transfer,
- Material science and materials engineering,
- Polymer science and specifically ionomer chemistry,
- Design, manufacturing and engineering optimization,
- Solid mechanics and mechanical engineering, and
- Electromagnetism and electrical engineering.

Since fuel cells require a multidisciplinary knowledge, interaction and integration, one individual may not possess the necessary background, and teamwork and collaboration is a must for a successful fuel cell R&D program.

The main focus on fuel cell design and engineering includes efforts for better performance, improved durability, cost reduction, and better cold-start characteristics. This focus need for identification, understanding, prediction, control, and optimization of various transport and electrochemical processes that occur in fuel cells.
Since PEMFC performance depends on a large number of coupled physical phenomena such as fluid flow, heat, mass and charge transport, and electrochemical processes; PEMFC design is not an easy task. These coupled processes are controlled by a large number of physical parameters that might have competing effects on the different physical phenomena. For instance, changing a specific parameter may help the mass transport but reduce reaction kinetics. As defined as fuel cell law in [9]: “First fuel cell law: One cannot change only one parameter in a fuel cell-change of one parameter causes a change in at least two other parameters, and at least one of them has an opposite effect of the one expected to be seen”. For this reason, in order to obtain an optimal PEMFC design, all design parameters must be varied simultaneously during the design process like in parametric studies.

Theoretical analysis, modeling and simulation may be performed for a particular phenomenon or a collection of phenomena that occur in a specific fuel cell system. The objective may be to understand and elucidate the phenomena and their impact on fuel cell performance, and how to design the various components of a fuel cell system to harvest the desirable effects or to avoid a detrimental influence. Hence, the ultimate objective is to carry out either performance evaluation of an existing fuel cell or attempt performance prediction for a new design. Because the relationship between cell voltage and current density drawn from the cell with constitute the primary measure of a fuel cell performance, other performance measures such as cell energy conversion efficiency and power density can be easily derived from the information, the ultimate goal of any fuel cell analysis and modeling is to calculate the cell polarization curve under various operating and design conditions.

The calculation of cell polarization curve begins typically with the Nernst equation, which gives the reversible (or the best possible) cell potential. Then all three modes of voltage losses, namely activation, ohmic and concentration overpotential are calculated from the conservation equations for total mass (continuity equation), species (including both neutral and charged species), momentum, and energy along with the transport equations for the transport phenomena of mass (including neutral and charged
species), momentum and energy. The mechanism and rate of electrochemical reactions are employed for the rate of mass and electric current production. Finally, the actual cell potential is determined by subtracting the overpotential from the reversible cell potential. From cell voltage and current density, the energy efficiency, power density, and rate of waste heat generation (which dictates the cooling requirement) can be easily established. Figure 1.5[17] illustrates the elements of a typical fuel cell analysis, modeling and simulation. Treatment of the conservation and transport equations gives rise to theoretical models of various degrees of complexity. With the advancement of computer science and numerical techniques, it may become possible to solve these equations for sophisticated geometrical designs[2].

![Flowchart](image)

**Figure 1.5. Elements of typical fuel cell analysis, modeling and simulation[17].**

Simulation models of PEMFCs already exist but most of them are only capable of individually addressing the performance issues described in the previous section and don’t include the complete fuel cell. Available experimental data and mathematical models have been obtained for very restricted and
idealized situations, and do not take into account of phenomena other than the one investigated. Both experimental and analytical/numerical studies need to be conducted and compared with each other for describing a complete fuel cell system. Much effort has been expended in the last decade upon development of numerical models with increasingly less restrictive assumptions and more physical complexities. Current development in PEMFC modeling is in the direction of applying computational fluid dynamics (CFD) to solve the complete set of transport equations governing mass, momentum, species, energy, and charge conservation. Computational modeling concept makes possible to investigate complex geometries and different situations by expending less time and effort than experimental investigations.

A computational fuel cell model is a mathematical representation of the physical phenomena (including electrochemical processes) governing fuel cell operation. This includes a set of differential equations which are conservation equations and boundary conditions, which define the transport processes within a fuel cell, and closure relations (or coupling equations) which express how the transport equations are related to one another. Additional equations that define the physical properties of the materials used in a given fuel cell are also needed. Once the mathematical model is developed, the resulting set of equations is solved numerically using a finite element or computational fluid dynamics (CFD) solver or other numerical method.

Computational models of PEMFC’s are primarily useful in two regards. First, they offer a means of learning more about the complex physical phenomena governing fuel cell performance. For example, due to the nature of fuel cells, it is difficult to evaluate many of the physical phenomena in situ [18]. Due to complex interactions, it is difficult to perform experimental investigation to understand all the details of physics in a PEMFC during operation. With a model, this information, which would otherwise be difficult to obtain, is readily accessible. Computational models are also useful design tools. For instance, one might use a fuel cell model to perform parametric studies on a given design to evaluate its
performance and identify areas in need of improvement. The models themselves can be simple, focusing on one or more physical phenomena, or complex and comprehensive in scope. The advantage of a simple model is that a great deal of information may be gained in a short period of time, since a simple model can be solved much more quickly than can a large, comprehensive model. Conversely, a comprehensive model will take longer to solve, but will yield much more information than a simple model. A comprehensive model is necessary when attempting to simulate how all of the phenomena occurring in a fuel cell are related to one another.

1.7. Thesis Objectives & Contributions to Literature

The principal objective of this research is to develop a comprehensive, computational model of a PEMFC that satisfies the following three criteria:

- The model is based on a mathematical description of fuel cell physics in a complete fuel cell including membrane, catalyst layers (CLs), gas diffusion layers (GDLs), gas channels and current collectors; and can be solved in one, two, and three dimensions.
- The model is useful as a learning tool in that it can facilitate a greater understanding of the physical phenomena that govern fuel cell behavior.
- The model is useful as a design tool in that it allows for the evaluation of fuel cell design concepts. This requires that the model be flexible with respect to geometry, material properties and operating conditions.

This model is capable of dealing with all the different performance issues in a PEMFC and will eventually act as a valuable design tool for future developments once a comprehensive solution scheme for the model has been developed and implemented.

In support of and in addition to the principal research objectives, the following objectives are also established:
to implement and solve the system of governing and constitutive equations and closure relations by using a computational model built in COMSOL Multiphysics and by using PEMFC Module in FLUENT,

to validate the model using numerically predicted data and experimental data found in the literature,

to generate an extensive set of results and perform a detailed analysis of the phenomena present by conducting parametric studies with particular attention given to the effects of the membrane structure on cell performance and water transport,

to develop recommendations for future work which could lead to improvements in the existing model and which couples this model to others in the fuel cell.

This work presented here contributes to the literature mainly by the followings:

- presenting a very comprehensive review of fuel cell modeling, especially in the physical representation of phenomena occurring in the fuel cell components,

- establishing a general mathematical fuel cell model which incorporates the most successful models of the fuel cell components while presenting the governing equations in a single domain approach,

- developing a combined pseudo-homogenous/agglomerate catalyst layer model which takes the advantage of the simplicity of pseudo-homogenous modeling while taking into account the effects of the agglomerates in the catalyst layer by using experimental geometric parameters published,

- comparing the stepped and tapered flow fields by simulating the polarization performance and the reactant distributions for similar entrance and exit channel dimensions and modeling approach,
developing computational fuel cell models by using COMSOL Multiphysics and ANSYS FLUENT tools besides analytical mathematical model,
performing parametric studies investigating the effect of temperature and water content on the membrane performance and accordingly on the overall fuel cell performance.

The present study differs from earlier studies in transport modeling, especially in the CL and the membrane. The CL model developed here proposes a novel approach considering the agglomerate structure while using the comparatively more robust and simpler pseudo-homogeneous modeling for CL. Also, the water transport through the membrane is accounted by considering the swelling effect and the convection transport which are mostly neglected in the previous models. As can be seen in Table 1.1, the main difference between the catalyst layer models: pseudo-homogenous and agglomerate models, is in the governing reactant transport, especially oxygen mass transfer.

<table>
<thead>
<tr>
<th>Table 1.1. Comparison of pseudo-homogeneous and agglomerate models for catalyst layer[7]</th>
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<tr>
<td><strong>Pseudo-homogeneous</strong></td>
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<tr>
<td>The catalyst is treated as a homogeneous phase.</td>
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<tr>
<td>The oxygen diffuses through the porous media.</td>
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In this study, the catalyst is treated as a homogeneous phase like in the pseudo-homogeneous modeling, which makes the model robust. On the other hand, it also considers the effect of the agglomerates on the reactant transport such as oxygen mass transfer as well as the conduct of electrons and protons by modifying diffusion coefficients and electron and proton conductivity of the catalyst layer according to
experimentally obtained agglomerate parameters and this improves prediction capability of the catalyst layer model. The modified model takes into 3 phases of catalyst layer account while a pseudo-homogeneous model treat catalyst layer as 2 phases. In agglomerate models, the effect of agglomerate structure is governed by the modification in Butler-Volmer equation but unfortunately, this increases the complexity of the computation as well as the number of geometric parameters to be computed or experimentally obtained. In summary, the CL model developed in this study proposes a simpler modified pseudo-homogeneous/agglomerate catalyst layer model which takes the advantage of the simplicity of pseudo-homogenous modeling while taking into account the effects of the agglomerates in the catalyst layer by using experimental geometric parameters published. The detailed comparison of catalyst layer models and the governing equations for the modified model can be reviewed in Sections 2.3.2 and 3.3, respectively.

The remainder of this thesis is organized into six chapters as follows:

- Chapter 2: A literature review containing summaries of existing fuel cell modeling work as well as research done in the area of physical property characterization,
- Chapter 3: A description of the mathematical foundation of the computational fuel cell model,
- Chapter 4: 2D MEA Model representation along with the assumptions, the boundary conditions(BCs) used, the results generated in the model, and its validation with experimental data as well as parametric study investigating the effect of water content and temperature on the conductivity and performance of the MEA,
- Chapter 5: 3D MEA Model representation along with the assumptions, the boundary conditions(BCs) used and the comparison of the simulation results obtained by using different flow field designs: straight, tapered and stepped,
- Chapter 6: ANSYS FLUENT Module two phase modeling framework along with the experimental validation,
 Chapter 7: A summary including the conclusions that may be drawn from the research presented in this thesis and the recommendations for future work.
2. LITERATURE REVIEW

2.1. Introduction

PEMFC was first developed at General Electric (GE) in the early 1960s, about 30 years after the invention of SOFC, through the work of Thomas Grubb and Leonard Niedrach. In mid-1960, GE developed a small fuel cell for a program with the U.S. Navy's Bureau of Ships (Electronics Division) and the U.S. Army Signal Corps[19]. PEMFC was also used in NASA's Project Gemini in the early days of the U.S. piloted space program. GE continued working on PEM cells and in the mid-1970s developed PEM water electrolysis technology for undersea life support, leading to the US Navy Oxygen Generating Plant. The British Royal Navy adopted this technology in early 1980s for their submarine fleet. Other groups also began looking at PEM cells[20].

Polymer electrolyte fuel cells (PEFC) are considered as one of the most promising alternative energy devices for many applications because of their high efficiency, low emissions, low operation temperature, and low noise. Therefore, since 1980s, a great number of experimental and modeling studies have been carried out to explore the performance, problems, and efficiency of fuel cells, with the ultimate goal of extensive commercialization of these energy devices. Models help a better understanding of parameters affecting the performance of fuel cells and fuel cell systems; therefore, they play an important role in fuel cell development. All fuel cell models, from empirical to mathematical models, intend to predict the behavior of the fuel cell by investigating the phenomena occurring inside the fuel cell and, in particular, in each one of its regions.

Empirical models [21-28] use an algebraic equation to fit experimentally obtained polarization curves by adjusting the coefficients of the algebraic expression as fitting parameters. Empirical models are very useful for fuel cell stack design; however they are able to predict only the behavior of the specific existing fuel cell which has been used to get the empirical relations. On the other hand,
physical/mechanistic/mathematical models can be used to predict the performance of new fuel cells, since they account for the phenomena that occur inside a fuel cell using the governing equations and incorporating some empirical determined model constants.

Mathematical models can be classified according to several criteria such as System boundary (single cell, stack, system), number of layers the model takes into account, the State (steady-state, transient), Spatial dimension (zero to three dimensions), and if it accounts for single or two phase flow and/or if it accounts for thermal changes or not (isothermal, non-isothermal).

The system boundary describes the area of interest of the model. It could include the fundamental cell level including the electrodes and the membrane, the fuel cell stack assembled with the individual fuel cells, or the fuel cell system consisting of a fuel cell stack with its auxiliary system components.

The fuel cell system can be modeled at steady-state or transient conditions (or a special case, the quasi steady-state) with respect to temporal changes. Steady-state models represent one operating point in each step and they are useful for parametric studies, sizing components in the system (e.g. heat exchanger area) and calculating amounts of materials such as catalysts[29]. Typically, laboratory fuel cells are operated at steady-state, that’s why there are more steady-state models than the transient/dynamic models. However, when the fuel cell is considered with the system components such as compressor, humidifiers, reformer, etc., the integrated system responds immediately to variations in load. For example, when the fuel cell is used in a vehicle, the model should account for the transient/dynamics characteristics to some degree since the fuel cell performance at steady-state would give only part of the operation. In order to investigate the start-up and shutdown procedures, the effects of various components on flows during a drive cycle and the optimum response time on load changes, transient models can be developed.
Spatial dimension and complexity/details are also important criteria. With respect to spatial changes, the problem can be zero-dimensional (0D, lumped model), one-dimensional (1D), two-dimensional (2D), or three-dimensional (3D), depending on the number of spatial independent variables of the resulting model (differential equations). The zero-dimensional (0D) models are mainly empirical and predict the fuel cell performance with a simple polarization equation; therefore, they can only be used for initial systems optimization. A better description of a fuel cell with the phenomena occurring inside the fuel cell, such as mass transport, needs at least one dimension. 1D models address the fuel cell sandwich composed of channel boundaries with diffusion medium and membrane with various complexities. The majority of the models are 1D sandwich models considering the different regions of the fuel cell sandwich with everything from simple equations to complex expressions derived. They also can combine the other non-geometric microscopic and macroscopic effects, such as consumption of reactant in a pore of a particle which is within a porous electrode. 2D models account for the phenomenon occurring in the fuel cell sandwich as well as in the other direction, either across or along the gas channel. Finally, 3D models take the effects in both directions in the flow field into account as well as comprising the fuel cell sandwich. Figure 2.1[30] below shows a schematic of a fuel cell, showing the different modeling dimensions.

![Figure 2.1. Schematic showing different modeling dimensions[30].](image)
The 1D models contain the fuel cell sandwich in z-direction, the 2D models include the 1D sandwich and either of the two other coordinate directions (x or y), and the 3D models consider all three coordinate directions.

In most of the models one major assumption made in order to simplify the numerical implementation is to treat the catalyst layers as an interface without thickness. Another major simplification is to assume the water is produced and transported in the vapor state only. However, the produced water vapor may condense into liquid water in the conditions which the water pressure is higher than the saturated vapor pressure at the local temperature. In this case, the flowing water in fuel cell components is in 2-phase: liquid and vapor. Mostly at high current density operations which excessive water is generated at the cathode, the liquid water accumulates within the cathode, and fills the pores of the diffusion medium where the reactant and product gases are transported. This situation so-called flooding causes mass transport limitations since the reactants, especially oxygen, cannot be transported to the active areas where the reactions occur; accordingly deteriorates the overall performance of the fuel cell. Therefore, a fundamental understanding of two-phase transport in porous diffusion media is essential in order to improve the performance. The most of the fuel cell models recently published investigates the two-phase phenomenon. The models which neglect the water liquid phase by assuming that all water is in vapor state are known as single-phase models while the models that account for gas and liquid water are known as two-phase models.

In single-phase models, the transport of the reactant gases and water vapor are modeled to be driven by pure diffusion [27, 31-35] or by diffusion and pressure convection [18, 31, 36]. The diffusion transport of the species is generally modeled by using Maxwell-Stefan equations which is equivalent to Fick’s Law in binary mixtures. Under simplifying assumptions, instead of Stefan-Maxwell equations, Fick’s Law can be used for mixtures with three-species [27, 33, 35]. Some models[31, 32, 37-43] also consider the Knudsen
diffusion[44] which is important when the mean-free path of the diffusing molecules is 10 times greater than the pore radius, especially in catalyst layers where pore is small.

Pressure effects can be assumed to be negligible for 1D and 2D through-the-channel models considering only one flow channel but they become important in 2D along-the-channel models and 3D models, especially with different flow field designs since the pressure drop in the channel can be quite different[31, 45]. The transport driven by both diffusion and pressure convection is modeled by using Maxwell-Stefan equations incorporating with Darcy's law as the momentum equation in the set of governing equations [18, 36, 46].

Modeling liquid water transport is very challenging since the mechanism of the two-phase transport through the porous media is still debatable and the two-phase transport properties of porous media are uncertain. The simplest method of treating liquid water is to consider its effect which deteriorates the ability of fuel and reactants to reach the reaction site by reducing the pore volume fraction available for gas transport in the porous media[31, 33, 47] while its transport is not modeled and its volume fraction is used as a fitting parameter[31]. The second method which is more sophisticated is to treat gases and liquid water as two different phases and use Darcy's law to model the liquid water transport [8, 31, 46, 48]. Both methods predict the effects of liquid water to some degree but they can't determine the local saturation of the porous medium which is the fraction of pore volume filled with liquid water. The saturation not only depends on the location but also the porous medium properties such as the porous size, the hydrophobicity/hydrophilicity and the capillarity pressure. Capillary pressure is the pressure difference across the interface between the gas phase and the liquid water and since it can be defined as a function of both pore structures and wetting features of the porous media, it can be used as a key parameter in predicting liquid water transport and distribution in the porous media. In most models, the relationship between the capillary pressure and saturation is represented using an empirical expression such as Leverett J-function[31, 49] while Darcy’s Law is used in order to estimate the
pressure of the liquid and vapor water[31, 50, 51]. Some more comprehensive models [51-54] propose two-phase flow mixture model which defines the flow in terms of mass averaged mixture velocity and a diffusive flux representing the differences between individual phase velocities and the mixture velocity.

Simple or complex, all models must be validated to some degree in order to assure the credibility of the model. On way to validate the model can be to use the experimental data from the literature when the sources are limited; however, it is a very challenging task when there is not enough data reachable. But as long as validated with the experimental data in the literature, mathematical models are very useful for fuel cell design by making possible to study complex and different situations with less time and effort than experimental investigations.

The objective of the present chapter is to provide a comprehensive review on mathematical modeling of polymer exchange membrane fuel cells (PEMFCs) and discuss the current models. Although the majority of the models in literature have been reviewed; there are, of course, some models that were not mentioned. In terms of time frame, the review focuses mainly on models that have been published through the end of 2010. Although there have been many experimental and mathematical models, all of them have been developed for limited and idealized conditions and don’t consider the phenomena investigated or the region included in another one. They vary in their approach and complexity and it is hard to make a direct comparison between them. The main differences may be the methodology used to describe the physical phenomena taking place in a specific region and dimension of the fuel cell or the assumptions made concerning the heat and water management. For these reasons, the review is organized in 4 sections. Firstly, the detailed review of the selected models will be given. Then the fuel cell sandwich including membrane, CL and GDL will be examined in details. The water management and two phase flow modeling are presented in the third section while the physical properties of each component required in PEMFC modeling are discussed shortly in the last section.
2.2. Review on PEMFC Models in Literature

There have been a great amount of mathematical studies on polymer electrolyte membrane fuel cells. Here mostly selected steady state models have been reviewed. If the state of the model is not specified, it can be interpreted as that the model is SS. The early models mostly emphasized the electrochemical modeling in 1D or pseudo-2D and accounted for transport phenomena in the membrane and the cathode side of the fuel cell. Later, single-phase multidimensional models solving transport equations governing conservation of mass, momentum, species and charge were developed in order to investigate the internal conditions such as the reactant and water distribution, the effects of the physical and operating parameters such as temperature, pressure, humidity, thickness of the membrane, the porosity of the diffusion medium, channel geometrical properties, etc. The computational fluid dynamics (CFD) approach has arrived with the development of multi-dimensional models using the commercial CFD packages like FLUENT, STAR-CDCFX, CFD-ACE+, CFDesign™. Then the treatment of liquid water started to get more attention and many two-phase models have been published. The review is divided by two main parts and based on a historical base. Firstly single-phase models and then two-phase models, mainly grouped regarding the dimension included have been presented.

2.2.1. Single Phase Models

One of the pioneering works in modeling PEMFCs is that of Bernardi[55] who developed 1D isothermal mathematical model for the membrane and cathode electrode in order to investigate the humidification requirements of inlet gases to maintain a state of water balance in PEMFC. In that model, electro-osmotic drag of water and pressure induced flow across the membrane were assumed to be insignificant next to the flow caused by concentration gradients due to the thin thickness of the membrane. The main conclusion of the study was that the current density needed to maintain a water balance increases with increasing temperature due to larger water evaporation and oxygen transport in
the cathode may limit fuel cell performance due to diffusion limitation. Bernardi and co-worker Verbrugge[8] improved this model by including cathode catalyst layer as a domain and taking into account the effect of electro-osmotic convection in the model for the first time. In order to model the motion of the water in the membrane, a modified form of Schlogl’s velocity equation which describes the generation of convection within pores of the ionomer by electric potential and pressure gradient was used. This model can be considered as the basis of two-phase models since it takes into account the possibility of liquid water as well as vapor flux in the electrode. Their results showed that water transport by both pressure difference and electric-potential forces were a strong function of the cell operating conditions, and the polarization resistance resulting from the oxygen reduction reaction was important at all current densities. The limitation of the model is that it is valid only for fully hydrated membranes. In their next model[48], they added the anode catalyst layer to their model region and investigated the influence of membrane and electrode properties such as porosity and thickness. They also compared Dow membrane to Nafion®®. This model is again valid only for fully hydrated membranes and does not account for the drag force on water molecules. The polarization curve obtained by the model diverges from experimental data at high current densities due to the inability to predict flooding, probably. The studies of Bernardi and Verbrugge[8, 48], can be taken as the starting point of contemporary PEMFC modeling study and the basis for further modeling investigation[56].

In the same time, Springer et al.[57] developed another 1D isothermal MEA model with a membrane having variable water content unlike Bernardi and Verbrugge models[8, 48]. In order to model water transport in the membrane, they incorporated the data for water diffusion coefficients, electro-osmotic drag coefficients, water sorption isotherms, and membrane conductivities which was obtained experimentally by other authors [58-60]. On the contrary the comprehensive model of water transport in the membrane, the presence of liquid water in the electrodes was ignored. They assumed equilibrium between membrane water and water vapor at the membrane-electrode interface. They concluded that
the membrane resistance increased with an increase in current density and a thinner membrane
extenuated the ohmic polarization significantly. The limitation of this model is that they used artificially
fitted parameters (such as cathode GDL effective diffusivity) to predict water flooding. However, since
this is the only such model, it is still widely used when a partially humidified membrane is considered.

In 1993, Fuller and Newman[61] presented a quasi-2D, non-isothermal MEA model in order to study
water management, thermal management, the effect of operating conditions on transport and
utilization of fuel. Quasi-2D model is built by first solving the modeling equations through the membrane
as 1D problem and then integrating the solutions at various points in the channel direction. They
concluded that the conductivity increased with hydration of membrane. Equilibrium sorption term of
water between the gas phase and the polymer electrolyte was shown to depend strongly on
temperature. They proposed that the rate of heat removal is a critical parameter in the operation of the
fuel cell and the thermal considerations must be included in an analysis of water management. This
model is valid as long as there is no condensation of water within the catalyst layer and it doesn’t
predict mass-transfer limitations in GDL until current densities of 5 A/cm².

Same year, Nguyen and White[62] also developed a 2D water and heat management model including
MEA and gas channels in order to predict the effect of humidification. In their model they greatly
simplified MEA assuming ultra-thin gas diffusion electrodes. Contrary to the other models in the same
years, they didn’t study the details of the membrane and the catalyst layers since the model groups
these elements in the electrodes but they included heat transfer from the solid phase to the gas phase,
and the latent heat associated with water evaporation and condensation in the flow channels and
investigated local current density along the gas channel as a function of resulting local conditions. They
claimed that at high current densities ohmic loss in the membrane had the strongest effect on the
voltage loss. They found that the anode stream should be humidified to minimize the ohmic loss, as well
as cathode if air is used instead of O₂, since the water back diffusion from the cathode side of the
membrane was not enough to keep the membrane sufficiently hydrated to provide high conductivity.

In the same year, in order to identify the improvements required to enhance the performance of air
cathodes, Springer and co-workers[15] published a 2D isothermal half-cell model considering voltage
losses caused by interfacial kinetics at the Pt/ionomer interface, gas-transport and ionic-conductivity
limitations in the catalyst layer, and gas-transport limitations in the cathode backing for the first time.
They also examined the distribution of current in catalyst layer thickness. They suggested assigning a
diminished-decreased porosity of porous medium in order to model partial flooding. They proposed that
limitations caused by gas-phase transport in the cathode determined the cell limiting current and also
deteriorated polarization curve in the medium current densities, particularly so at low air pressures.
They pointed out that for a given overall catalyst loading; a distributed catalyst-layer thickness increased
the effective conductivity and permeability.

Weisbrod et al. [63] enhanced membrane water model by Springer et al.[57] in order to analyze the
water balance in GDLs, the impact of the catalyst layer thickness and platinum loadings and the effect of
temperature and cathode pressure on the performance. They defined the catalyst particles to be
covered by a thin film of ionomer and neglected the diffusion through this film. They assumed the gas
stream to be saturated in the presence of liquid water. They found out that fuel cell performance is
moderate for catalyst loadings less than 0.1 mg/cm². They concluded that the performance drops when
the cell temperature was increased to approximately 100 °C with a gas stream pressure of 2 atm.

In 1998, Eikerling and co-workers[64] presented a 2D MEA model in order to look into the effect of
membrane parameters and compare the diffusion and convection model of the membrane. Their
experimental data showed that water transport through the membrane was convection dominant.
Divisek et al.[65], in their 1D physical model, also reported that convective based model explained the
water transport through the membrane better than the diffusion based models. In these models, only capillary forces are assumed to have an effect on the equilibrium water content in the membrane, unfortunately.

Lee et al. [66] developed an MEA model with a set of empirical correlations and studied temperature, pressure, and oxygen partial pressure distributions. They pointed out a strong relation between the distributions of oxygen partial pressure and the cell current. They discovered that in all the distribution curves which were very similar in shape, the region of highest current production corresponding to the region of highest oxygen concentration.

In the same year, Wohr and co-workers [38] built a comprehensive transient, 1D, isothermal half-cell model and investigated the effects of structural and material parameters, such as thickness and porosity of GDL, and the structure of catalytic layer on the performance of single and cell stacks. They took into account the condensation and evaporation of water, heat conduction and convective heat transfer, and joule heating and ohmic heating. In GDL, gas transport within the pores was represented by Dusty-Gas Model combining Stefan-Maxwell and Knudsen diffusion with convective transport driven by a pressure gradient. They stated that the transport of liquid water in the porous system of the electrodes was driven by surface diffusion or capillary transport and they included the effect of the decrease of pore volume with increasing water loading. They claimed that the exchange current density does not depend on the active catalytic surface but on the geometric surface of the electrode. The transport of proton as well as water in the membrane was considered for the first time. They found out that the activation overpotential of the anodic reaction might be negligible compared to that of the cathodic reaction since the exchange current density of the hydrogen oxidation on platinum is several orders of magnitude higher than that of oxygen. They concluded that the decrease of the oxygen partial pressure causes a decrease in cell voltage. They also explained the decrease in the performance due to the inhibition of reactants at high temperatures (>90°C).
Gurau and co-workers[36] constructed a non-isothermal 2D complete fuel cell including membrane, anode and cathode catalyst layer, GDLs and gas channels and used the methods of computational fluid dynamics (CFD) for PEMFC modeling for the first time. They also used the single-domain approach which eliminates the need to define boundary conditions at the interfaces between different parts of the fuel cell sandwich. They investigated the effects of various parameters such as GDL porosity, cathode velocity, on the performance. They analyzed the oxygen and water concentration distribution at the gas channel/gas diffusion interface and their effect on the current density. Moreover, they examined the current density distribution at the membrane/cathode catalyst layer interface and liquid water velocity distributions in the membrane. According to the results, they pointed out the importance effect of a non-uniform reactant distribution on the current density. Although this model is very comprehensive, it lacks the overpotential due to transport limitation in the catalyst layer by assuming an indefinitely thin catalyst layer.

Singh and co-workers[67] published a 2D isothermal MEA model in order to explore the transport processes in order to improve heat and water management, and to mitigate mass transport limitations. They used Finite Volume Method (FVM) to solve the governing equations and analyzed the two-dimensional effects ignored in previous studies. They reported that 2D model predicted the fuel cell performance more conservatively than 1D models, with lower cell voltage, serious concentration losses and increased humidification needs at lower current densities. They also studied the effects of flow configuration and electrode porosity. They found that the cathode polarization due to the sluggish oxygen reaction rate was more dominant in polarization curve at all practical current densities. They pointed out the importance of two-dimensional effects by showing that the anode and cathode water fluxes varied considerably along the oxidant and fuel flow channels and comparing the water processes and concentration polarization at low current densities for counter-flow and co-flow cases.
Yi and Nguyen[68, 69] refined the model of Nguyen and White[62] and built 2D along-the channel model including cathode electrode and cathode gas channels in order to investigate the effect of operating parameters such as gas distributor design, electrode dimensions, and humidification. Their model accounted for the convective water transport across the membrane by a pressure gradient, temperature distribution in the solid phase along the flow channel, and heat removal by natural convection and concurrent and counter-current heat exchangers. They also examined the effect of humidification and concluded that anode humidification and positive differential pressure between the anode and cathode to increase the back transport rate of water across the membrane could enhance the performance. In the investigation of electrode dimensions, they found out that the electrode average current density decreased with increasing in the electrode thickness and the shoulder width of the gas distributor. They also reported that excessive temperature rise leaded to local membrane dehydration so efficient heat removal was necessary for better performance. For this purpose, they claimed that the counter-flow heat exchanger was the most effective. They found that when an interdigitated gas distributor is used, pressure drop produced b/w the non-interconnected region of inlet and outlet channels make oxygen and water transport to and from the inner layer of the electrode by not only with diffusion but also by convection. Thus, this design improves the electrode performance with a higher gas flow rate through the electrode. Moreover, they indicated that higher gas flow rate helped the remove of entrapped liquid water, occurred with water condensation in the electrode, from inner layers of electrode. Later, Kazim et al. [70] also developed a 2D half-cell model with interdigitated flow field design and made a performance comparison between fuel cells with conventional and interdigitated flow fields. They presented the superiority of the interdigitated one over the conventional one by showing that the limit current density increases threefold and the maximum power doubles the interdigitated flow field compared with the conventional one.
In these years, many authors[71-75] published 1D and 2D microscopic agglomerate models of catalyst layer in order to examine the influence of geometry through agglomerate model (a Carbon, Pt and Nafion® mixture separated by pores). Broka & Ekdunge[75] reported that the thickness of the Nafion® film surrounding Carbon-Pt agglomerates is a crucial parameter at medium and high current densities due to the influence of diffusion through the Nafion® from the pores to the Pt catalyst surfaces. Bultel and co-workers [71, 74] developed a modified agglomerate model, called as Modified Thin Film Model in order to predict the behavior of the electrodes. Marr and Li[76] presented an isothermal 1D catalyst layer model with fully hydrated membrane. They described the catalyst layer performance by its reaction surface area and the resistance to the reactant diffusion and showed that the utilization of platinum catalyst decreased with increasing current density and lower loadings of platinum at higher current densities can be used without an adverse effect on cell performance. However, it should be noted that the void region in the catalyst layer was assumed to be fully flooded and Knudsen diffusion is assumed to be unimportant compared to the bulk diffusion.

In 2000, Gurau et al.[77] and Dannenberg et al.[78] kept on using agglomerate approach for cathode catalyst layer. Gurau et al.[77] used a 1D isothermal half-cell model in which they used expressions for cathode internal and overall effectiveness factors, active fraction of catalyst layer, catalyst layer resistance, limiting current density slope of polarization curve. They analyzed oxygen mass fraction distribution, current density and membrane phase potential in terms of physical and thermodynamic parameters of fuel cell. Additionally, they explored the liquid water gradient in GDL and catalyst layer by modeling GDL in parallel layers defined by different porosity and tortuosity coefficients and assuming thermodynamic and hydrodynamic equilibrium. They reported that for given thermodynamic and operating conditions, there were bijective relationships between any two: external load, fuel cell voltage, current density and average surface overpotential at the cathode catalyst layer; and for specified thermodynamic and operating conditions, interestingly, catalyst utilization deteriorated when
the catalyst loading was increased or/and the interface between catalyst particles and ionomer (polymer membrane) was enhanced. They pointed out the importance of catalyst layer porosity especially if the diffusion is the rate-determining step, but on the other hand, they claimed that limiting current density doesn’t depend on the properties of catalyst layer and it could be increased with temperature and pressure. They also took attention to the 3 typical polarization regions in polarization curve: kinetic or activation limitations at low current densities, ohmic losses at moderate current densities and mass transfer limitations at high current densities. Dannenberg and co-workers [78], in their 2D whole fuel cell model, presented the calculation of water content in the membrane and the oxygen permeability in the catalyst layer, and investigated ohmic resistance and water profile in the membrane. They treated non –isothermal along the channels, isothermal in other regions and analyzed the current distribution & variation of temperature in the gas channels. They also performed simulations for different humidities of inlet gases, several different stoichiometric ratios, cooling media (air, water) with different heat transfer coefficients. Their analysis revealed that the best performance of the PEMFC occurred with well-humidified gases at conditions close to isothermal and at a stoichiometry of gases only somewhat higher than that corresponding to complete reactant consumption. The limitation of the model is that it doesn’t consider the anode overpotential and two phase transport of water. Another 2D whole fuel cell model in which catalyst layer was based on an agglomerate geometry was developed by Siegel and co-workers[18] in 2003. They obtained the data related to catalyst morphology by electron microscopy. Their results revealed that the fuel cell performance, especially in high current densities where the concentration polarization is dominant, significantly depends on catalyst structure, specifically the void fraction and polymer membrane contained within the active region as well as the geometry of the individual agglomerates such as the characteristic agglomerate length and size. They claimed that a void fraction of 0.04 in the catalyst layer was optimal. CFDesign™ was used to solve the governing equations defined on single-domain approach.
In order to study the influence of catalyst area and membrane thickness in addition to operation conditions, Mann and co-workers[24], developed a 1D isothermal electrochemical MEA model by using mostly theoretical coefficients. They took into account membrane ageing and presented an approach for the prediction of proton resistance of the Nafion® membrane. They concluded that Nafion® resistivity altered with the method of membrane preparation /preconditioning, the type of flow field and the method of performing experimental measurements (in situ or ex situ).

In 1999, Kulikovsky and co-workers[32] developed the first 2D cathode compartment model in order to investigate the influence of two-dimensional effects on cathode performance. They carried out the simulations for high and low values of carbon phase conductivity and reported that increasing the carbon phase conductivity created more uniform distribution of reactions. On the other hand, they stated that decreasing conductivity one may improve gas transport since typically, low conductivity of the carbon phase was shown to be a result of its high porosity. Moreover, it was revealed that the removal of platinum could be allowed with almost no loss in performance with low conductivity of the carbon phase. Later Kulikovsky [40, 79] presented the first quasi 3D model including whole fuel cell regions with a fully hydrated membrane and with meander like gas channels in order to compare the catalyst layer performance. His model didn’t account for the effect of liquid water on the transportation of gases to/from the catalyst sites as well as the water flux through the membrane. The results showed that the reaction rate was non-uniform along the catalyst layers; in both anode and cathode side, it was higher in front of the gas channels and was lower in front of the current collectors. On the other hand, the polarization was found to be nearly constant across the catalyst layer and exponentially variable across the anode side. A simple equation for optimal anode catalyst layer thickness was formulated.

Um et al.[80] constructed a transient, isothermal, 2D whole fuel cell model solved by FVM based CFD technique using single-domain approach in order to examine the effects of hydrogen dilution in the anode feed as well as looking into other reactant and product distributions. The validation has been
done not only on the polarization curve but also on the product and reactant distributions. Their results showed that the hydrogen dilution caused significant mass transport polarization due to limited diffusive transport of hydrogen from the fuel stream to the reaction site and consequently a lower current density. On the other hand, their model is not capable of predicting cathode concentration polarization. They only considered liquid phase of water but they reported that single-phase simulation still could give a good approximation for current densities as high as 0.6 A/cm².

The first fully 3D model was published by Dutta and co-workers [81] in 2000. In their isothermal whole fuel cell CFD model, Dutta et al.[82], investigated the effects of the membrane thickness and the cell voltage on the axial distribution of the local current density and calculated species concentrations along the flow channels. They also examined the net rate of water transport and considered the two-phase flow in a simple fashion that neglected the volume of liquid water inside the GDL. Their results of water transport between the cathode and anode sides showed that the mass transport toward the membrane was driven by both the pressure and concentration gradients rather than by diffusion alone. They also pointed out the fragile balance of diffusion and electro-osmosis and their impact on the current distribution along channel. They enhanced their study by including both anode and cathode flow channels in the following year in order to examine the mass flow between channels with a serpentine flow path. They also analyzed the velocity distribution, the gas-mixture distribution, and the detailed reactant consumption in the MEA. Their results revealed that flow directions importantly hinge upon the mass consumption pattern on the MEA and the computation technique should include gas-mixture density change due to significant variation. They found that in a serpentine channel, the overall pressure drop was lower than that expected since the transport through GDL was enhanced.

The other study using FLUENT in their 3D CFD isothermal model was the one built by Hontanon and co-workers[83]. They studied to enhance the performance by optimizing the gas flow distribution and to simulate the gas flow in the assembly, consisting of the fuel side of the bipolar plate and the anode.
the same year, Hsing and Futerko [84, 85], published a 2D whole fuel cell CFD model using Finite Element Method (FEM) in order to predict the dependence of product water leaving the anode on hydrogen stoichiometry, oxygen stoichiometry, current density, and cell temperature.

Djilali & Lu [37], used a 1D relatively simplified numerical model including whole fuel cell in order to look into the effects of temperature and pressure on transport since it has not been addressed previously. They found out that polarization was not affected significantly by temperature and pressure non-uniformity while water transport was strongly affected by non-uniform temperature and gas pressure distributions. They also examined the micro-hydrodynamics in very small pores (Knudsen diffusion). This model was extended by using parallel straight flow gas channels, in order to analyze the 3D distributions of reactant concentrations, current densities, and water and temperature fluxes in all domains, by Berning and co-workers [46, 50]. The main conclusions they have made are the following: 3D domain is necessary to determine current distribution and limiting current density and analyze the nature of transport correctly; a uniform current density generation can be attained with a non-uniform catalyst distribution in order to have optimum cell performance. The maximum temperature occurs inside the membrane due to low electron conductivity while cathode temperature is higher than the anode temperature due to the reversible and irreversible entropy generation. The degree of diffusive transport of water through the membrane is negligible when compared to the convection and the electro-osmotic drag. Phase change is driven by the balance of temperature change, reactant gas depletion, and pressure drop inside the GDL. In the latter models by Berning & Djilali[50], phase change was modeled by defining local evaporation as a function of the saturation and liquid water concentration while the former didn’t. The models mentioned here are all single-phase models even though they account for phase change in some degree. Further capability enhancement requires the modeling of two-phase transport and phase change in all regions, especially in GDL and catalyst layers.
The first 3D single-phase, isothermal whole fuel cell in order to investigate the electron transport through GDL was built by Meng and Wang[86, 87]. In the model in which the effects of electrode electronic resistance and electrolyte ionic resistance were examined, the lateral electronic resistance, the gas channel width and the oxygen concentration were found to significantly affect the current distribution in different cell voltages.

Shimpalee et al.[88] developed a 3D CFD model technique based on STAR-CD software by including all fuel cell domains with the patented J.A. Rock flow-field[89] with a symmetric pattern in order to analyze the distributions of current, temperature, and species mole fractions as a function of the operating conditions for stationary and automotive operating conditions. Their results showed that the performance was improved by increasing the humidity in the cathode. It was pointed out that with the optimization of water management, a combination of proper flow-field design and operating condition could give more uniform distribution of reactants and consequently a better fuel cell performance.

In 2004, Weber and Newman [42, 90] developed a 3D membrane model that account for both the vapor- and liquid-equilibrated transport modes and bridged the gap between the one phase and two phase macroscopic models developed until that time. Moreover, they examined the effect of temperature on water uptake by membrane from water vapor and its related impacts on the transport properties such as the conductivity of the membrane, the transport coefficient, and the electro-osmotic coefficient, as well as membrane structural properties, including the effective contact angle of a liquid-equilibrated membrane channel.

In 2006, the same authors[91] published a 1D half-cell heat transfer model in order to investigate the transport of water due to temperature gradient and its related effects on performance. The incorporation of non-isothermal effects was found to be necessary in fuel cell modeling, especially in the presence of saturated gas streams. It was reported that the temperature gradient can cause a heat-pipe
effect[91] making water to evaporate near the catalyst layers and move and condense down the
temperature gradient towards the gas channels. Thus the reactant gas mass transport reaching the
catalyst layers decreases and on the other hand, more water moves from cathode to anode than for the
similar isothermal case. The optimum operating temperature was found to be around 65°C at 1 bar and
increase with gas pressure and/or with subsaturated feeds.

Cao and Djilali[92] constructed a 2D non-isothermal, non-isobaric whole fuel cell model in which the
water transport and electrical potential were defined with variable water content variation in the
membrane. An empirical equation describing the electro-osmotic drag as a function of water content
and a new equation for electric potential rigorously accounted for water content variation were derived
while proton and water transport were modeled with Nernst-Plank equation and Schlogl equation,
respectively. The importance of two-dimensionality, temperature and pressure non-uniformities and the
relationship between humidification and membrane ohmic polarization were examined. It was found
that the higher pressure on the cathode side had more positive effect on the performance than on the
anode side. While the evaporation and condensation rates were predicted to be significantly impacted
by the temperature and pressure, the phase was not accounted in the model.

In the same year, Guvelioglu ans Stenger[93] developed a 2D isothermal, MEA model in order to study
the complex water balance in the membrane and to determine the operating conditions making the
membrane dehydrated. Moreover, the effects of channel width and bipolar plate shoulder dimensions,
porosity, and the relative humidity of the inlet streams on the fuel cell performance were examined. It
was observed that smaller width channels and bipolar plate shoulders provided better performance for
high current density operations, and higher porosity can create a positive impact on the performance
when the electrode area under the bipolar plate shoulder is increased. It was found that the anode gas
stream’s relative humidity was more effective on fuel cell performance than the cathode gas relative
humidity. Although this model cannot predict the concentration changes along the channel and their
effect on the performance of the entire fuel cell, the application of finite element method using FEMLAB enabled a robust and fast convergent optimization.

Sivertsen and Djilali[94] constructed 3D non-isothermal whole fuel cell model with a fast CFD optimization using the parallel processing of the FLUENT. The model accounted for convective and diffusive transport; distributed heat generation associated with the electrochemical reactions; local activation, ohmic losses and concentration losses as well as ionic and electronic potentials in the electrodes and membrane in order to estimate the local current density distribution more accurately. The maximum current density was found to occur under the land areas due to the dominant ohmic losses and it was observed that by modifying the conductivity significantly changes the current distribution by changing the relative effect of ohmic to activation losses. The parametric simulations demonstrated that by changing the asymmetry parameter, substantially different spatial distributions can be obtained without a noticeable change in the voltage-current characteristics. These results pointed out the fact the global comparison between experimental and predicted results may be insufficient in validating the computational model.

Liu and co-workers[95] investigated the effect of diffusion resistance through the catalyst particle and the local effectiveness factor in the catalyst layer by building a isothermal full 3D agglomerate model with straight gas channels. The 3D distribution patterns of oxygen concentration, local current density and cathode activation overpotential were found to be uniform at low average current density while they were significantly non-uniform at higher current density due to the mass transfer limitation.

In the same year, Huang and co-workers[96] developed an isothermal single-phase along-the-channel model in order to analyze the pressure effects, open circuit voltage dependence on pressure and stack temperature, and membrane conductivity dependence on the water vapor from both anode and cathode sides. The entrance and exit effects on the pressure drop were assumed to be negligible. The
results pointed out the importance of humidification of both anode and cathode for the performance while indicating that this effect is more announced with the anode humidification. Increasing the temperature and pressure within a reasonable range was reported to enhance the performance.

Meng[97] presented an isothermal 3D model using mixed-domain method in order to define water transport in the MEA. In the model, by integrating the Springer’s[57] 1D interfacial treatment into a 3D framework, the conservation equations used in membrane and in the other regions of the fuel cell were linked with set of internal boundary conditions based on the thermodynamic phase equilibrium and flux equality at the interface of the membrane and the catalyst layer. The comparison between the results from this mixed-domain approach and those from the single-domain method, demonstrated that mixed-domain approach provided more accurate results in predicting cell performances, current distributions and water content variations in the membrane.

By building a 3D single-phase isothermal whole fuel cell model, Wang and co-workers [98] investigated the structure performance relationship of carbon cloth and carbon paper as gas diffusion media. The results showed that at high-humidity operations, the carbon cloth gave better performance because of the low tortuosity of its pore structure and its rough textural surface. On the other hand, it was reported that more tortuous structure of the carbon paper decreased the loss of product water to dry gas streams which helped increasing the membrane hydration level and reducing the ohmic loss; therefore, under dry conditions, the carbon paper was a better choice.

With the development of multi-dimensional models, it has been explored that the flow field design in bipolar plates as well as the geometric parameters is very important for improving the fuel cell performance. The main objective to develop new flow field design is to obtain more uniform distribution and thus, better performance. Starting in 2004, in order to investigate the influences of the geometry and pattern of the flow channel on the performance, many authors developed 3D single-phase
iso thermal whole fuel cell model with different flow field designs: serpentine, parallel, interdigitated, micro parallel, tapered, bio-inspired (leaf and lung), stepped and porous-media flow fields.

Nguyen and co-workers[99] applied a voltage-to-current (VTC) algorithm that solves for the potential fields and allows for the computation of the local activation overpotential to determine the local current density distribution more accurately. The simulation results clearly demonstrated the dependency of current density distribution on loading conditions and pointed out the incapability of the previous models assuming constant overpotential. It was discovered that at low loads, the maximum current density occurred under the collector plate land areas while it moved towards the center of serpentine channels as the load increased. In their study based on the work of Um and co-workers[80, 100] and Ju and Wang [101] indicated that the global polarization curves were deficient and sometimes deceptive in order to validate a model and pointed out the effect of current distribution profiles on the validation of the model. In the experimental work of Wang and Liu[102], experiments focusing on the effects of the cell temperature, gas humidification, cell operating pressure and reactant gas flow rate in an interdigitated flow field design revealed the following information. The performance enhances when the temperature is increased as long as sufficient humidification was furnished. Unlike in serpentine flow filed, interdigitated flow field performance is affected by both anode and cathode humidification. Hongthong and co-workers[103] performed simulations with conventional and interdigitated gas flow channel using FLUENT 4.5. The results revealed that the flow channel pattern created a strong impact on the cathode cell performance, while it did not change the anode cell performance. The interdigitated flow field design was found to generate a higher limiting current density and improve the cathode cell performance by 120-150% over the conventional design if a larger shoulder width was used. On the other hand, the inlet and outlet channel widths of the interdigitated design didn’t have a significant effect on the performance. Wang and co-workers’ models [104, 105] investigated the effects of various design parameters for the serpentine, parallel, interdigitated flow fields, including the number of flow
channel bends, number of flow channels, the flow channel width ratio, flow channel aspect ratio and flow channel cross-sectional area, on the cell performance and local transport phenomena based on the local oxygen mass flow rates and liquid water distributions. They considered the effect of the liquid water formation on the porosities of the porous layers while the complex two-phase flow was neglected. The results revealed that for high voltages (greater than 0.7 V), the electrochemical reactions were very slow due to flooding and limited oxygen concentration and the design parameters such as channel aspect ratio and channel cross-sectional area couldn’t overcome this effect; therefore, the type of the channel design had small impact at these voltages. On the other hand, at lower voltages (lower that 0.7 V), the electrochemical reactions became faster with increased oxygen consumption and liquid water production as the operating voltage decreased. However, liquid water may block the oxygen transport to the reaction zone by accumulating in the pores of GDL and catalyst layer. In this case, since the removal of the water can be changed with flow design, the various bipolar plate design parameters strongly change the performance at low voltages. More specifically, smaller channel aspect ratios and cross-sectional areas in the parallel design enhanced the water removal and accordingly, the cell performance. This effect was not seen in the interdigitated design, since the water removal was mainly driven by the high shear forces. For the single serpentine flow loop field, it was found to give better performance than the double and triple loop flow fields and the performance was shown to increase with the number of flow channel bends. The pressure drop was found to be different for the various flow field designs; however they were negligible compared to the cell output power. Lee et al.[106] analyzed the performance of the micro flow field design of which much narrower and longer channels increased the pressure drop and pumping power, and reported that pressure drop was 11 Pa at anode and 22.5 Pa at the cathode flow channel for 0.5 V. They also showed that reactant streams were transported to the membrane by diffusion mechanism rather than convection. In order to reduce the negative effect of the reduction of the reactant concentration in streamwise direction and accelerate
the reactant flow into the GDL by forced diffusion, Liu et al.\cite{107, 108} proposed a tapered flow channel design and their simulations showed the improvement in the fuel cell performance with the new channel design, especially at lower voltages at which the mass limited polarization becomes significant. The bio-inspired designs proposed by Kloess and co-workers\cite{109} incorporates the advantages of the existing serpentine and interdigitated patterns with patterns found in nature: leaf and lung. The simulations performed with four different flow channels: leaf, lung, serpentine and interdigitated, revealed that the leaf or lung design established a more uniform flow to GDLs, a lower pressure drop from the inlet to outlet and better performance up to 30\% in peak power density when compared to the existing serpentine or interdigitated flow patterns. Wang\cite{110} presented a new flow design by filling porous media in the channel space. The new design allowed the transport of gaseous reactants and heat/electrons through the channel via a void space and a solid matrix, respectively; thus, improved the performance with the added functions and lessening the contact resistance under the channel. A theoretical analysis was performed in order to investigate the factors affecting the heat transfer, electronic conduction and pumping power consumption for both hollow channel and porous-media-channel fuel cells operating at low-humidity, omitting liquid water impact. Besides demonstrating the enhanced heat and electron transport and design flexibility gained with porous-media flow field, the simulations showed the importance of in-plane channel dimension and diffusion media thermal property on the local temperature variation and electronic ohmic loss in the hollow channel design. Zhang and co-workers\cite{111} presented a 3D non-isothermal mathematical model of a whole fuel cell with serpentine flow field in order to optimize the performance by investigating the effects of parameters such as porosity, permeability, and the thickness of the GDL, and the inlet gas stoichiometric ratio on the performance. The optimum values of these parameters were obtained by applying the Powell multi-parameter optimization algorithm. The results indicated that at a large permeability creates a higher potential since more oxygen is transferred from the gas channel to the catalyst layer,
resulting in a more active electrochemical reaction. In addition, the pressure drop across the cathode GDL was found not to be affected much with the gas inlet stoichiometric ratio. In 2011, Sierra et al.[112], examined the species concentration, transfer current and ionic conductivity distributions in a whole fuel cell employed with different modes of gas feeding in a serpentine design (cross-flow, non-symmetrical flow, similar flow, counter flow) in order to find out the correct form of injecting gases in the serpentine flow-field. The simulations performed using ANSYS FLUENT 12.0, indicated that the most uniform local current distribution on cathode catalyst layer can be obtained by feeding gases in similar mode while feeding gases at counter-flow mode would give the highest current density values. In addition, it was reported that the channel height for serpentine flow field should be reduced to enhance the mass transport on both the electrodes. It was concluded that a time dependent study accounting for the degradation of membrane/electrodes assembly could determine the best form of gas feeding mode better. In 2009, Zhou and co-workers[113] investigated the effect of the assembly pressure on the performance by developing a full multiphysics model accounting for the mechanical deformation, mass transfer resistance, and electrical contact resistance. First, GDL deformation was obtained numerically, then a 3D overall performance model was built incorporating a mass transfer resistance and a microscale electrical contact resistance model based on the deformed geometry and associated parameters. The simulations demonstrating current density and O2 mass fraction distribution indicated that generally high assembly pressure increased mass transfer resistance and decreased the current density. Another novel flow field design, stepped flow field, has been recently proposed by Min[114]. In the 3D model with this novel flow field developed, the activation, ohmic and concentration polarizations were considered separately and the results showed that the cathode polarizations are greater than the ones at anode with an increasing order: concentration, ohmic, activation polarizations. Moreover, they pointed out the enhancement in the reactant, local current density distribution and accordingly in the fuel cell performance with the stepped flow field, especially with the lower number of steps and the
height of the outlet channel. They also mentioned that the tapered flow field is a stepped flow field with infinite number of steps and has the lowest cell performance.

The following year, Wen and co-workers[115] built a 2D unsteady/transient numerical model in order to investigate the variations of important operating and physical parameters along the cathode channel such as velocity field, concentrations of species and local current density like many authors did so far but they used the Vorticity-Stream Function Method and Alternating Direction Implicit (ADI) scheme in order to solve coupled governing equations more efficiently. They reported that a 2D numerical model is time-efficient to predict the location of liquid water formation and the performance effectively in some conditions. The results indicated that increasing pressure improves the performance better than increasing the inlet velocity or the inlet flow rate.

Recently, Tohidi et al.[116] published a 1D isothermal MEA model investigating the effects of the primary parameters such as temperature, pressure, membrane thickness, relative humidity, stoichiometric flow ratio as well as the distribution of oxygen in the cathode catalyst layer and the molar fraction of nitrogen gas. The results agree with the previous studies: Increasing temperature, pressure, relative humidity of inlet gases and anode and cathode stoichiometric flow ratio, and decreasing membrane thickness increase membrane performance and accordingly the overall fuel cell performance. On the other hand, increasing the molar fraction of nitrogen gas was found to deteriorate the performance by making the cathode activation loss higher. Additionally, the oxygen concentration was found to become zero in about 8 percent depth of cathode catalyst layer and therefore; it was concluded that the catalyst layer thickness could be decreased 92 percent (from $10^{-5}$ m to $10^{-7}$ m) without any potential loss in output voltage.
2.2.2. Two Phase Models

The models mentioned above are not capable of predicting flooding or two-phase transport. In 2000s, many studies accounting for liquid water transport and flooding issues in several degrees have been published. Many authors have developed 3D whole fuel cell models as well as 1D and 2D, and partial models of which many have used CFD methods.

1D 2-Phase Models

Baschuk and Li[47] developed a 1D isothermal half-cell model with a fully hydrated membrane in order to investigate the effect of the degree of water flooding in the cathode catalyst layer on the cell performance. They showed that flooding limited the concentration of oxygen needed for reaction and, thus, increased the mass transport polarization in the catalyst layer and caused a significant performance loss in the fuel cell. Their results demonstrated that the use of air as the cathode gas cut down the degree of flooding due to a higher gas flow rate in the cathode flow channel. Temperature rise was found to postpone the onset of flooding to higher current densities. Contrarily, the increase in the pressure resulted in significant degree of flooding in the electrode and gave rise to the maximum flooding at low current densities. One of the limitations of this simple two-phase model is that it doesn’t account for the Knudsen diffusion in the electrode.

In 2000s, many authors continued to develop 1D two-phase isothermal model. Wang et al.[51], constructed a 1D isothermal half-cell model in order to numerically and analytically study two-phase flow and transport of reactants and products in the air cathode of PEMFCs including hydrogen and direct methanol fuel cells. They used a finite-volume-based computational fluid dynamics (CFD) technique for numerical solution. The polarization curve as well as water and oxygen concentration distributions covering single- and two-phase regimes of the air cathode was presented for the first time. Single- and two-phase regimes of water distribution and transport are separated by a threshold current density at
which first liquid water appears at the membrane/cathode interface and the cell starts to operate in two phase within the porous cathode. Their results showed that capillary action is the dominant mechanism for water transport inside the two-phase region of the hydrophilic structure. The limitation of this model is that catalyst layer is treated as an interface instead of a physical domain. In their 1D isothermal MEA model, Maggio et al.[117] investigated mass transport (diffusional) and ohmic losses due to the electrode flooding as well as membrane dehydration, which are two main water management problems in fuel cell modeling. They used variable gas porosity approach for GDL for the first time; in the model GDL gas porosity changed with the gas composition and pressure. They also calculated electrochemical parameters for Nafion® 117 membrane and made comparison with Dow membrane in terms of performance. They reported that DOW membrane performed better than Nafion® 117 due to higher conductivity of the former although their electro-kinetic properties such as the balance in the volume of pores and their sizes were the same. They also found that GDL effective porosity (liquid water-free pores) and membrane conductivity decreased with increasing current density due to higher degree of flooding. In 2004, Pasaogullari and Wang[118] presented a 1D two-phase in which water transport in both hydrophilic and hydrophobic diffusion media were considered and solved analytically, and clarified the important role of GDL wettability in detail for the first time. They reported that the capillary transport caused by the gradient in phase saturation was the dominant force driving the transport to remove water from flooded GDLs. They predicted the onset of two-phase regime in GDLs and the related threshold current density in different combinations of the anode and cathode humidification. In 2005, Birgersson and co-workers[119] published a non-isothermal two-phase MEA model which was solved numerically under three different thermal (assuming effective heat conductivities, isothermal flow, and interfacial and bulk conductivities), and two hydrodynamic (lowering the capillary pressure, negligible buoyancy effect) modeling assumptions. A scale analysis was performed to quantify the transport mechanisms in the porous backings of the cathode and anode as well as in the membrane,
with proper scales. The results significantly depending on the choice of capillary pressure expression for the GDLs provided the following conclusions: (a) The convective contribution can be ignored compared to the conduction of heat throughout the cell; (b) The ohmic heating in GDLs can be eliminated without affecting the model results while it is of the same magnitude as the heat conduction in the membrane, whence it must be considered there; (c) The diffusion is the dominating mechanism for species transfer on the cathode side as long as the flow field does not cause a forced flow (like in interdigitated flow field). More recently, in 2010, Liu et al. [120] presented a 1D two-phase model of cathode GDL and CL in order to examine the coupled phenomena of cathode flooding and mass transport limitation and to determine how to remove effectively the liquid water accumulated in the cathode by studying the effects of some important parameters, such as the boundary value of the saturation, the net transport coefficient and the permeability, on the saturation level. According to the numerical results, the saturation level inside the cathode depended on the surface overpotential, the absolute permeability of the porous electrode, and the boundary value of saturation at the gas diffusion layer-gas channel interface. The capillary properties of GDL and CL are different so in order to meet the continuity interfacial condition of the capillary pressure and the conservation of the mass flux at the GDL–CL interface, the catch of the huge of jump saturation was very important in the model. Moreover, the results proposed that the flooding in the CL is much more important than that in the GDL, since liquid water produced in the electrochemical reaction arises and accumulates in the catalyst layer first. Therefore, it was concluded that firstly the liquid water accumulated inside the CL pores should be taken out in order to control the flooding effectively.

2D 2-Phase Models

The first detailed two-phase model has been built by He, Yi & Nguyen, 2000 [121]. Their isothermal 2D half-cell model with interdigitated flow field, studied the effects of liquid water and its transport on the performance of the cathode. They proposed that the liquid water transport through the porous
electrode was driven by the shear force of gas flow and capillary force and in order to model the liquid phase transport, they derived an equation accounting for both forces. They observed that higher differential pressures between inlet and outlet channels resulted higher electrode performance, due to the higher rates of the oxygen transport and the more effective liquid water removal. They also concluded that an optimization for the electrode thickness was required for optimal performance since a thinner electrode decreases gas flow rate while a thicker electrode reduces the diffusion. They suggested more channels and shoulder widths for a fixed size electrode.

In 2001, Janssen\cite{122}, and Natarajan and Nguyen\cite{123} published two-phase isothermal 2D models. Janssen\cite{122}, applied Concentrated Solution Theory in order to model the transport of water in the membrane, and of water vapor and liquid water in the electrodes. He found out that incorporating the liquid water transport into the model was necessary in order to explain the observed characteristics of electro-osmotic drag coefficient and its dependence on operating conditions and variations in MEA. His model also allowed the calculation of the partial water pressure distribution and the results were validated by the direct measurements of the water transport. Natarajan & Nguyen’s multi-component, transient cathode model\cite{123} provided qualitative information on the effects of various operating conditions and design parameters and the transient phenomena upon cathodic polarization. They adjusted Darcy’s Law in order to model the capillary flow of liquid water in GDL. They stated that the dynamics of liquid water dominated the performance of the cathode, especially at high current densities. By the help of the transient profiles, they clearly showed that liquid water transport was the slowest mass transfer phenomenon in the cathode while gas transport in itself was noticeably faster. Therefore, the liquid water transport was found to be mainly responsible for mass transfer limitations at the cathode, especially over the shoulder. They reported the operating conditions and design parameters that increased the liquid water removal rate and promoted the cathode performance: increased temperature, dryness of the inlet gas stream, reduced diffusion layer thickness, and higher
porosity. Natarajan and Nyugen[124], upgraded this 2D model to 3D in order to account for the dimension along the length of the channel and to predict the distance from the inlet where the liquid water first was formed in the channel at various operating conditions.

You and Liu[52] published a 2D cathode model giving important insides for two-phase transport in the GDL and gas channels. They used a two-phase flow mixture model where the multiphase flow was described in terms of a mass averaged mixture velocity and a diffusive flux representing the differences between individual phase velocities and the mixture velocity and which was solved by a single-domain approach. They clearly showed the dependency of current density, operating temperature, anode and cathode humidification temperature on two-phase characteristics at the cathode side such as the threshold current density needed to form two-phase flow and the distribution of liquid saturation. According to their results, the magnitude of liquid saturation increases with increasing current density and with further increase the two-phase region extends to the beginning of flow passage. In the humidification simulations, it was found that anode humidification temperature was more important factor to form liquid water in the cathode side as well as being the most common and effective way to hydrate the membrane. Moreover, they discovered that the liquid velocity vector headed to the gas channel/GDL interface so liquid water was removed from GDL where it was claimed to be formed first, and liquid saturation increased in gas channel; therefore, the characteristics of porous media also determine two-phase flow characteristics significantly. However, the model was not capable of predict the influence of these characteristics on two-phase flow. Weber et al. [42], studied the effect of the characteristics of the diffusion media such as the bulk porosity, wettability, thickness, and pore-size distribution on the maximum power as well as flooding, by developing a porous-medium model which included analytic expressions and a methodology for handling both liquid and gas flow in GDL. The presented model was one of the first robust models enabling to investigate the wettability effects and flooding in the diffusion media. However, the catalyst layer flooding was mainly ignored. Their
simulations showed the interactions between mass transport effects associated with flooding of the diffusion media and ohmic effects.

In their 2D isothermal, two-phase whole fuel cell model, Ge and Yi [125], examined the effects of flow modes (co-flow and counter-flow) as well as various operation conditions, such as relative humidity, temperature, pressure and the membrane thickness while neglecting the pressure drop along the channel and water transport in the membrane was taken into account only along the y-direction. In the model, electrode pores for gas flow were separated from pores for liquid water and the effective porosity for oxygen gas transport in GDL was defined due to liquid water but how liquid water was transferred was not considered. The results indicated that counter-flow mode had advantageous on current distribution when the reactant gases were dry or low humidified, compared to co-flow. They also stated the improvement in cell performance with increased temperature.

In contrast to the mixture model used by You and Liu[52], Chan et al.[126] used the locally homogeneous flow model (LHFM) where the slip velocity between the liquid and gas is assumed negligibly small in order to model the two-phase transport in 2D and implemented the governing equations for two phases separately. In the solution of the equations, the SIMPLE algorithm was applied with a single-domain approach. The results indicated that most of the liquid phase was accumulated in the cathode, giving maximum value near the cathode catalyst layer-membrane interface. A new design of the serpentine flow field with blocked outlets pushing the fluids to diffuse into the catalyst layers more was proposed to increase the reactant concentrations at the active areas and accordingly promote the performance.

Ziegler et al.’s transient 2D MEA model[127] accounted for phase transition between liquid and vapor water and Schroeder’s paradox in the membrane and investigated the effect of the double-layer capacitance and the reduction of the effective active area in the catalyst layers due to flooding as well as
the dynamic effect of liquid water formation and transport on the current-voltage characteristics. The dynamics results revealed the hysteresis of current voltage relation and the time dependency of limiting current density.

In 2007, Meng[128] published 2D non-isothermal two-phase MEA model based on the previously developed mixed-domain model along with water transport in MEA. The model was established using the traditional two-fluid method in order to assess condensation and evaporation rate coefficients and to perform numerical studies concerning the effects of the inlet humidity condition and temperature variation on liquid water distribution with or without a condensation/evaporation interface. The condensation rate coefficient ($5000 \text{ s}^{-1}$) was found to be consistent with the detailed theoretical analyses in Nam and Kaviany[129]. Meng[130] upgraded this model using two-phase mixed-domain approach in order to examine the effects of liquid water transport and heat transfer phenomena on the transient responses of the PEMFC to a step change in the cell voltage, with and without condensation/evaporation interfaces. Simulations showed that the liquid droplet coverage model at the GDL and gas channel interface had significant effects on liquid water distribution and cell performance. Under a low-humidity inlet condition, a condensation/evaporation interface of which location depends on the inlet humidity value would appear while a non-isothermal operation causes a condensation/evaporation interface resulting in a dry region in the porous materials directly under the gas channel. Numerical simulations revealed that the liquid water in GDL appears in two regions: near the current collecting land owing to the low temperature and further inside the GDL but still away from the catalyst layer. They suggested that the micro-porous layer at the inlet region of the cell can be used to prevent liquid water from entering the catalyst layer and thus prevent severe liquid flooding in the region. It was observed that the heat transfer process significantly increased the transient response time under non-isothermal two-phase conditions while isothermal two-phase conditions established an
increase in the current density overshoot and undershoots in the presence of liquid water in the porous media.

In 2008, another transient 2D two-phase model including an open area (gas delivery channel) linked to a porous GDL was published by Baboli and Kermani[131]. In their study, the saturation levels were solved by a separate PDE for the mass conservation of the liquid water and the slip velocity between the phases was determined by the capillary pressure. A recently developed finite volume SIMPLER scheme of [132] was used in order to solve the strongly coupled equations including a full compressible form of the momentum equation and Maxwell–Stefan equation. The results showed that the saturation in some regions around the GDL/CL was 0.4 or even more when the cell was operating near to the limiting current density. The development of the transient solution toward the steady state condition at three current densities with one dry case and two wet cases was analyzed and the time required to achieve the steady state solution for dry case was found to be 3s (O(1)s) while the two-phase cases were two orders higher (O(100)s. Similar observations were also reported by Song et al.[133].

In 2009, Sun et al. [134] built a 2D two-phase CL model including cathode GDL and gas channel in order to get a fast numerical simulation of two-phase transport in the cathode. They reported that the main difficulty in the numerical simulation of two-phase transport model in the cathode was the oscillating nonlinear iteration mainly caused by discontinuous and degenerate diffusivity in concentration equation and the dominant convection coefficients in gas channel. Their numerical solution was based on the mixed finite element method for the modified Navier-Stokes equation and standard finite element method for water equation. They applied streamline-diffusion and Galerkin-least-squares to deal with the dominant convection arising from the gas channel; and Kirchhoff transformation to overcome the discontinuous and degenerate diffusivity in water concentration and their numerical treatment provided accurate results with fast convergence.
3D 2-Phase Models

In order to examine the critical conditions, flooding, membrane drying and degradation, Costamagna[135] presented a 3D whole fuel cell model solving for the distribution of the physicochemical parameters, such as temperature, gas composition, and electrical current. They discovered that local temperature peaks above 130°C (at 1 atm) induced irreversible degradation of the membrane. Moreover, they observed the blockage of the gas channels due to water condensation, leading to periodical interruptions of the operation of the system.

Mazumder and Cole[53] built a comprehensive whole fuel model (with bipolar plates) which the fluid flow in porous medium were addressed considering nonlinear anisotropic resistances, spatially varying porosity and permeability, and the effects of catalyst loading and pore size, and making corrections of heat and mass transfer coefficients in porous regions with the effect of tortuosity. Coupled iterative solution of the governing equations for numerical stability was performed using a fully integrated finite-volume solver. The simulations obtained for 2D and 3D geometries revealed that 3D modeling is required in order to predict the performance at higher current densities while 2D and 3D simulations produced the same results at low current densities where the performance is rate limited. The liquid water formation and transport which were not considered were addressed in the next part of two-part paper[136]. This two-phase model included water condensation and/or evaporation via equilibrium phase transformation and transport processes driven by pressure (advection), surface tension (capillary diffusion), electro-osmotic drag, and gravity. Two-phase model simulations showed that under the assumption of no liquid water formation, the single-phase model over predicted the measured polarization behavior. While the level of electro-osmotic drag played an important role in the water distribution, accordingly in local saturation, the overall performance with and without electro-osmotic drag was not that different. On the other hand, the effect of electro-osmotic drag on the overall performance was claimed to be more detectable in cells with more complex channel configurations. It
was observed that at critical current density, saturation levels turned out be more than 50%, and highest in the cathode. Incorporating of clogging effects of liquid water was concluded to be necessary for precise prediction of polarization curve.

Hu and co-workers[137] presented a full 3D model accounting for not only the rib resistance to the species but both the single and two phase flow and transport in the gas channels and GDLs. The numerical techniques for the solution were analyzed to give an overview of the solution procedure and the solution was obtained for two sets of boundary conditions, one for a conventional flow field and the other for an interdigitated one, using the FORTRAN language with SIMPLE algorithm coupled with the shooting method and fourth order Runge–Kutta method. By the comparison of the model developed by Um et al.[80], it was observed that a 2D, single phase model always overestimated the performance. In the second part of this study[138] the internal transport mechanisms obtained were analyzed and compared for both flow fields. The results demonstrated that in an interdigitated flow field, the oxygen concentration fraction was higher while the liquid water saturation was much less, both decreasing the losses and accordingly improving the performance. On the other hand, interdigitated flow field was found to establish poorer performance than the conventional one when the cathode inlet air was not humidified with water, because of a larger ohmic overpotential.

In 2005, Pasogullari and Wang[139], presented a new theory for the liquid water transport in hydrophobic GDLs incorporating a 3D isothermal, two-phase model in a single domain with serpentine flow field after their 1D two phase study in 2004[118]. In the model, the liquid water in the gas channel was assumed to occur in very small droplets (homogeneous two phase flow) and not involve with the gas phase transport; therefore, single phase transport is assumed in the gas channels. However, at high current densities flooding effects become more severe and water comes out of the GDL in liquid droplets. The formation, size, and shape as well as the transport of these droplets significantly affect the PEMFC operation. The effects of the humidity level and flow rate of the reactant streams on two phase
transport and the performance were studied and the results demonstrated that the flooding of the cathode deteriorated the oxygen transport to the reaction site, and thus raised the cathode polarization.

In the same year, Wang and co-workers [140, 141] published 3D isothermal two-phase whole fuel cell models. Meng and Wang [140] used the multiphase mixture M2 model in order to define liquid water transport in the GDL while employing a mist flow model in the gas channel. They built an interfacial coverage model by liquid water at the GDL/GC interface to take into account the water droplet emergence on the GDL surface for the first time. This interfacial model was capable of simulating the effects of gas velocity or stoichiometry on cell performance without using unrealistic GDL permeability, in contrast to the previous two-phase models. Moreover, two distinctive mechanisms for electrode flooding were presented: one is operated by the bulk transport of liquid water across the GDL thickness, and the other prescribed by the interfacial processes occurring at the GDL surface. The assumption of a linear water profile within the membrane was found to induce large errors in cases where the diffusion and electro-osmotic drag were in opposite directions and grid refinement was reported to be imperative for the estimation of the net water flux across the membrane accurately. Creating an off-line database that can be coupled to large-scale calculation was proposed as a solution to the grid problem since it may enable the precise calculation of water transport and current transport within the membrane with better accuracy and efficiency.

Wang and Wang [141] investigated transient processes of membrane hydration and gas transport and step changes in the cell voltage and cathode inlet relative humidity. It was found that it takes 10 s for fuel cells to reach steady state due to the water accumulation in the membrane, consistent with theoretical estimation. Step changes in certain operating conditions were observed to result in overshoot and undershoot in the current densities. 3D simulations for a full fuel cell, investigating the liquid water distribution and flooding under non-isothermal conditions were presented in another study of these authors [142] for the first time. Irreversible heat and entropic heat generated due to
electrochemical reactions, Joule heating arising from protonic/electronic resistance, and latent heat of water condensation and/or evaporation were all included in the model.

Gurau and co-workers[143] developed a 3D multi-phase, multi-fluid transient cathode model in order to predict the liquid water accumulation at the channel-gas diffusion layer interface by considering the liquid water produced by electrochemical reaction, phase change, and water transfer between the ionomer distributed in the catalyst layer and the catalyst layer pores. Sorption/desorption and electro-osmotic drag were reported to be two competing mechanisms of water transfer between the ionomer-phase distributed in the catalyst layer and the catalyst layer pores. The water accumulation in GDLs is operated by the saturation equilibrium at the GDL-channel interface; while in the catalyst layer, it is controlled by the GDL permeability and the saturation equilibrium at the GDL-catalyst layer interface. It was claimed that homogeneous multi-phase models based on the two-phase mixture model were not sufficient enough to model two phase phenomena. Increase in liquid saturation at the catalyst layer was observed as water approached a steady-state level.

By developing a 3D non-isothermal whole fuel cell model in 2007, Matamoros and Bruggeman [144] investigated the effects of geometrical parameters which were thickness of the polymer membrane, cathode catalyst layer as well as gas channel to rib width ratio, on the ohmic and concentration losses, under different relative humidities of inlet flows (50 and 100%) for every change of characteristic length. The simulation results demonstrated the importance of simultaneously calculating both the water absorption and desorption through the polymer electrolyte and the liquid saturation in the cathode and anode porous mediums, in order to predict ohmic and concentration losses accurately under different hydrating conditions. Thicker membrane and catalyst layers were reported to have significant ohmic losses. Moreover, thin catalyst layer also was found to improve performance by decreasing the concentration losses. It was shown that high permeabilities (greater than 1e−15m2) could improve the removal of liquid water from GDL, keeping the saturation less than 0.2 in porous mediums.
Furthermore, the results demonstrated that wide gas channels enhanced the performance by inducing lower concentration losses under fully humidifying conditions, especially at high current densities as long as ribs width were wide enough to avoid ohmic losses by electron transport from anode to cathode.

Same year, in order to predict the liquid water saturation in the GDL and CL and to investigate the effects of liquid water on oxygen transport and cell performance, Ye and Nguyen [145] built a single-domain 3D non-isothermal whole fuel cell model in which experimentally measured capillary pressure representing both pore structures and wetting features of the porous media was used. The results indicated that the water distribution in the porous electrode strongly depends on both local current density and liquid water transport resistance and the sharp changes of the capillary pressure and relative permeability with liquid saturation demonstrates the highly nonlinear phenomenon of capillary action in the porous medium consisting of both hydrophilic and hydrophobic pores. At high current densities, the average water saturation levels were predicted to fall in the range of 0.2–0.5 (in the range of 0.4–0.5 in the CL and 0.2–0.3 in the GDL). The liquid water saturation in cathode CL was observed to be higher under the channel than that under the ribs while it was found to be lower under the channel than under the ribs in the cathode GDL. The effect of temperature on capillary functions was not accounted in the model.

Until 2008, multiphase computational fluid dynamics models for proton exchange membrane (PEM) fuel cells failed to provide even a qualitative depiction of the fuel cell water management. This was primarily due to the inability to capture two-phase phenomena in the cathode catalyst layer and the water saturation equilibrium at the interface between the fuel cell components. A model without the cathode catalyst layer cannot capture dominant mechanisms of water transfer and cannot explain correctly the fuel cell performance. In order to complete this deficiency, Gurau and co-workers[146, 147], Wang and co-workers[54, 110, 148] and Ren et al.[149] published 3D 2-phase isothermal models.
In their MEA model, Ren et al.[149] explored the physical insight and fundamental understanding of the transport mechanism by analyzing the detailed distributions of velocity vector, oxygen concentration, water vapor concentration, liquid water concentration, water content in the PEM, net water flux per proton flux, local current density, and overpotential which all were found to be similar to each other. Specifically, their results demonstrated that the oxygen concentration was smaller in the rib corresponding area of GDL, in the back part of gas channels, and at higher current density; and the performance could be enhanced by increasing the inlet gas velocity, and decreasing the PEM thickness and rib width.

Wang et al.[148] used mini-gas channels as structured and ordered porous media in their continuum model of two-phase channel flow based on two-phase Darcy’s law and the M2 formalism and they investigated three issues important in optimizing channel design and mitigating channel flooding in PEMFCs: liquid water buildup towards the fuel cell outlet, saturation spike in the vicinity of flow cross-sectional heterogeneity, and two-phase pressure drop. Additionally, a two-phase pressure factor expressing two-phase flow mal distribution in the channels was defined and an analytical solution of the liquid water saturation was obtained as a function of the stoichiometric ratio, relative humidity, and axial location. Under full-humidification inlet conditions, the liquid water was found to develop quickly at the entrance region followed by a slow increase downstream and the liquid saturation was predicted to become as high as 20%. Wang[54] examined the two-phase transport in both anode and cathode gas diffusion media and explored that the multiphase flows might exist in both anode and cathode diffusion media at low-humidity conditions. Moreover, the numerical solutions demonstrated that the liquid water emerged downstream/near the outlet due to water production in the co-flow configuration while flooding become severe in the middle due to the internal humidification in the counter-flow configuration. Later, Wang[110, 150] published the two-phase version of the Porous-Media Flow Field model. Moreover, a 1D analysis was presented in order to get analytical solutions for the profiles of the
gas/liquid superficial velocity, two-phase pressures, and liquid water saturation along the channel. The simulations indicated that the proposed channel configuration results in a modest flooding (the liquid saturation=20%) for all considered cases. In addition, the effect of the capillary action on liquid transport along the channel was found to be negligibly small while the superficial gas velocity were different in single and two-phase regions.

Recently, Dalasm and co-worker[151] presented a 3D isothermal and transient two-phase model of the cathode side with a straight channel in order to study the effects and the time variation of liquid water formation and distribution in along-channel and through plane directions as well as the gas phase transport under the startup condition. It was found that the liquid water first accumulated above the channel under the CL at the start up, then moved with capillary pressure gradient in the domain and finally accumulated above the rib and near the CL at the steady state condition. Besides, the two-phase mixture density decreased from the inlet and the reduction in the through-plane direction was found to be much higher than the along-channel direction while the liquid saturation level was approximately the same in the along-channel direction when compared to the through plane direction. The required time to attain the steady state condition (steady state time) was found to be much lower for the low average current density due to the capillary pressure gradient inside the porous media. According to the simulations, the time variation of the average current density profile showed very steep behavior within the first second due to gas phase transport (For example, it is reported that at the average current density of 1.45 A/cm², it reaches 80 percent of its final value within the first second). The highest power was obtained after 120 s. They have also presented a thermal management model in order to investigate the phase change in the cathode[152].

In the meantime, Min[153] proposed a novel 3D two-phase non-isothermal whole fuel cell model based on the two-fluid method. The model considered the intrinsic heat transfer between the reactant fluids and the solid matrices while neglecting the ohmic heating in the bipolar plates and the diffusion layers
due to their high conductivities. According to the numerical results obtained by using SIMPLEC algorithm[154], a lower cathode humidity enhances the oxygen concentration at the cathode, the liquid water saturation increases along the channel in the cathode electrode while the liquid water can occur at high current density at the anode due to the less water vapor transport than the hydrogen consumption rate. Additionally, temperature difference between the reactant fluid and solid matrix was found to be the highest in the cathode CL while it decreases far from the CL. Near the catalyst layer, the reactant fluid temperature was predicted to be higher than the solid matrix temperature while the opposite was seen near the channel.

The overall summary of the models presented here are given in Appendix A.

### 2.3. Review on Modeling of Fuel Cell Sandwich

A PEMFC consists of four main components: the bipolar plate, which contain the current collectors and gas channels; the gas diffusion layer (GDL); the catalyst layer (CL) or active gas diffusion layer, and; the proton exchange membrane. In the subsections of this section, a short description is given of the composition and the physical phenomena taking place in each layer as well as a brief outline of the most relevant literature. Because this thesis is focused on optimization of the composition of MEA, catalyst layer models and membrane models are described in detail. More general fuel cell reviews can be found in references [10, 17, 19, 29, 30, 90, 155-162].

#### 2.3.1. Membrane Modeling

One of the most important parts-maybe the most important-of the polymer exchange membrane fuel cells is the electrolyte which is a single ion conducting or specifically proton conducting membrane.

The functionality of a polymer exchange membrane or polymer electrolyte membrane depends on the water content of which the amount affects the ionic conductivity and other transport properties of the
membrane. Therefore, the membranes are humidified with water vapor or liquid water which the humidified reactants include. The structure of the membrane also depends on the water content as well as operating temperature, pressure and pretreatment procedures.

The modeling of the membrane focuses on the transport of water and protons which are two species that are directly related to the functionality of the membrane. Before looking into the mechanisms governing their transport, it is necessary to review some of the background regarding the model formulation such as the morphology and hydration behavior of the polymer exchange membranes. Although several membranes have been studied experimentally, Nafion® manufactured by DuPont, is the most thoroughly used and studied membranes for PEMFCs. The good thing is that by only modifying the property values, the other membranes can be modeled with the same governing equations used for Nafion® [30]. Therefore, the review presented here gives the necessary background information and analyzes the modeling efforts in the literature, focusing on Nafion®.

1. Structure & morphology

The function of the membrane is to provide a path for the ions to move from anode to cathode and separate the oxidation and reductions equations[31]. Therefore, a fuel cell membrane must have relatively high ionic conductivity, must prevent of mixing of fuel and reactant gases, and must be chemically and mechanically stable within the operating environment of the fuel cell[9, 163]. PEMFCs use a solid polymer typically sulfonated fluropolymer membrane providing the ionic migration/conduction as well as isolating the anode and cathode electrically and mechanically[163].

Sulfonated fluropolymer membranes also referred to as perfluorinated ion exchange membranes or perfluorosulfonic acid membranes (PFSAs) such as Nafion®ª, are currently the best option for low-temperature fuel cells since they have the necessary properties in the fuel cell environment: high
conductivity (when sufficiently hydrated), good stability (both mechanical and chemical), and high permselectivity for nonionized molecules to block crossover of reactants[163].

PFSA is basically a copolymer of tetrafluorethylene (TFE) and various perfluorosulfonate monomers[9]. Sulfonated fluoropolymer membranes start with a polytetrafluoroethylene (PTFE) backbone that is sulfonated by adding a side chain ending in a sulfonic acid group (SO₂H) to the PTFE backbone[9, 164]. The schematic demonstrating the microstructure of NAFION® is given in Figure 2.2[165].

The schematic demonstrating the microstructure of NAFION® is given in Figure 2.2[165].

**Figure 2.2. Schematic representation of the microstructure of NAFION®[165].**

The SO₃H group is ionically bonded: the end of the side chain is actually an SO₃⁻ ion with H⁺ ion, that’s why such structure is called ionomer[9]. The ends of the side chains tend to cluster within the overall structure of the membrane due to their ionic nature. This macromolecule contains both highly
hydropobic (Teflon-like backbone) and highly hydrophilic (sulphonic acid groups at the end of the side chain) regions[9, 164]. The hydrophilic clusters of sulphonated side chains is capable of absorbing relatively large amounts of water (in some cases up to 50% by weight) which enables H+ movement and make these materials proton conductive[9].

Varying the length of the chains, and location of the side chain on the backbone, the equivalent weights (EWs) of sulfonated fluoropolymer membranes can be modified. EW is practically a measure of ionic concentration within the ionomer, it is inverse of the ion exchange capacity (IEC), and is defined as the weight of dry polymer sample in grams per number of moles of acid groups[9, 164]:

$$\frac{1}{IEC} = \frac{W_{dry}}{N_{A^{-}}}$$

(2.1)

where $W_{dry}$ is the weight of dry polymer sample in grams and $N_{A^{-}}$ is the number of moles of acid groups.

Nafion® is a copolymer of poly(tetrafluoroethylene) and polysulfonyl fluoride vinyl ether, which uses perfluoro-sulfonylfluoride ethyl-propyl-vinyl ether (PSEPVE)[9]. Nafion®TM membranes are built in different sizes and thicknesses and noted with a letter N, followed by a 3- or 4- digit number. The first 2 digits expresses EW divided by 100, and the last digit or two digits describes the membrane thickness in mill (1 mill=1/1000 inch=0.0254 mm). Nafion®TM is produced in several thicknesses, namely 2, 3.5, 5.5, 7, and 10 mills (50, 89, 127, 178, 254 µm, respectively). For example, Nafion®TM N115 has equivalent weight of 1100 and it is 5 mills (0.127 mm) thick. (EW) in g eq$^{-1}$ of a polymer membrane can also be formulated with the formulation[9]: $EW = 100n + 446$ where n is the number of TFE groups on average per PSEPVE monomer[9, 166].

Typical EW for Nafion®TM membranes is 1100 since this EW has the mechanical stability while the membranes with EW as low as 700 don’t. On the other hand, copolymers with EW greater than
approximately 1500 g eq⁻¹ cannot provide enough ionic conductivity for practical fuel cell applications [9].

Other manufacturers such as Asahi Glass (Flemion), Asahi Chemical (Aciplex), Chlorine Engineers (Membrane C) and Dow Chemical have developed and sold similar materials. Furthermore, a composite membrane made up of a Teflon-like component featuring mechanical strength and dimensional stability and a perfluorosulfonic acid component providing protonic conductivity has been presented by W.L. Gore and Associates[9].

Research on other types of membranes such as sulfonated polyaromatic membranes, typically sulfonated polyetherketones and hybrid membranes is being performed in order to have cheaper and better membranes, especially being able to operate at higher temperatures [164, 167-176].

2. Membrane hydration & Transport

The structure and the water content of the membrane are significantly important factors on the protonic conductivity of a solid polymer membrane. Therefore, the hydration of the membrane including the water transport and the processes occurring while the membrane sorbs the water molecules should be understood.

Water sorption behavior of PEMs is usually presented in terms of water content or water uptake. The water uptake in certain ionomeric membranes, mostly Nafion® and Dow membranes from water vapor and liquid water at various temperatures has been studied by many authors. However, more data for water uptake from the vapor and liquid phases, especially at the operating temperatures of PEMFC (e.g., 80⁰C) is required in order to model these membranes[177]. The data for the water uptake of Nafion® is the most available one among the membranes. On the other hand, due to the similarities in the morphology, other membranes are predicted to demonstrate similar trends to those of Nafion®[164].
The water content or water uptake in membrane is commonly expressed as grams of water per gram of polymer dry weight, or as number of sorbed water molecules per sulfonic acid groups, i.e. per sulfonate head, present in the polymer:

\[
\lambda = \frac{N(H_2O)}{N(\sim SO_3H)}
\]  

In order to completely remove the water from a membrane, the temperature is raised but this anhydrous form (\(\lambda = 0\)) form is not usual since this temperature will be the point where the membrane starts to decompose\[164\]. Therefore, there is always an amount of water (approximately one and a half waters per sulfonate head (\(\lambda=1.5\)) persists to stay in the membrane when it is not in contact with any vapor or liquid water \[164, 178\]. As mentioned before, the backbone of the polymer membrane is hydrophobic and the sulfonate heads are hydrophilic so the first water molecules sorbed are distinct from the hydrophobic fluorocarbon and strongly linked to the sulfonate heads, and they make sulfonate heads dissociate and from hydronium ions\[45, 164, 177-180\] This structure of the sorbed water associated with/localized on the sulfonate heads, i.e. ion exchange sites is called as counter-ion cluster/inverted micelle or this water is called to be in ion cluster phase\[45, 90, 164, 177-179, 181\], while the sulfonate heads are called as nucleation sites\[45, 90, 164, 178, 181\].

Figure 2.3\[164\] demonstrates the state of a membrane for in the range of \(\lambda= [1, 2]\). In this range of \(\lambda= [1, 2]\), the hydrogen bonds have approximately 80% of the strength of those in pure water since the cluster shape doesn’t allow for the formation of stronger bonds. Moreover, the hydrogen bonds become weaker as more water contributes to counter-ion clusters \[164, 178\]. On the other hand, distance between sulfonate heads will become less in an actual membrane as sulfonate heads cluster together; thus, some proton transport is possible even at lower water contents of 2 although it is extremely low due to insufficient amount of water sorbed which cannot form continuous water phase\[158\].
In the range of $\lambda = [3, 5]$, as the water content increases, the counter-ion clusters become larger and the excess charge protons become mobile over the entire cluster which provides the pathways to allow for conductivity\cite{164, 178}.

Figure 2.4\cite{164} is the schematic of the hydration state for $\lambda = [3, 5]$\cite{164}. As $\lambda$ approaches 5, some ion-clusters begins to connect, therefore; the membrane becomes more conductive \cite{164, 178, 182}. For $\lambda$ larger than 5-6, all ion-clusters become much larger and form interconnections with each other/coalesce which enables any additional water to form a free, continuous phase with properties approaching those of bulk water\cite{45, 90, 164, 178, 181-184} since the additional water are not strongly tied to sulphonate heads\cite{4, 164, 183, 184}. The cluster network of the connections, or collapsed channels, is based on a percolation-type phenomenon so a transport pathway is formed as the clusters grow, get closer and become connected by the collapsed channels which are transitory and hydrophobic compared to polymer matrix \cite{45, 90, 181}.
Figure 2.4. Schematic hydration diagram for NAFION® for water contents of $\lambda = [3-5]$ [164].

The measurements of water mobility and water self-diffusion values [185] as well as the mobility of protonic charge carriers [4] confirmed that these properties approach the bulk water values. The amount of water needed to connect the ion-clusters depends on the strength of the charge on the acid group and the distance between sulfonate heads [164] so the variation in the hydration among PFSA membranes will also cause variation in the threshold conductivity. Based on conductivity data obtained for Nafion®, the percolation threshold is shown practically to occur around $\lambda = 2$ [45, 90, 181].

Figure 2.5 [164] illustrates the hydration states for $\lambda = 6$ near the conductivity threshold and $\lambda = 14$ which is the maximum water content for a fully saturated/vapor equilibrated membrane [164].
The maximum amount of water that can be sorbed in the membrane strongly depends on the state of water used to equilibrate the membrane. A Nafion® membrane equilibrated with liquid water takes about 22 water molecules per sulfonate group, while the maximum water sorption from the vapor phase is roughly 14 water molecules per sulfonate group. This phenomenon was first described in 1903 by Schroeder and is therefore known as Schroeder's Paradox [164, 186, 187]. Since this phenomenon is important in modeling of water transport in the membrane, it is discussed in detail.

**Schroeder's paradox:** Schroeder’s paradox is the difference in water uptake due to the type of reservoir in contact with the membrane as mentioned above. At the same chemical potential, liquid water or saturated water vapor, the uptake will be different as seen in Figure 2.6[45] below.
According to the physical model proposed by Weber and Newman [45], the reason for the difference in uptake is basically structural: due to the filling and expansion of the channels connecting the clusters. When the membrane is in contact with saturated water vapor, a complete cluster channel network has formed as can be seen in the 3\textsuperscript{rd} picture in Figure 2.7 [45] demonstrating the cross-sectional representations of the membrane where the gray area is the fluorocarbon matrix, the black is the polymer side chain, the light gray is the liquid water, and the dotted line is a collapsed channel [90]. On the other hand, when the liquid water is present at the boundary, due to repelling of the fluorocarbon-rich skin of the ionomer by the aqueous environment, a structural organization takes place letting liquid water infiltrate and expand the channels [45, 90]. As the channels which are still hydrophobic on average become stable and the clusters pile/agglomerate along them, a pore-like structure which are now filled with liquid water forms and the uptake of the membrane has increased without a change in the chemical potential of the water [45, 90]. In other words, the liquid water has sufficient pressure and energy to penetrate and expand the channels while the water vapor does not have enough energy to
condense in the channels due to their hydrophobicity and consequently the liquid-equilibrated membrane acquires higher water content[45].

![Figure 2.7. Evolution of membrane structure as a function of water content[45].](image)

The schematic of vapor-equilibrated membrane showing the collapsed interconnecting channel and liquid-equilibrated membrane showing the interconnecting channel swollen are given in Figure 2.8 and Figure 2.9, respectively. In vapor-equilibrated membrane, a hydronium ion (and maybe water) moves diffusion from cluster to cluster through the hydrated sulfonic acid site in the polymer matrix (collapsed channel); in liquid-equilibrated membrane, the complete liquid network is formed and the hydrated proton moves from cluster to cluster while water move down its pressure gradient[45, 90].
A similar explanation to this difference in uptake from vapor and liquid phases is given by Fimrite et al. [164] as the following: “As sorption from the vapor phase involves condensation of water inside the polymer, most probably on the strongly hydrophobic polymer backbone, and the resulting uptake is lower than if sorption and imbibition\(^1\) directly from the liquid phase [164, 177, 179].”

Another explanation for this phenomenon given as the best explanation according to Fimrite et al.[164] is that proposed by Choi and Datta[182] who presented a physicochemical model for water sorption. Their model agrees with the experimental data for vapor equilibrated membrane as seen in Figure

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1 Imbibition is described as the absorption of a liquid by a solid or gel.
2.10[164]. They proposed that water molecules sorbed by the membrane are either strongly chemically bound to the sulfonate heads of which number is set by chemical equilibrium, or are “free” waters, which physically equilibrate with the external solvent while their number is determined by phase equilibrium [164, 182]. They reasoned the difference by an additional capillary pressure causing the vapor-equilibrated membrane to sorb less water than the liquid-equilibrated membrane from an external solvent with the same activity [164, 182].

![Figure 2.10. Water sorption isotherm for vapor-equilibrated membrane[164].](image)

Temperature dependency/independency is another difference between the water sorption of vapor- and liquid-equilibrated membranes [45, 188]. In the former case, the interactions of water with the polymer, the formation of clusters and the existence of the transitory channels, both have energies that change with the temperature [45, 188]. On the other hand, the structure for the latter case through which the water moves as if it were inert, is stable; therefore, the uptake doesn’t depend on the temperature [45, 188].
Fuel cells are usually operated with humidified gases in order to increase the performance, and this may yield situations where there is liquid water on the cathodic side of the membrane, but only water vapor on the anodic side[3]. However, water uptake from the vapor phase may be more relevant for fuel cell operation[164].

3. Modeling Approaches

Membrane modeling is a subject that has been explored in a great amount since the membrane is one of the most important key elements in the fuel cells. In their review, Weber and Newman[45] pointed out the fact that PEMs have been modeled within two extremes in terms of both quantitative and qualitative modeling: the macroscopic and the microscopic[45]. Kreuer et al. [189] published a comprehensive review of both microscopic and macroscopic modeling regarding the transport phenomena in PEMs.

The microscopic models exclusively concentrate on the microscopic structure of the membrane, study molecular dynamics simulations[30, 190] and statistical mechanics modeling[191-194] as well as they allow for the fundamental understanding of processes like diffusion and conduction in the membrane on a microscopic scale. They provide valuable information about how small perturbations like non-homogeneity of pores and electric fields impact the transport and how to incorporate the small-scale effects including single ions and pore-level effect[30, 45, 164, 184, 190, 191, 195-197], besides all microscopic models consider the membrane as a two-phase system[45]. However, unfortunately microscopic models are generally too complicated in order to predict the overall FC performance and characteristics[45]. In contrast, the macroscopic models deals with the transport and relevant parameters of the membrane in a macro-homogeneous fashion based on mainly empirical results[30, 45].
In order to examine a multidimensional model of the complete fuel cell taking the membrane transport into account, the use of macroscopic membrane models is practically prescribed [99, 100, 164]; therefore, the focus here is on macroscopic models.

In membrane modeling, the main need is to accurately predict the ohmic losses related to the protonic current which strongly depends on a set of coupled transport phenomena that determine water content and conductivity. As mentioned above in details, with the decrease in the water content in the membrane, the protonic conductivity decreases and this increases the ohmic losses. On the other hand, in order to avoid flooding in CLs and GDLs and obtain better transport of both reactants and products, the amount of the water in the membrane is restricted to achieve a well management of water in all regions. Therefore, a comprehensive membrane model considers water transport in addition to proton transport, that’s why most models describe the membrane system with three main components: membrane itself, protons, and sorbed water. Since the membrane is stationary, only the water and protons move in the membrane system. In addition, most models don’t take the penetration of the reactants through the membrane since these crossover are almost negligible and don’t significantly affect the proton or water transport [30, 31]. There are some exceptional models [8, 30, 31] considering the fuel or oxygen crossover effects which can be easily incorporated into any membrane model [30, 31, 42, 90].

The work presented here provides a comprehensive review of recently proposed macroscopic membrane models in order to understand the phenomena occurring in the membrane and determine a general framework for developing a computational fuel cell model which may allow for the analysis and optimization of fuel cells.
Macroscopic models

As demonstrated in Figure 2.11, macroscopic membrane models can be sorted into two general categories: 1. Membrane Conductivity Models, and 2. models presenting fuel cell processes mostly for water management purposes, so-called Membrane Transport Models. The second generally requires the use of a conductivity model, a fit to empirical data, or the assumption of constant conductivity e.g., fully hydrated membrane at all times [30, 45, 164]; therefore, here only membrane transport models will be discussed. The review about membrane conductivity models can be found in Fimrite et al.[164].

Fuel Cell Models

![Fuel Cell Models Diagram](image)

Figure 2.11. Classification of membrane modeling approaches.

Membrane Transport Models: Physical models for water and proton transport

The membrane transport models can be classified in two main categories, those that assume the membrane system is a single phase, and those that assume it is two phases[164]. The former results in a diffusion-type model [30, 45, 57, 122, 164] and the latter in a hydraulic-type model [8, 30, 45, 48, 64, 164, 192]. Although both types of models agree with experimental data to some degree, neither can be used for satisfying the full range of data nor predicting all of the observed effects, like Schroeder’s paradox. Therefore, there is combination models developed including some properties of each.
Diffusion Models

Diffusion models treat the membrane as a homogeneous, nonporous matrix in which the sorbed/dissolved water molecules are transported by diffusion, electro-osmotic drag and pressure gradient [30, 31, 164]. Since the diffusion models assume the membrane system as a single phase, they represent the vapor-equilibrated membranes[30]. In diffusion models, for the transport, Dilute Solution Theory [139] and Concentrated Solution Theory [85, 198] are commonly used.

There are many models [18, 30, 43, 57, 78, 81, 82, 199-207] including some of the earliest ones that used Dilute Solution Theory along with Ohm’s law (conductivity model) successfully. Dilute solution theory takes only the interactions between each dissolved species and the solvent into account and uses Nernst-Planck equation[208, 209]. Nernst-Planck equation incorporates the migration flux and diffusive flux of the charged species resulting from a potential gradient and concentration gradient, respectively; and convective flux of the species due to the bulk motion of the solvent carrying it along[30]. The motion of each charged species is characterized by its transport properties, namely, the mobility and the diffusion coefficient which can be related to one another at infinite dilution via the Nernst-Einstein equation [30, 208, 210, 211]. For the analysis of the one-phase systems, the convective term is neglected since velocity of membrane being the solvent is zero[30]. The water itself is not a charged species, having zero valence so the Nernst-Planck equation is reduced to Fick’s Law to model the water movement[30]. Though, there are some simplest models either neglecting the water movement totally or treat it as a known constant[30].

On the other hand, in the literature, it is well reported that while the protons move across the membrane, they drag the water in the same direction, which is defined as the electro-osmotic drag. Technically, this effect is a result of the proton-water interaction, not a dilute solution since the membrane itself is the solvent[30]. Although the proton-water interaction generally assumed not to be
too significant, when there is a large gradient in the water (e.g., low humidity or high current-density conditions), it should be taken into account[30]. In contrast to Dilute Solution Theory, Concentrated Solution Theory takes this interaction, the electro-osmotic drag into account; actually it considers all binary interactions between all of the species [61, 84, 85, 209, 212-215]. It is reported that it is simpler but more accurate to use Concentrated Solution Theory for an electrolyte with three species, that’s why there are many models that used Concentrated Solution theory [34, 42, 61, 84, 85, 122, 213].

Hydraulic Models

In contrast to the single-phase treatment of the membrane system mentioned above, hydraulic models representing the liquid-equilibrate membranes, treat the membrane as two-phases: the polymer phase and the liquid water filled pores, essentially water[30, 31]. The additional degree of freedom created by the addition of the second phase, allows for the membrane system to maintain a pressure gradient in the water due to an unknown stress relation between the membrane and the fluid at every point in the membrane so the movement of water can be modeled as it is transported by a potential gradient and a pressure gradient[30, 31, 164]. The movement of water by the pressure gradient can be determined mainly by describing an effective permeability of water moving through the pore structure and this treatment is used for the fuel systems of which the membrane is fully hydrated, assuming the transport properties to be uniform across the membrane and the pressure gradient to be the only driving force for water transport, which give a linear distribution of pressure[30]. However, when the membrane is not fully-hydrated, this approach cannot predict the resulting water flux; therefore, concentration gradient can be more promising as a driving force for the water transport [45, 164].

The hydraulic models developed by Bernardi and Verbrugge [8, 48] were based on earlier work of Verbrugge and Hill [216, 217] and these were the first of the earliest and most referenced models where the membrane is fully hydrated/saturated with water of which most is in liquid phase while transported
through the pores[122]. In order to describe the proton movement, Dilute Solution approach incorporating Nernst-Planck equation was used whereas Schlogl equation was used in order to obtain the liquid water velocity[216, 218]. In addition, Bernardi and Verbrugge[8, 48] take the transport of oxygen through the membrane into account in this cathode model. This model is very popular among the literature; many other models [36, 46, 47, 67, 219-221] use the same approach and equations as Bernardi and Verbrugge, when the membrane is assumed to be well hydrated, mostly assuming the transport properties to be constant. Eikerling et al. [64] developed a more general hydraulic model accounting for the variation in the water content and the dependency of conductivity, permeability and electro-osmotic drag coefficient on the local water content. More recently, in order to model liquid-equilibrated membranes, Weber and Newman[90] used Concentrated Solution Approach instead of Dilute Solution Theory for their hydraulic model. The limit of these hydraulic models is that they assume that membrane has two different pore pathways for gas and liquid which physically is not reasonable[45].

Combination Models

Both diffusive-type and hydraulic-type models mentioned above have limitation although they are still popular for having the ability to predict some part of the transport phenomena. They fail to predict completely the correct water profiles and transport. For example, Buechi and Scherer[222] discovered that only a hydraulic model can explain the experimentally observed sharp drying boundary on the anodic side of the membrane, which only a two-phase model can do[45]. Moreover, any of the above models can’t effectively give a physical picture of Schroeder’s paradox.

Diffusion models exclude the effect of pressure gradient as a separating force resulting with a constant concentration while accounting for the diffusion in the full hydrated membrane[30]. On the other hand, hydraulic models only account for the pressure driven flow assuming the liquid water in the pores is
pure[30]. In summary, diffusion model provides a better prediction for transport in membrane with low water content [31, 45, 164] while the transport behavior of a fully saturated membrane is represented better by the hydraulic models [31, 64, 164].

The most accurate model is the superposition between them since the model must account for both types of behavior reflecting the experimental data that includes Schroeder’s paradox.

There have been various models [26, 52, 135, 223, 224] based on Concentrated Solution Theory employing both the diffusive and convective flow with pressure and concentration driven forces, respectively. Thampan et al. [223] and Janssen [122] in their diffusive-type models, described the water transport through the membrane by the chemical potential gradients only, instead of separating diffusive and pressure-driven flow components.

Primarily focusing on convective transport, Eikerling and co-workers [64, 194] coupled the capillary pressure isotherms with the phenomenological transport equations accounting for the electro-osmotic drag and pressure-driven flow with the capillary pressure isotherms in addition to considering the effect of local water content on the conductivity, permeability and electro-osmotic drag coefficient. They also used the percolation phenomena in order to describe the flow through two different pore types in the membrane by incorporating the pore-size distribution for Nafion®.

Recently, Weber and Newman [45], presented a novel combination model in which they assume that two transport modes occur in parallel and are shifted between simultaneously using the fraction of channels that are expanded by the liquid water. The transport for vapor-equilibrated membrane is defined by the chemical potential gradient and hydraulic pressure gradient is used for liquid-equilibrated membrane. For the continuous transition between vapor- and liquid-equilibrated regimes, the electro-osmotic drag coefficient is treated to transit from 1 to 2.5. They also considered the microscopic effects such as the channel-size distribution and the surface energy of the pores.
There are different kinds of voltage losses in a fuel cell caused by many irreversibilities due to kinetics of electrochemical reactions, internal electrical and ionic resistance, difficulties in getting the reactants to reaction sites, internal(stray) currents and crossover of reactants[9, 10]. These factors are grouped mainly in three polarization types which are activation, ohmic and concentration, respectively missing the last one.

2.3.2. Catalyst Layer Modeling

1. Structure & Morphology

At the anode and cathode, hydrogen is oxidized and oxygen is reduced, respectively; these reactions are known as half-cell reactions. The oxygen reduction reaction (ORR) occurs in the cathode catalyst layer, and the hydrogen oxidation reaction (HOR) occurs in the anode catalyst layer. At the low-temperature environment of a PEMFC, these electrochemical reactions cannot take place so both reactions require breaking the molecular bond in the diatomic gaseous reactant molecules. Pt or Pt alloys are mostly used catalysts due to the acid nature of the polymer electrolyte[156]. In order to enable the reactions, the catalyst layers must allow for the transport of reactant gas molecules, protons, and electrons so the catalyst layers can be viewed as porous diffuse regions containing both electrolyte and electron conducting phases [10, 30, 31, 95, 156, 225]. Therefore, the catalyst layer is three-phase interface consisting of 3 components: the ionomer to allow for a passage for protons to be transported in or out (the protonic phase volume fraction), carbon support composed metal catalysts supported on carbon (the electronic phase volume fraction) to allow for electron conduction, and sufficient porosity for the gas molecules to be transferred to catalyst sites (the void/gas phase volume fraction). The sum of all volume fractions is equal to unity, and individual volume fractions must be optimized to obtain the best overall performance of a catalyst layer. The state of the art catalyst layer for PEMFCs is presented as a triply percolating mixture of the polymer electrolyte, carbon support, and gas pores [10, 18, 31, 75, 226,
The structure of a catalyst layer in details in Ref. [10]: Carbon support is composed of a nanodispersed carbon support powder (30–40 nanometer carbon black particles), previously distributed with 5–10 nanometer platinum particles; the carbon particulates naturally assemble into 150–250 nanometer agglomerates due to residual charges and surface interactions. The agglomerated carbon is mixed with an aqueous solution of perfluorosulfonic acid polymer and isopropyl alcohol which serves as a binder and proton conductor, constituting the catalyst ink. Catalyst ink is typically applied to the PEMFC in a 10–20 micrometer film [10, 31] which is essentially the thickness of catalyst layer. The cross-section of the MEA cut by a glass knife (a) Nafion® 117 membrane, (b) impregnated active catalyst layer, (c) electrode[75] can be seen in Figure 2.12[75] and Figure 2.13[10] gives a schematic of the catalyst layer structure. The effective Pt surface area of the catalyst ink is determined by the structural distribution of carbon support/gas phase/ionomer phase of the resulting mixture. Following the mixing process, evaporation of alcohol leading to cracking and leaving residual pores (residual pore formation) occurs [10].

Figure 2.12. Cross section of MEA[75].
In summary, being the thinnest layer in the fuel cell sandwich, catalyst layers are the functional core of the PEMFC and are responsible for

- promoting reaction kinetics with the inclusion of catalyst particles,
- transporting electrons and protons from/to the active catalyst sites with the carbon agglomerate phase,
- transporting fuel and reactants via diffusion through the gas phase (pores), liquid water, and electrolyte phase,
- transporting water to the GDL or membrane.

2. Modeling Efforts

Electrochemical reactions take place at the catalyst layers of the fuel cell. At the anode and cathode, hydrogen is oxidized and oxygen is reduced. The cathode reaction where the water is produced, is much
slower that the anode reaction so mass transfer effects become more important; actually it represents the principal inefficiency of the fuel cell[30]. Because of this reason, there are many more cathode models than anode ones and in fact, basically every electrode-only model is for the cathode[30]. Therefore, the review below focuses mainly on the cathode models. The anode models are almost always modeled as a simplified cathode model along with the change in the kinetic expressions and property values.

These layers are often the thinnest but the most complex component in the fuel-cell sandwich because all of the different types of phases (membrane, gas diffusion medium, pores) exist in the same region and they are all essential for the catalyst layer to function. Since the catalyst layer includes the membrane and diffusion media, the proposed models can be used in the catalyst layer incorporating the additional expressions associated with the electrochemical kinetics on the supported electro-catalyst particles. The transported species in the catalyst layer can be seen in Figure 2.14[7]. Due to complexity of catalyst layers, the approach of various modeling efforts usually depends on how the other components are being modeled and what the overall aim of the model is.

![Figure 2.14. Species transported in cathode catalyst layer[7].](Image)
Like membrane models, they can be classified in two main categories: microscopic models and macroscopic models. The classification of the catalyst layers is demonstrated in Table 2.1[7]. The microscopic models include pore-level models and more detailed quantum models. The quantum models deal with detailed reaction mechanisms and elementary transfer reactions and transition states [30]. They are beyond the scope of this literature review and not to be given here.

Table 2.1. Comparison of macroscopic and microscopic models for catalyst layer[7]

<table>
<thead>
<tr>
<th>Macroscopic models</th>
<th>Microscopic models</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Pseudo-homogeneous</strong></td>
<td><strong>Agglomerate</strong></td>
</tr>
<tr>
<td>The catalyst is treated as a homogeneous phase.</td>
<td>The catalyst is assumed to form agglomerates of certain ordered geometry.</td>
</tr>
<tr>
<td>The oxygen diffuses through the porous media.</td>
<td>The oxygen diffuses from the pores to the agglomerates.</td>
</tr>
<tr>
<td>The oxygen concentration in the pores is constant.</td>
<td></td>
</tr>
</tbody>
</table>

In the macrohomogeneous models, all phases are assumed to exist at all points in each volume element and they provide for more physically realistic simulations, therefore; in the literature, almost all of the models used for fuel-cell electrodes are macrohomogeneous. The catalyst layer was not the main point of interest in most of the macroscopic models reported in the literature but the classification is puzzling.

Weber and Newman[30] proposed that the macrohomogeneous models can be subdivided on the basis of the length scale of the model, being analogous to dimensionality for the overall fuel cell models. In this strategy, the first type of model is the 0-D type models or interface models. The structure of catalyst layer is not taken into consideration so just a single equation is used in the interface of gas diffusion layer and membrane. The second group, simple macrohomogeneous model, includes two types of 1-D
models: porous-electrode and agglomerate models, which accounts for changes across the layer or only local effects in the agglomerate, respectively. Porous-electrode models sometimes can be called thin-film models in the literature. Agglomerate models may include the effects across the layer as well and porous-electrode models also may include agglomerate scale interactions[30]. In other words, porous-electrode and agglomerate correspond to the length scales of the layer and agglomerate, respectively. If the model considers the effects on both length scales, they are called as 2-D type models and known as embedded macrohomogeneous models. There are only two primary length scales (the catalyst layer and the agglomerate) in catalyst layer regions so there are no 3-D-type models[30] according to the classification on the basis of the length scale. Catalyst layer models can also be categorized on the basis of assumed oxygen transport mechanism[31], these are interface models, pseudo-homogeneous models and agglomerate models[30]. Pseudo-homogeneous models are essentially the same with porous electrode models. In all these models, Ohm’s Law is used for modeling electron and proton transport and Butler-Volmer equation is used for the reaction kinetics but the modeling of oxygen transport differs.

In this section, the catalyst layer models are discussed on the basis of length scale. The review starts with microscopic models and then macrohomogeneous models including interface, simple and embedded macrohomogeneous models are examined.

**Microscopic Models: Single-Pore Models**

The earliest models of fuel cell catalyst layers are microscopic because these models are conformable to analytic solutions because of the assumption of first-order reaction with Tafel kinetics. In microscopic models, effective values for the parameters like diffusivity and conductivity, involving averaging over the microstructure, are not used, therefore; they require a detailed microstructure of the catalyst layer[30].
The original single-pore models were done for phosphoric-acid fuel cells in which the catalyst layer contains Teflon coated pores for gas diffusion, with the rest of the electrode being flooded with the liquid electrolyte. There are two main types of single-pore models depending on the structure of the gas pores modeled. The first type is called gas pore models and they are based on the scheme of Giner and Hunter[30, 228]. In this type of models, gas pores are straight and cylindrical with a defined radius and they extend along the length of the catalyst layer. The reactions occur at the surface of these gas pores. The second type of pore-level models are termed as the flooded-agglomerate models and they use the approach of Grens[229, 230] and Cutlip[30, 231]. They still use gas pores but the difference is that these gas pores are filled with electrolyte and catalyst particles. Both models mainly use the diffusion equation with reactions but the flooded-agglomerate models also take account into the diffusion across the electrolyte incorporating the equilibrium condition for the dissolved gas concentration in the electrolyte. The gas pore models were able to match the experimental findings but the flooded-agglomerate one shows better agreement with experimental data since it probably models the actual microstructure better and also has more parameters[30].

In reality there are multiple pores that are tortuous so this is the backside of the single-pore models but overall, they give a good first start in simulation of fuel cell electrodes and build a basis for more complicated models as to be discussed below. However, since these models were essentially built for phosphoric acid fuel cells, it is questionable that they can be used in the modeling of polymer electrolyte fuel cells in which the electrolyte is solid. Further detailed information about the different equations and limiting cases can be found in the literature [30, 232, 233].

The other microscopic models for the catalyst layers are built by Bultel and co-workers [30, 71, 74, 234, 235]. These models assume that in the catalyst layers, spherical agglomerate structures exist in regular 3-D hexagonal arrays and either there are gas pores or the region is flooded with electrolyte between
these agglomerates and they can be used to study the detailed placement of the electro-catalyst particles if these arrangement can also be experimentally succeed, which may not be even possible[30].

**Macrohomogeneous Models**

**Interface Models**

The simplest macrohomogeneous catalyst layer models are the interface models. The major characteristic of these models is that they all treat the catalyst layers as an interface between the membrane and the gas diffusion layer rather than a different medium in the fuel cell model. In other words, the catalyst layer is assumed to be infinitely thin, and its composition and structure can be ignored by assuming that all properties are uniform throughout this layer.

HOR is very fast compared to the ionic resistance of proton movement, which means charge-transfer resistance is very low in the anode and so the reaction distribution is found to be relatively sharp front next to the membrane[30]. Therefore, in order to utilize the most catalyst and increase the efficiency of the electrode, the catalyst layer should be relatively thin. In that situation, treating the anode catalyst layer as an interface is reasonable. On the other hand, since ORR is sluggish, the charge-transfer resistance is relatively high and thus, the reaction distribution across the cathode is seen basically uniform[30]. In this situation, uniform surface overpotential can be used as a simplifying assumption. As long as the mass transfer of oxygen continues, basically all of the catalyst is being utilized in the layer. When oxygen transfer becomes limiting, the resistance next to the membrane becomes much severe, since there is less oxygen and accordingly less utilization of the catalyst in that region[30].

In interface models, a single equation for the reaction kinetics is used in the cell model as a boundary condition between the GDL and the membrane and it defines the effect of the catalyst layer in the overall cell performance. This interface assumption simplifies fuel cell modeling and facilitates numerical implementation[54]; therefore, they are commonly used when the primary interest is not the catalyst
layer composition but the membrane or the multidimensional effects of a complete cell, or when studying water or heat management[46, 236]. However, this approach does not resolve the cathode overpotential adequately[94, 237] due to neglect of electrolyte phase potential variation in the through-plane direction of the catalyst layer[31]. In addition, oxygen transport in the catalyst layer is only represented by the kinetic reaction equation and essentially it does not account for the transport of oxygen through the catalyst. Therefore, interface models are concluded that they are not suitable for catalyst optimization [31, 54].

**Simple Macrohomogeneous Models**

Simple macrohomogeneous models use essentially only one length scale averaged over the microscopic details of a region based on the theory of volume averaging and they do not include microstructural details although they are based on the same physical ideas and use similar equations with the single-pore models[30]. As mentioned before, the two main length scales studied are over the whole catalyst layer or over the agglomerate and each are discussed below. Figure 2.15 is given by Weber and Newman[30] as an idealized schematic of the catalyst layer going from z=0 to z=L between the membrane and cathode gas diffusion layer showing two main length scales: the agglomerate and the entire porous electrode[30]. The membrane, the gases, and catalyst particles are shown by gray, white and black colors, respectively; the gray region outside of the dotted circle represents an external film of membrane or the liquid water on the agglomerate[30].

**Porous-Electrode Models**

The single-pore models create a basis for the porous electrode models but in the porous electrode models don’t consider only a single pore and also the exact geometric details are not taken into account.
Figure 2.15. Idealized schematic of cathode catalyst layer showing two main length scales [27].

Porous-electrode theory is first described by Euler and Nonnenmacher[238] and Newman and Tobias[27][239]. In porous-electrode theory, the overall reaction distribution in the catalyst layer is examined as the main effect of the catalyst layer without considering the agglomerate effects[30]. The agglomerates are assumed to have a uniform concentration and potential. Weber and Newman[30] visualizes porous electrode theory as a resistor network in which electron, proton and kinetic resistances govern the reaction distribution. Thus, they modeled the overpotential and transfer current in the electrode as a function of position considering the fact that the current travels along the path of least resistance. The overall charge-transfer resistance may be nonlinear since it is derived from the kinetic expressions and calculated by accounting the effect of[30].

The simple porous-electrode models have some variations in treatment. In the first treatment, the cell potential or current density are calculated by integrating over the catalyst layer boundaries [30, 32, 219, 240]. Being very similar to the interface models, they also consider the potential drops for the matrix and solution phases.

The next set of models treats the catalyst layers using the complete simple porous-electrode modeling approach described above, which all of the variables are determined with a length scale of the catalyst layer. The gas-phase reactant concentration is assumed to be uniform in the catalyst layers in some of
these models[30, 40, 61, 79] but most of them account for diffusion in the gas phase[8, 26, 30, 36, 48, 241, 242] as being fundamentally macrohomogeneous versions of the single-gas-pore models[30].

Lastly, there are simple porous-electrode models more similar to thin film models where the difference in the treatment is that the reactant gas dissolves in the electrolyte and moves by diffusion and reaction, instead of gas diffusion in the catalyst layer[15, 47, 76, 204, 221, 243, 244] and thus, a concentration instead of a partial pressure appears in the kinetic expressions[30].

All porous electrode models assume the concentrations of the species to be in equilibrium with their respective gas-phase partial pressures, i.e., use Henry’s law [30].

**Agglomerate Models**

The simple macrohomogeneous agglomerate models are very similar to the microscopic models of Bultel and co-workers discussed above. The difference is in the geometric arrangement averaged over the agglomerate scale incorporating with the use of effectiveness factors internally and in overall while each phase exists in each volume element[30]. In these models, only effects occurring in the agglomerate length scale are accounted and the characteristic length scale is the radius of the agglomerate.

All of the agglomerates are assumed to be the same shape and size[30] being either spheres of electrolyte-filled with carbon and Pt particles and approximately of one micron in radius[18, 75, 226, 227, 237, 245] or spheres of carbon particles and platinum of around 50nm in radius that are void and are filled with liquid water during cell operation[31, 246]. Depending on the pore geometry, agglomerates are also modeled being planar, cylindrical, and spherical[95]. But in general, there are two types of agglomerate models: electrolyte-filled and water-filled agglomerate models.

According to both models, the reactant or product diffuses through the gas pores, dissolves into the electrolyte/water film surrounding the agglomerate, diffuses through the electrolyte/water film into the
agglomerate in which the reactions occur[30, 31]. They both assume that gas concentration and surface overpotential through the thickness of the catalyst layer are uniform, accordingly the reaction rate is uniform although there is a concentration and possibly a potential distribution within the agglomerate[30, 31]. In electrolyte filled agglomerates, the electrolyte is assumed to transport oxygen inside the agglomerate, and protons in the CL while the electrolyte is assumed to transport proton and the oxygen is transported inside the agglomerate by the liquid water in water filled agglomerates. As a result, each type of agglomerate models finds the optimal catalyst layer structure differently, expecting a lower optimal electrolyte content in water filled agglomerate model[31].

The reaction inside the agglomerate can be modeled in a similar way to the reaction in the porous electrode models since the transport process similar except that porous electrode models don’t consider the characteristics of agglomerates or the diffusion of reactant and product into the agglomerate[31].

Model Comparison

Between the two simple macrohomogeneous models, the major distinction is the length scales of the effects being studied. There have been many researchers [30, 39, 75, 247-249] who have compared them to each other and experimental data. Boyer et al. [39] examined the characteristic length scales for the various processes such as diffusion in the gas phase, diffusion in the agglomerate, proton migration in the catalyst layer in order to understand which scale is more important in which process. The process comparisons were done for the cathode and the results all showed that the agglomerate model fits the data better than the porous-electrode model. They also concluded that the simple agglomerate model gives more accurate results for the cathode in which has approximately uniform distribution due to slow kinetics and on the other hand, in the anode in which there is highly nonuniform reaction distribution due to fast kinetics.
According to Gloaguen and co-workers[247, 248], the porous-electrode models overestimate oxygen transport limitations due to the use of thin-film models that did not contain gas pores[30]. Chan and Tun[249], showed that the agglomerate model is more sensitive to changes in mass transport resistances caused by flooding than the porous-electrode models[30]. Broka and Ekdunge[75] arrived at the same conclusion with the previous models by comparing the models to experimental data and microscopy. They also showed that porous electrode models can give the same accuracy with the agglomerate models by adding a mass transfer coefficient into the model.

In summary, several studies in literature [31, 39, 75, 247-249] that in general, agglomerate models give more accurate prediction of experimental data, especially at low current densities where the reaction distribution is uniform and the most important effects happen at the agglomerate scale. On the other hand, at high current densities, the reactions become more nonuniform and both models give similar accuracy with the experimental data. As mentioned before, HOR is facile so reaction distribution is nonuniform; therefore, porous electrode model gives better results for anode simulations. In terms of computation, porous electrode simulations may take less time while agglomerate models need more empirically determined parameters which could be a reason for the better suit to the experimental data[31].

Besides to these two simple, there is another simpler approach considering the catalyst layer as a two phase system consisting of ionic and electronic phases only, without gas voids, so-called homogeneous models[156]. In these models, the gases are transported through the catalyst layer by the electrolyte phase as dissolved species while in the porous-electrode ones, the pores are assumed to exist along with the electronic particles covered by a thin film of polymer electrolyte. In agglomerate models, on the other hand, there is a 3-phase system composed of the gas pores surrounding the agglomerates consisting of electrolyte films and electronic particles.
The simple models belonging to the macroscopic theory account for many effects but they cannot really capture reaction distributions and proton migration across the catalyst layer. In certain circumstances such as the existence of the anode catalyst layer, a flooded catalyst layer, and a catalyst layer with a dehydrated membrane, these effects are more important. Therefore, in order to get more accurate results with the experimental data, a more complex embedded model where both length scales are used, should be used. The embedded models are described in the next section.

**Embedded Macrohomogeneous Models**

The simple macrohomogeneous models account for only one length scale, either catalyst layer thickness length scale or agglomerate radius scale. Embedded macrohomogeneous models are essentially built in order to explain both the local agglomerate level and effects across the porous electrode[30].

According to Weber and Newman[30], the embedded models can be developed in two ways. The first one can be built by improving the porous electrode modeling with the addition of a mass transfer term in order to account for the diffusion flux to/from the agglomerate. Basically, by doing this, a film between the reaction site and the gas pore is created and averaged over in the macrohomogeneous approach. This approach is not more computationally costly than the porous-electrode model in addition to making possible to use an extra fitting parameter and giving more realistic simulations especially when flooding effects are accounted[30]. Mazumder and Cole [53, 136] have used this approach. The other approach can be built by using porous electrode equations along with the effectiveness factor and incorporating the agglomerate equations as well. The change of gas composition and the overpotential across the catalyst layer due to ohmic, mass transfer, and reaction effects are considered. As a fitting parameter, the overall effectiveness factor accounting for both external and internal mass transfer to and through the agglomerate can be used without the detailed calculations and multiple fitting parameters[30]. Although, this approach is more complicated by
needing more knowledge of the agglomerate structure or yielding more fitting parameters, there have been more catalyst layer models[78, 220, 227, 243, 250, 251] using this one since it constitutes the physical phenomena in the catalyst layer better including more relevant effects[30]. Overall, the embedded models are the most complex and best in catalyst layer modeling. Unfortunately, they require more parameters as expected, and not all of them may be known. Therefore, a modified pseudo-homogeneous catalyst layer model accounting for agglomerate structure is used in the thesis although the pure agglomerate models give better predicting results at higher cell voltages.

2.3.3. Gas Diffusion Layer Modeling

1. Structure & Morphology

The diffusion media are the porous backings between the catalyst layers and the gas channels. The diffusion media are often composed of either a single gas diffusion layer (GDL) or a composite structure of a gas diffusion layer and a micro porous layer[30]. There are only a few models that consider composite diffusion media[129, 252]. Most models treat only gas diffusion layers [GDL].

The GDLs are responsible for;

- transporting electrons from the catalyst site to the bipolar plates or vice versa,
- transporting the fuel and reactant from the gas channels to the catalyst or reaction site,
- transporting product water (vapor or liquid) and heat away from the catalyst layer,
- providing structural support to the membrane electrode assembly (MEA).

GDL is much thicker and more porous than the catalyst layer. The catalyst layer has significantly less void space because of the high content of required proton conducting ionomer[253]. Gas diffusion layers [GDLs] are constructed of carbon fibers, in the form of carbon cloth or carbon paper which are both highly porous materials, in order to allow for transport of gases besides to electron conduction. Carbon
cloth is made of woven tows consisting of individual carbon fibers while carbon paper is formed from randomly laced carbon fibers[253]. Both Mathias et al.[254] and Ihonen et al.[255] published studies about characterizations of gas diffusion layer materials. Carbon paper has a much more porous structure than the carbon cloth of which values such as pore diameter and porosity are difficult to obtain [253-255]. Carbon cloth is only available in thicknesses between 350 and 1000 μm while carbon paper is available in thicknesses as low as 90 μm[253-255]. Because of thicker structure of carbon cloth, carbon cloth electrodes yield more polarization due to increased Joule heating and mass transfer resistance. Moreover, carbon cloth, because of its woven structure, is spatially heterogeneous on a macroscopic scale, whereas carbon paper is roughly spatially homogeneous due to its random lacing[10]. The two gas diffusion layer structures are both not isotropic. The anisotropic values of material parameters such as permeability and electron conductivity can be determined by 3D scans as first developed to characterize the permeability of rocks in oil reservoirs[10]. Therefore, the behavior of GDL materials in dry conditions can be predicted without experimental testing in operating fuel cells[10]. However, the behavior of GDL materials in two-phase situations cannot be predicted in the same level yet[10, 256]. Carbon cloth and carbon paper also varies in their degree of anisotropy: carbon paper has an anisotropy in only two degrees while carbon cloth has three degrees of macroscopic anisotropy due to its woven structure[253]. The differences between two GDL materials and catalyst layer in terms of geometrical properties are summarized in the table below [253-255].

Table 2.2. Comparison of porous media used in PEMFC [253-255]

<table>
<thead>
<tr>
<th>Porous Media</th>
<th>Spatial Uniformity</th>
<th>Thickness</th>
<th>Porosity</th>
<th>Mean Pore Diameter</th>
<th>Dimension of Anisotropy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Catalyst Layer</td>
<td>Homogenous</td>
<td>~15 μm</td>
<td>0.05-0.55</td>
<td>~1 μm</td>
<td>Isotropic</td>
</tr>
<tr>
<td>Carbon Cloth GDL</td>
<td>Heterogeneous</td>
<td>350-1000 μm</td>
<td>0.3-0.4</td>
<td>~10 μm</td>
<td>2D</td>
</tr>
<tr>
<td>Carbon Paper GDL</td>
<td>Homogenous</td>
<td>90-350 μm</td>
<td>0.7-0.9</td>
<td>~30-40 μm</td>
<td>3D</td>
</tr>
</tbody>
</table>

GDL materials are generally treated with a PTFE solution (Teflon) in order to increase the hydrophobicity of the GDL. Hydrophobicity improves the water management issues in the electrode by inducing the water droplets expelled from the GDL to agglomerate and preventing liquid water from reentering the
GDL in addition to reducing the condensation of the water vapor[253] which is found to occur in hydrophilic cracks in the carbon fibers[129, 253].

2. Electron transport

One of the most important functions of GDL is to serve for electron conduction operating as a bridge between the catalyst layer and the current-collecting land and GDL performs this function with the solid phase, i.e. carbon fibers. In the most of the models, electron transport in the catalyst layer/ GDL as well as in the current collector plate is ignored due to the high conductivity of the carbon in the diffusion media, and consequently, uniform electronic phase potential in these materials. While the current collector has an electric conductivity on the order of 104 S/m for graphite plates, the effective electric conductivities of GDL and catalyst layers are only in the range of 300-500 S/m in the through-plane direction and these comparatively low values could significantly affect the current distribution, both macroscopically along the flow direction and mesoscopically between the channel and land areas[156]. Therefore, the electron conductivities of porous media can become a limiting factor due to geometry[86] or the composition of the porous media[30].

In order to model the electron transport in the solid phases, the charge conservation equation, Ohm's law is used, mostly incorporating with Bruggemann's correction[257] accounting for the porosity and the tortuosity of the media to determine the effective electron conductivity[32, 61, 62, 200, 237]. Bruggemann's expression can underestimate the tortuosity at low porosity values[30, 129, 258] and Nam and Kaviany[129] presented a comprehensive discussion of the appropriate relationship for the tortuosity. The anisotropic electronic transport in the GDL has also received some attention in modeling and the requirement for new function between the GDL porosity and effective conductivity has been pointed out recently[31, 259, 260].

Although the electron transport equation was solved in 1D PEMFC models[8, 48] the lateral electronic conduction in GDL can only be demonstrated in a 3D geometry[86, 156] like Meng and Wang[86]
performed. As can be seen in Figure 2.16 showing the current distribution in a straight-channel fuel cell with an effective electric conductivity value of 300 S/m, while the current density is highest in the middle of the channel without considering the lateral electron transport in GDL(a), this region is shifted toward the edges of the channel when the electronic resistivity of GDL in the in-plane direction is accounted(b); since these locations are the most suitable places for easy access to oxygen and the shortest path for electron transport onto the current-collecting land.

3. Reactant transport

The other important function of the GDL is to transport the fuel, reactants, water vapor, and liquid water and performs this duty via the pores (void phase). As mentioned before, single phase models, ignore the transport of the liquid water by assuming that all water is in vapor state, while two-phase models account for both gas and liquid phase transport.

Gas transport

In single phase models, the transport of the reactant gases and water vapor are modeled to be driven by pure diffusion [27, 32-35] or by diffusion and pressure convection [18, 36, 46]. The gases are mostly assumed to obey Ideal Gas Law. The diffusion transport of the species is generally modeled by using
Maxwell-Stefan equations since the transport of the species is dependent on the others and their partial pressures sum to unity [10, 30, 63, 261]. Maxwell-Stefan equation is equivalent to Fick’s Law[129] in binary mixtures. Under simplifying assumptions, instead of Stefan-Maxwell equations, Fick’s Law can be used for mixtures with three-species [27, 31, 33, 35].

Some models[26, 32, 37-40, 42, 241] also consider the Knudsen diffusion[44] which is important when the mean free path of the diffusing molecules is 10 times greater than the pore radius, especially in catalyst layers where pore is small[30]. As the pores of the diffusing medium becomes smaller, gas molecules collide more often with the pore walls than with each other and Knudsen diffusion account for these molecule-pore wall interactions[44]. Therefore, the diffusion coefficient is a direct function of the pore radius[30, 214]. The pore radius in a typical carbon GDC range between 5 and 20 μm[254, 255] while it changes between 0.05 and 2 μm in a microporous layer[30, 262, 263]. According to an order-of-magnitude analysis[30], bulk diffusion is the dominant transport mechanism when the mean free path of a molecule is less than 0.01 times the pore radius while Knudsen diffusion becomes dominant when the mean free path is greater than 10 times the pore radius. According to this analysis[30], Knudsen diffusion may not have to be accounted for GDL while modeling of microporous and catalyst layers shouldn’t be ignored.

While most models account for pure diffusion which total gas pressure and concentration stays uniform, some other models[18, 26, 36, 38, 46, 50, 69, 81, 85, 121, 199, 221, 264-266], mainly the CFD ones, also consider the convection in the gas phase by either using Darcy’s Law as a separate momentum function or incorporating the Darcy’s law and Maxwell-Stefan equations and using effective permeability as per the dusty-gas model[30].

The results of almost all of the models indicate the insignificant effect of the pressure-driven flow in the GDL since the pressure difference through the fuel cell sandwich (through all layers) is found to be
minimal, therefore; the gas transport only driven by pure diffusion by assuming uniform pressure is acceptable for most of the conditions [30, 48, 51, 90, 123]. This can be explained by the fact that the gases flow parallel to the sandwich, along the channel, and, due to a no slip condition at channel walls, they move through the diffusion media primarily by diffusion. From another point of view, a small pressure difference in the direction out of the sandwich may alter mass transfer depending on the permeability of the diffusion medium and this effect may become more important when combined with thermal effects[30]. However, independent from the permeability and thermal effects, the GDL transport model should consider the convection in fuel cells with interdigitated flow channels since the gas channels in this flow design are not continuous through the fuel cell, and so, the gases are transported by both forced convection and diffusion through the diffusion media to reach the next gas channel [30, 69, 121].

2.4. Water Management and Two Phase Flow Modeling

In a Proton Exchange Membrane Fuel Cells (PEMFCs), the presence of water plays an important role since the ionic conductivity of the proton-conducting membrane is strongly dependent on its degree of humidification, or water content, with high ionic conductivities at maximum humidification. When the water removal rate exceeds the water generation rate, membrane dehydration occurs and this leads degradation of the membrane and significant ohmic losses within the cell. On the other hand, at high current density operations of the fuel cell, the excess amount of water is generated and condenses filling the pores of the GDL and CL with liquid water, especially at the cathode side of the fuel cell. This phenomenon in the porous medium is known as flooding (Figure 2.17[10]). Although flooding is generally related to the high current density operation, it can also been observed at lower current densities under certain operating conditions, such as low temperatures, low gas flow rates and high humidity ratios of the gas streams due to faster saturation of the gas phase by water vapor. and it is a
limiting factor for the overall fuel cell performance because the accumulation of the liquid water in the pores hinders the reactant transport to the catalyst sites and accordingly deteriorates/limits the current production and fuel cell performance, even may stop the operation completely under severe flooding conditions due to the accumulation of water in the gas channels.

Figure 2.17[161] demonstrates the effect of flooding on the fuel cell performance. As it can be seen, the effect increases with the degree of flooding by causing more steep decreases in the voltage. Therefore, proper water management in PEMFCs is critically important for the design and modeling in order to avoid flooding in porous medium for reactant/product transport while providing sufficient water to fully hydrate the membrane. These two requirements are totally conflict to each other. This makes the fuel cell modeling more challenging since it includes multiphase mass transport in catalyst sites, gas diffusion layers and flow channels, i.e. the coupled flow of liquid water and gaseous reactants in porous media, besides the solution of fundamental equations which consists of conservation of mass, momentum, species and charge coupled with electrochemical processes through source terms to describe reaction kinetics and water transport in polymer electrolyte.

Since the fundamental understanding of the water management including the analysis of the membrane water transport, the treatment of the liquid water, modeling two-phase transport and the mitigating of flooding is essential for the optimum performance; it is one of the most critical and widely studied issues in the fuel cell literature. Studies on the water management have ranged from numerical simulation and prediction, to experimental investigation and diagnosis, with the ultimate goal of developing mitigation strategies.
Experimental efforts such as direct visualization and pressure drop measurements have provided qualitative understanding of the phenomena while the modeling studies have been useful in understanding the importance of water management, designing the fuel cell components and determining the optimum operating conditions. Strategies such as the hydrophobic treatment of GDL with PTFE, the addition of a micro-porous layer (MPL) in the MEA and the serpentine layout of flow field design have been successful at mitigation of the flooding in PEMFCs[10]. Although this operating condition cut down the degree of flooding, still clearly the fundamental understanding of water generation, transport and distribution within PEMFC is very important requirement in modeling.
The purpose of this section is to review the modeling efforts on management of water focusing on the transport mechanisms and treatment in PEMFC components including the polymer membrane and the porous media.

### 2.4.1. Modeling Efforts on Water Management

The studies done in order to simulate the water management in PEMFCs can be roughly divided into 3 categories. The first group focused on the water transport and mechanism through the polymer membrane [43, 48, 57, 61, 85, 122, 200, 222, 267, 268] mostly by using diffusion model and considering the nonlinearity of the transport properties more or less. The early models [8, 36, 57, 61, 81, 200, 203, 221, 269] mostly focused on the fuel cell operation with fully humidified fuel/air streams which assures a well hydrated membrane in order to have a maximum proton conductivity and minimum ohmic loss. However, it was observed that under these full humidification conditions, even at low current densities,
the oversaturation of gases leading the condensation of water vapor at the cathode occurs which obstructs the access of oxygen to the catalyst layer and causes a significant concentration losses. Moreover, full humidification of the gas streams externally needs additional volume and power which are undesirable in the fuel cell system. That’s why the movement is towards to the operation under low humidity conditions while sustaining the membrane well hydrated[156]. While the models focusing on the water transport through the membrane give the insides of the water transport, they are not capable in managing the overall effect of the water transport.

The second group of models [46, 53, 123] tried to model water transport within the entire fuel cell using the CFD approach while ignoring the water transport through the membrane. Finally, the last group composed of more recent models [47, 52, 57, 63, 81, 82, 121, 123, 124, 129, 133, 139, 188, 221, 270] attempted to develop a comprehensive water transport model by incorporating the water transport in all regions with the correct physics and including a wide range of operating conditions including low humidity.

Wang[156], Ma et al.[17] and Biyikoglu[157] have presented a comprehensive review of fundamental models for PEM fuel cell engineering, and Weber et al.[30] and Choe et al.[160] have given a detailed overview of transport modeling in PEM fuel cells. Recently, Bazylak[162] and Litster et al.[253] published review papers about the liquid water visualization in PEMFCs while Li et al.[161] reviewed the water flooding issues in PEMFCs.

2.4.2. Water Transport in Polymer Membrane

Water transport across the membrane in an isothermal PEMFC, from one electrode to the other, is mainly controlled by three processes driven due to the gradients of electrical potential, water concentration (or water content) and hydrodynamic pressure. The effect of temperature gradient
should be included when there is a temperature difference within the fuel cell components. These 3 mechanisms are called as electro-osmotic drag, back diffusion and hydraulic permeation, respectively.

**Electro-osmotic water transport:** During the operation of PEMFC, while the protons are migrating through the membrane from the anode to the cathode, they drag the water with them from anode to cathode and this transport mechanism is called electro-osmotic drag (EOD) since the electric current through an ion exchange membrane causes the flow of water in the same direction as the migration of the free ionic charges. The larger the number of ions moving to the cathode, the more the water will be dragged along with them; therefore, the water flux due to the EOD effect is represented directly proportional to the protonic flux (i_{cell}/F).
**Back Diffusion:** Both the EOD and the water generation at the cathode catalyst–membrane interface as a result of ORR, create a large concentration gradient across the membrane by building water up near the cathode. Because of this gradient, some amount of water diffuses back from the cathode to anode in order to equilibrate the water concentration profile across the membrane. This diffusion flux of water in the membrane is usually represented by diffusion coefficient and the concentration gradient of water through the ionomer. The rate of diffusion of water is essentially given by Fick’s Law.

**Convection/Hydraulic Permeation:** In addition to concentration gradient, water also may be hydraulically pushed from one side to another side of the membrane to the other side if there is a pressure difference between the anode and cathode. The rate of hydraulic permeation is represented by a combination of Darcy’s Law and Fick’s Law.

In addition to the water transport processes occurring through the membrane, the excess water at the cathode may be carried away from the CL by evaporation, water vapor diffusion and capillary transport of the liquid water through the GDL into the flow channels and exhausted at the outlet, which is actually desirable since the accumulated water at the cathode would cause flooding. These additional transport mechanisms would change the transport through the membrane and vice versa, the overall water management is critical. Therefore, the water transport through the membrane not only depends in the membrane transport properties, but also the operating conditions, MEA properties and flow field design of the fuel cell.

### 2.4.3. Treatment of Liquid Water in Porous Media

Liquid water has been modeled in fuel cells by many different methods[30, 31]. The simplest method to account for liquid water is to treat it essentially as a solid species that occupies a certain volume fraction which decrease the gas phase volume[30, 31]. Its only effect will be to reduce the ability of fuel and reactants to reach the reaction site[33, 47, 133] by decreasing the effective diffusion coefficients of the
gas species so its transport essentially is not modeled even if its effect on flooding would be included[30, 31]. In these models that do this approach the volume fraction of water is used as a fitting parameter [15, 26, 30, 31, 33, 47, 57, 77, 133, 272] The liquid volume fraction should be predicted as a function of position to mimic the flooding successfully[47, 77] but this type of models are not capable of this.

The next and more sophisticated approach to treat liquid water is to include also its transport by assuming that the liquid water exists as droplets that are carried along in the gas stream, so as a component of the gas [30, 31, 135, 200]. It is predicted to be a small component of gas mixture so it is assumed to be negligible on the gas-phase flow and velocity and a separate liquid phase is not considered while its effect on the gas-phase volume fraction and the evaporation and condensation processes are taken into account[30]. In order to determine the existence and the location of the liquid water, this type of models can be used but they cannot predict the water pressure and concentration distribution exactly.

In order to model the liquid water transport correctly, the gases and liquid water should be considered as two different phases as in the two-phase models. The treatments of liquid water described above are fundamentally one phase. Liquid water transport is similar to the gas transport driven by the pressure but it doesn’t include the diffusion contribution since the liquid water is assumed to be pure and all transport properties used are related to the pure water[30]. As a third type of treatment, many models use the flux form of Darcy’s Law[30] with a set value of the liquid phase volume fraction [8, 46, 48, 67, 68, 121, 219, 220] by assuming there are isolated gas and liquid pores in the medium, although there is a transfer between them as well as a changing volume fraction in reality[30]. Due to the existence of hydrophilic and hydrophobic materials and pores, liquid water can also be treated as a thin film of liquid covering a hydrophilic surface[30].

There are similar models (using the flux form of Darcy’s Law) that differ in the formulation such as using a surface diffusion coefficient instead of the effective permeability divided by the viscosity and a water-
loading gradient related to a water pressure[38, 78, 241] or using a driving force of chemical potential[122] or a liquid-pressure gradient driving force[90] and the permeability as a fitting parameter[30].

In addition to the models considering the liquid-phase as a separate phase, there are some models[81, 82, 199, 206] treating the two phases combined in a single phase mixture by defining all transport parameters as mixture parameters for the two phases while still using the Darcy’s Law to describe the transport for the liquid water. Since the gas and liquid are assumed to move with the same velocity as the mixture moves with a single velocity, the liquid pressure does not have a separate driving force, which not physically correct[30, 129]. This approach can be seen as a simplified version of the multiphase mixture model by Wang and Cheng [273, 274].

Although the models mentioned above describe liquid-water transport to some extent, the simplifications made, usually help in numerical stability and computation time, so these models do a reasonable job in predicting the water balance of the fuel cell. However, they don’t account for the saturation level of the porous medium (i.e. the amount of pore volume fraction filled with liquid water) depending on the location, porous medium properties such as porous size, the hydrophobicity and the capillarity pressure (i.e. the difference in pressure across the interface between the gaseous phase and the liquid water), therefore; still the existence of partially saturated media requires the use of capillary equations and a strict two-phase description of flow[156].

2.4.4. Two-Phase Flow

In the porous medium, as mentioned above, the gas and liquid phases interact with each other while they have different velocities and separate transport mechanisms. In order to simulate this two-phase flow, many different modeling approaches that range from a simple bundle-of-capillaries model to very complex 3-D network models incorporating a detailed description of a medium’s microstructure[30].
Here only macroscopic models[46, 50, 51, 53, 123, 124, 129, 220] [42] used for modeling the diffusion media including GDL and CL in fuel cells are examined.

As mentioned before, in the porous medium, the amount of pore volume fraction filled with liquid water can be described by a local average saturation $s$ ($0 \leq s \leq 1$). As an interpretation, the meaning of $s=0$, there is no liquid water in the medium so there is only gas transport that can be defined by Fick’s Law in binary mixture gases or Stefan-Maxwell equations for more than 2 species of gases. When the liquid saturation is greater than 0, there is liquid water in the medium in addition to the gases so two-phase transport with quite different mechanisms occur while gas and liquid phases are in interaction. The two-phase boundary $s = 0$ is a free interface of the problem[10].

In the two-phase models, the saturation is normally calculated by relating the capillary pressure to the saturation by an empirical relationship. Nguyen and co-workers[123, 124] derived a function by fitting the experimental data and Pisani et al.[220] use a function with an unknown fitting parameter, while the most of the other models[46, 50, 51, 53, 129] use the empirically determined Leverett J-function[275] which was originally derived for 1D SS transport on packed sand[49]. Gostick et al.[276] pointed out the well agreement between the Leverett J-function and experimental data from different GDLs. Weber and Newman[42] followed a different approach using a random cut-and-rejoin bundle-of-capillaries model[30] in order to consider the pore-size distribution of the diffusion media to get the saturation analytically in addition to account for the mixed wettability of the diffusion media consisting of separate hydrophobic and hydrophilic pores. The other model considering such effects is Nam and Kaviany’s model[129] which is a very comprehensive model explaining the liquid water transport in diffusion media. According to Nam and Kaviany[129], the liquid water in a hydrophobic porous medium is transported with a branching type geometry distribution (percolation) in the shape of micro and macro spherical droplets by two types of mechanisms, occurring simultaneously: macro and micro. The transfer of condensed water from the condensation sites is called as micro-transport since they are in micro-
droplets, then these micro-droplets starts to agglomerate by filling the pores of the porous medium until macro-droplets (a continuous liquid-phase) are formed by reaching the threshold of inmobile saturation[129]. Macro-transport actualizes when the macro-droplets are connected and move toward lower saturation region (toward channel) since pressure of liquid water is higher in high saturation region regardless of the porous medium, hydrophobic or hydrophilic[129]. While flowing towards the porous medium, water prefers larger pores since it requires smaller capillary pressure and lower flow resistance[129]. In summary, the water vapor condenses at the surface of the micro-droplets which intermittently agglomerate to provide the macro-droplets with liquid-water[129]; therefore, the distribution of liquid water is controlled by condensation (micro-droplets) and liquid phase capillary flow (macro droplets)(Figure 2.20[129]). However, this bundle of capillaries type of model is not rigidly accurate because it idealizes the actual porous network[30].

Pasaogullari and Wang[118] presented a similar mechanism to that of Nam and Kaviany[129] in which the liquid water flow was proposed as an “upside-down tree” capillary network and a high number of small capillaries scattered evenly within the GDL that agglomerate to larger capillaries and finally result in one very large capillary that reaches the surface. Litster et al.[253] proposed a transport mechanism which is different from these and claimed that the transport is dominated by fingering and channeling and features numerous “dead ends”, where water transport moves back when a neighbor crack channel forms[253]. Their explanation for this hypothesis is the fact that the dominant path is not larger than an average-sized fiber cross-section in addition to that the liquid is seen to fill the entire void space surrounded by other fiber cross-sections after it has broken through a chokepoint (constriction). They concluded that the convergence of small capillaries into successively larger ones is not the observed mechanism in the non-woven GDLs[253].
Figure 2.20. Schematic of the branching micro- to macro-transport of water in porous media[129].

Within the two-phase region the water vapor pressure can be taken equal to the saturation pressure[10]. The surface tension on the curved surface between liquid and vapor makes the liquid pressure $P_L$ different from the vapor pressure $P_G$. The jump in pressure across the gas/liquid interface due the fluid surface curvature is characterized by a capillary pressure, $P_C$, which is the difference in pressure between the liquid water, and water vapor $(P_C = P_L - P_G)$[118].

In any of the two-phase models discussed above, in order to determine the saturation, the capillary pressure must be known at every position within a diffusion medium which requires the gas and liquid pressure profiles. In many models [30, 31, 50, 51], the movement of both liquid and gas in porous media is determined by Darcy’s law for each phase with additional diffusivity parameters and by using the capillary pressure description the two pressures are related to each other.

As the fraction of void spaces occupied by liquid water, i.e. saturation, increases, the liquid pressure increases; therefore, a liquid pressure gradient takes place from higher to lower liquid saturation regions[118]. The liquid saturation at the GDL-CL interface due to the water generation and EOD is higher than the saturation in GDL-channel interface, the pressure gradient in GDL pushes the liquid
water from the reaction sites toward the open channel[118]. The pores in the medium in the fuel cells are assumed to be in spherical shape[129] so the capillary pressure as a function of contact angle, $\theta_c$, surface tension, $\sigma$, and pore radius, $r$, is given by[30, 129]:

$$P_C = P_L - P_G = \frac{2\sigma \cos(\theta_c)}{r}$$

(2.3)

Note that $\theta_c$ is the internal contact angle that a drop of water forms with a solid[30]. The capillary pressure relation is founded on how liquid water wets the material: For a hydrophilic pore structure, the contact angle is $0 \leq \theta_c < 90^\circ$, and for a hydrophobic one, it is $90^\circ < \theta_c \leq 180^\circ$[118, 129]; therefore, contact angle is dependent upon the hydrophilic or hydrophobic nature of the GDL, and varies with the Teflon content[118]. In the hydrophobic porous medium, the liquid pressure is larger than the gas phase pressure while the gas phase pressure is higher than the liquid phase in hydrophilic medium[118].

The liquid saturation is the volume of the total void space of porous media, $V$, occupied by the liquid phase, $V_L$, so in two phase model, it represents the ratio of the volume fraction of liquid phase, $\varepsilon_L$, to the bulk porosity, $\varepsilon_0$[30].

$$s = \frac{V_L}{V} = \frac{\varepsilon_L}{\varepsilon_0}$$

(2.4)

In order to relate the capillary pressure to the liquid saturation, Leverett-J function is mostly used[118] and it is formulated as[118]:

$$P_C = \sigma \cos \theta_c \left( \frac{\varepsilon}{K} \right)^{1/2} J(s)$$

(2.5)
Where \( J(s) \) Leverett function, \( K \) is the absolute permeability of the porous medium and \( \varepsilon \) is the porosity of the medium. \( (K/\varepsilon)^{1/2} \) is also defined as the characteristic capillary radius of the porous medium[129].

In a hydrophilic medium, the wetting phase is the liquid phase while the gas phase becomes the wetting phase. Therefore, Leverett J-function is expressed in the gas phase saturation, \( (1-s) \), in hydrophilic medium and in the liquid phase saturation in the hydrophobic medium[118]:

\[
J(s) = \begin{cases} 
1.417(1-s) - 2.120(1-s)^2 + 1.263(1-s)^3, & \text{if } \theta_c < 90^\circ \\
1.417s - 2.120s^2 + 1.263s^3, & \text{if } \theta_c > 90^\circ
\end{cases}
\]

(2.6)

The permeability of the porous medium has been assumed to depend only on the structure of the medium[51, 53], in some models[42, 123] it has been used as a fitting parameter and generally it is estimated by using empirical Kozeny-Carman relation[30, 129]:

\[
K = \frac{\varepsilon^3 D}{16k_k (1-\varepsilon)^2}
\]

(2.7)

Where \( k_k \) is the Kozeny constant and for fibrous porous media \( (0.5 < \varepsilon < 0.7) \), this constant is taken as 6[129].

Nam and Kaviany[129] used reduced water saturation in order to relate the capillary pressure to the reduced water saturation, \( S \), incorporating the inmobile saturation, \( s_{im} \):

\[
S = \frac{s - s_{im}}{1 - s_{im}}
\]

(2.8)

Then the capillary pressure can be expressed by[129]:

\[
P_c = \frac{\sigma \cos(\theta_c)}{(K/\varepsilon)^{1/2}} \left[ 1.417S - 2.120S^2 + 1.263S^3 \right]
\]

(2.9)
In the two-phase flow in the porous media, since the available pore space is shared by the liquid and gas phase, the cross-sectional area available for each fluid is less that the total available pore space and this phenomenon is modeled by the creation of the relative permeability, \( K_{rk} \), which defines the ratio the ratio of intrinsic permeability of a phase \( k \) at a given saturation level to the total intrinsic permeability of the porous medium[118]. Therefore, both the vapor velocity and liquid water velocity are generally modeled by using the effective permeability which is the multiplication of the absolute permeability, \( K \), and relative permeability of the phase essentially accounting for the influence of the liquid water, \( K_{rk} \) [10, 30, 42, 118, 129]:

\[
v_k = -\frac{KK_{rk}(s)}{\mu_k} \nabla P_k\tag{2.10}
\]

The dependence of \( K_{rk} \) on saturation is hard to determine. While Nguyen and co-workers[123, 124] and Berning and Djilali[50] used a linear relationship for the saturation dependence, most of the other models have used the cubic dependence[10, 53, 118, 129, 220, 225]:

\[
K_{rk} = s^3
\]

\[
K_{rg} = (1-s)^3\tag{2.11}
\]

Furthermore, Weber and Newman[42] derived an analytical expression of \( K_{rk} \) as a function of the capillary pressure which is close to cubic dependence. They also used the residual or irreducible saturations in order to calculate the effective saturation like Kam and Naviany[129], and Pisani et al.[220]. In summary the cubic dependence is the most used and observed one with respect to the typical data while the other similar and simpler relations may help in the mathematical convergence of the models without increasing the overall error of the simulations too much[30].

Similar to the implementation of saturation into the permeability, the gas diffusion coefficients of the other gases are also modified in order to account for the existence of liquid water in the pores[225] in
addition to Bruggeman correction[257] used for correction in the porosity and tortuosity of the porous medium.

Promislow and Wetton[10], presented a comprehensive review about the mathematical representation of the fuel cell and they reported that at the two-phase zone interface seen in Figure 2.21, five boundary conditions are used: \( s = 0 \), \( T \) is continuous, \( P_g \) is continuous and has the value \( P_{sat}(T) \), mass flux is continuous, and the thermal flux is continuous taking into account the evaporation front at the interface[10]. As a solution to this free boundary value problem, a simple asymptotic description of the region near the two-phase zone boundary is given in [10]. In this study, it is reported that the main difficulty is the ellipticity in saturation which is degenerate at the interface since the forms for \( K_{rl}(s) \) have \( K_{rl}(s = 0) = 0 \), leading to the degeneracy; therefore, the degeneracy causes a singularity in the saturation at the two-phase zone interface[10].

The fundamental difficulty in two-phase models mentioned above is the elliptic degeneracy at the two-phase zone boundary[10]. Furthermore, the addition of the gas and water mass balances along with the transport equations and constitutive relationships including additional convection and advection terms create a closed set of equations but unfortunately, mostly it is very hard to get a converged solution, especially the model is multidimensional[30]. Therefore, Wang and Cheng [273, 274] proposed Multiphase Mixture Model (M2) replacing the saturation in the two-phase zone and the vapor pressure in the dry zone by the total water density defined by[10]:

\[
\rho = s \rho_f + (1 - s) \rho_g
\]  

(2.12)
Figure 2.21. Schematic showing typical single-phase, two-phase, and mixed regions in a fuel cell[10].

In both regions, the variables $\rho$ and $T$ can be used while the vapor pressure $P_G$ is treated with the below formulation[10]:

$$P = \min \left( P_{sat}(T), \frac{\rho RT}{M} \right)$$  \hspace{1cm} (2.13)

In M2 approach, the mixture is composed of each phase along with the mixture parameters averaged usually by saturation[30] like the density description given above. The vapor density $\rho$ can be determined by the vapor pressure and temperature and then the saturation can be calculated by using the total water density equation[10]. Moreover, although the mixture moves with the mass averaged velocity, mixture velocity is determined from Darcy’s Law using the mixture properties, the separate motion of each phase due to the interfacial drag between each other and other conditions are determined[30] incorporating the relative mobilities of the phases[30, 52, 134, 225, 273, 274]:
\[ \lambda_k = \frac{K_{rl}}{v_k} \]

\( v_k \) is the kinematic viscosity of the phase \( k \).

Thus, the liquid-phase velocity accounting for the convection, the capillary flow and interfacial drag between the phases [30, 52, 134, 225, 273, 274] can be calculated by the using M2 approach.

There are also some modified models [50, 53, 134] using M2 approach in order to describe the liquid water transport, \( N_L \), along with the concept of capillary diffusivity, \( D_S \), which is defined by:

\[ N_L = -D_S \nabla S \] (2.15)

The capillary diffusivity, \( D_S \), is calculated by[30]:

\[ D_S = \frac{K}{\mu V} \frac{dP_c}{dS} \] (2.16)

\( K \) is the permeability, \( \mu \) is the viscosity and \( V \) is the velocity of the multiphase mixture.

The relation described above can give a notion like that the driving force for fluid flow is the saturation and a saturation condition should be used as a boundary condition; but it is not correct although it is valid when the capillary diffusivity is interpreted correctly[30].

Recently, Sun et al. [134], presented a discontinuous and degenerate capillary diffusivity function to ensure a smooth transition between the two phases while the transport is modified with the advection correction factor which is a continuous function with respect to concentration[52, 134, 225]. When the water is only vapor, the water concentration is below the saturated water concentration (16mol/m³ at 80°C), and the diffusivity is the normal gas diffusivity which is nonzero[134]. When the water concentration exceeds the saturated water concentration value, it means that there is an excess gaseous water to be condensed to liquid water. At that point, the diffusivity of water suddenly
decreases to zero and then gives a smooth functional relation with respect to liquid water concentration[134].

The advantage of multiphase mixture (M2) model is that the simulations have only to solve pseudophase equations while the two phase flow is captured. However, it should be noted that this treatment may not account for pore size distribution and mixed wettability effects and moreover, problems may occur when the equations are not averaged correctly[10]. Bridge and Wetton[277] showed that a version of this method can converge numerically to traveling wave solutions[10] and due to the practical implementation and convergence verification, this technique is considered to be the current state of the art for this problem[10, 277].

On the other hand, according to the models of Natarajan and Nguyen[123, 124] and Weber and Newman[42], M2 approach predict much lower saturations and due to lack of experimental data on relative permeabilities and the rigorous mathematical work, the validation of the method is questionable[10, 30].

According to Wang[156], all two phase models mentioned above can be roughly categorized into two classes: Unsaturated Flow Theory(UFT) and M2 model. Whereas UFT models [50, 118, 121, 123, 124, 129] assume a constant gas phase pressure, i.e. saturation pressure and liquid water transport completely separated from the gas flow, M2 models [51-53] take the motions of both phases into account, also considering the interaction with each other.

Different than the models above, Promislow et al.[278] developed a model with a large inmobile water saturation level and an asymptotically large capillary pressure since the asymptotic problem contributed to a simple description of the transport without the singularity at the two-phase interface.

Most of the models reviewed above described macroscopic two-phase model by using the correlations of relative permeabilities and capillary pressure as a function of liquid saturation. Although Darcy’s Law gives the correct path to model one phase porous media flow, for the transport of two phase flow, it is
not a validated theory since there are experimental results showing hysteresis in the physical systems modeled with it[10].

Furthermore, GDL materials are found to have two types of pores: hydrophobic teflonated ones and hydrophilic unteflonated ones[10]. Due to the GDL microstructure composed of two types of pores, the alternative path for modeling two-phase flow in GDL regions may be the pore network model[279].

As known, two phase flow and flooding may take place in both GDL and CL. One of the most important problems may be to determine the degree of the effect of flooding on the performance when it occurs at both regions, which one decreases the performance more or less. The gas diffusion layer is much thicker and more hydrophilic with larger pores. Also, catalyst layers normally have a high active surface area and this may suppress the detrimental effect on performance even if there is some flooding[118]. These may suggest that the flooding of gas diffusion layer needs more attention but on the other hand, GDL is more porous. There have been more GDL models examining the flooding in this region. The models above considering the two phase flow in porous medium actually accounted for GDL but not necessarily for CL. Moreover, in contrast to the intensive research activities studying the effects of the GDL, the role of the CL in water balance has never been explored in depth either experimentally or numerically[161].

Eikerling and Kornyshev[242] recently developed a structure based model considering the spatial distributions of processes across the CCL and its effect on water transport and cell performance. The simulation results showed that the CCL is the primary region that the liquid water is converted to vapor and it adjusts the balance between the opposing water fluxes toward the membrane and the GDL[161]. Qi and Kaufman[280], Wilson et al.[281], and Janssen et al.[268] examined the water transport in GDL and CL experimentally by placing microporous layers between the catalyst layer and diffusion media. Either of the following results is proposed: The diffusion layers due to their hydrophobic nature throw
the water out or the catalyst layers wick water out due to their small pores. Therefore, the discussion is inconclusive and the flooding should be considered in both regions. [30]

For the treatment of flooding in the catalyst layer, in their review, Weber and Newman [30] proposes two main ways. The first one is to assume that a liquid film covers the membrane film of the agglomerates in the existence of liquid water in the fuel cell. This water film, as well as the membrane layer, creates a resistance for the diffusion of the reactant gases and products and the effect can be incorporated by the means of external mass-transfer [47, 76]. All of the agglomerate models can easily contain flooding by using this approach and the thickness of the film can be used as a fitting parameter [30]. In the cathode, only a very thin liquid film is enough to decrease the transport of reactants and accordingly, even inhibit the reaction, especially for oxygen transport due to the low diffusivity and solubility of oxygen in water [30]. The second one is to use the two phase modeling approach described above. In two phase modeling, the liquid saturation is calculated and the reduced active is adjusted by using a linear expression for the effect of saturation. Nguyen and co-workers [121, 123, 124], Wang et al. [51] and Ge et al. [125] have used this approach.

2.5. Physical Properties and Characterization

In order to use the governing equations explaining the physical phenomena in a simulation, various parameter values are required. The physical characterization of these parameters is very important in fuel cell modeling since the model predictions can be accurate and validated when the material and transport properties are put into the model accurately.

In a fuel cell model, in general the material and transport properties can be classified in 5 groups:

1. Transport properties of membrane (electrolyte)
2. Electrokinetic properties of catalyst layers or electrodes
3. Transport properties of GDLs and CLs,
4. Properties of bipolar plates, and

5. Thermodynamic and transport properties of species (chemical reactants and products).

Due to the objective of thesis dealing with the membrane modeling intensively, the characterization of the membrane transport properties are reviewed in detailed while the other properties are mentioned briefly. The transport properties used in the model presented in this thesis will be given in the next chapter in the mathematical model representation.

2.5.1. Membrane Properties

In order to obtain optimal performance from a fuel cell membrane, it is important to have a good water balance. The membrane should be hydrated for sufficient proton conductivity while cathode flooding and anode dehydration are avoided as mentioned before.

Water transport in the membrane occurs by two main mechanisms: electro-osmotic drag (EOD) of water with protons from the anode to cathode and by diffusion due to the concentration gradient. An additional source of water comes from the reaction of oxygen reduction at the cathode. Both the EOD and water production result in buildup of water near the cathode. Back diffusion of water from the cathode to anode decreases this trend and flattens the water concentration profile across the membrane[156, 271]. If there is pressure difference between anode and cathode side, there is also hydraulic permeation from the side having higher pressure.

The accurate estimation of net water flux across the membrane requires a correct description of the transport properties related to ionic transport and water transport. Therefore, there are three main important properties of the membrane required for fuel cell modeling and of which characterization will be reviewed here: proton (ionic) conductivity, water diffusion coefficient and electro-osmotic drag coefficient (EOD). These are dependent on water content and temperature. The other properties put into a fuel cell model are density, molecular weight and equivalent weight (EW) as well as other
membrane structural properties, including the pore distribution[65, 282, 283] and the effective contact angle of a liquid-equilibrated membrane channel[284] depending on the complexity of the model. The dry density of a Nafion® membrane is reported to be 2.0 gr/cm$^3$[68] and 2.16 kg/m$^3$[52]. The gas permeation through the membrane is assumed to be negligible by most of the models due to the very small diffusivity values of oxygen and hydrogen in the membrane (1.22*10$^{-10}$ and 2.59*10$^{-10}$ m$^2$/s, respectively)[48].

Since the transport in the membrane is one of the key elements in modeling of PEMFCs, in order to explore these properties of the electrolytes/polymer membranes used, extensive efforts have been made. There have been many studies on the characterization of Nafion® membranes so here the review of the properties will be mainly based on Nafion® membranes. However, Kreuer[4, 285] published a very comprehensive discussion of materials and transport properties of proton conducting membranes other than Nafion®.

The water content of Nafion® membranes have been measured by many studies [58, 59, 177, 188, 286-292] and the results reported by these several studies are similar. The main objective of these studies is to define a relationship between membrane water content and water activity. Water activity can be explained as the moisture of the surrounding environment[156] and it is calculated by the ratio of the water partial pressure to the saturated pressure, corresponding to the cell temperature.

The shape of the relationship between water activity and water content for a Nafion® membrane is shown in Figure 2.22[156].
The relationship between water activity and water content for a Nafion® membrane can be obtained by fitting a polynomial equation based on the experimental data performed by Zawodzinski et al. [188] and Springer et al.[57] Ge et al.[294] proposed a different relationship in order to define the water content of a Nafion® 117 membrane in contact with vapor as a function of temperature by using the experimental data obtained at 303 K and 353 K by Zawodzinski et al.[293] and Hinatsu et al.[177], respectively [57, 177, 294].

Zawodzinski et al. [188, 293] measured water content of membranes immersed in liquid water and membranes exposed to water vapor at variable activities. They observed the obvious discontinuity in the membrane water content between equilibration of the membrane with liquid water and with saturated water vapor, both of which correspond to unit water activity, which is defined as Schroeder’s Paradox. Wang[54] proposed the following relationship by accounting for the liquid saturation, s, in two phase systems by using the experimental data by Springer et al.[57].

It is proposed that the water uptake for a membrane equilibrated with water vapor is more relevant for fuel cell operation[164] where the reactant gases are fed as humidified at 5-15 °C above the operating
fuel cell temperature[295] for better performance and thus, the water is presented in the vapor phase mostly.

**Proton Conductivity**

In PEMFCs, high proton conductivity is the most important property of ionomer membranes under humidification conditions and at current densities typically required in PEMFCs. Proton conductivity is a function of water content in the membrane like the other transport properties, since water and proton transport takes place at the same time. As the water activity and water content vary spatially throughout the membrane, the proton conductivity also varies.

The conduction of protons is accomplished by both the vehicle and Grotthuss mechanisms[296] in both the liquid and vapor equilibrated membrane. In the Grotthuss mechanism proposed by Theodor Grotthuss[297] in 1806 and known as proton-hopping mechanism, an excess proton dissolved diffuses through the hydrogen bond network of water molecules or other hydrogen-bonded liquids through the formation or cleavage of covalent bonds by two plausible forms: Eigen($\text{H}_3\text{O}_4^+$ cation) to Zundel($\text{H}_3\text{O}_4^+$ cation) to Eigen (E–Z–E), on the basis of experimental NMR data and Zundel to Zundel (Z–Z), on the basis of molecular dynamics simulation[298]. In the vehicle mechanism proposed by Kreuer et al.[299] in 1982, the proton does not migrate as H$^+$ but as OH$^-$, NH$_3^-$, etc. bonded to a “vehicle” such as H$_2$O, NH$_3$, etc. showing a diffusion coefficient corresponding to the proton conduction and behaving like a Bronsted base (proton acceptor) towards its crystallographic environment[299]. The schematic below[299] demonstrates the two mechanisms of proton conduction. In the top one, the protons are passed along the hydrogen bonds while the movement takes place with the aid of a moving “vehicle”, e.g., H$_2$O or NH, as complex ion (H$_2$O$^+$ or NH$_2^-$) in the bottom one[299].
Figure 2.23. Schematic showing two mechanisms of proton conduction. Top: Grotthuss Mechanism; Bottom: Vehicle Mechanism[299].

Although the Grotthuss mechanism is more dominant in liquid equilibrated membranes, for modeling purposes, it is assumed that there is only one functional form of the conductivity with the water content as a parameter[90]. The detailed and microscopic models for conductivity are not within the scope of review here but further information can be obtained by references [90, 192, 194, 197, 265, 282, 300].

The measurement of the conductivity is usually done by alternating-current impedance using either two four electrodes across the membrane thickness dimension[90] or two electrodes placed on the same major surface of the membrane, where a much larger inter-electrode spacing can be employed[301], as well as by some other techniques[174, 188, 203, 222, 291, 302, 303].

Zawodzinski et al.[301] demonstrated the dependency of proton conductivity on the water content experimentally; their test results explored the roughly linear relationship. Then Springer et al.[57] proposed a correlation for proton conductivity (in S/cm) of a Nafion® membrane with the water content as a function of temperature, which has been mostly used in the modeling literature. Another empirical relationship between the conductivity and water content is used by using the data of Sone et al.[302].

In their comparison study made with several different Nafion® and Dow membranes, Verbrugge and Hill[216] reported that the acid-immersed Nafion® samples showed lower proton conductivity (0.06–0.085 S/cm) than the immersed Dow membrane samples (0.13–0.14 S/cm) at 22°C.
Unlike Springer et al. [57], Hsu et al. [304] reported the power law for proton conductivity of Na-Nafion® which agrees with the physical model, by proposing percolation theory for the first time. Percolation theory is founded on the initial formation of continuous conductive pathways across the membrane [90]. A threshold volume fraction is defined as the volume fraction where the sulfonic acid sites are hydrated and form a conductive pathway through the membrane and found to be 0.06 at λ=2 for Nafion® in the acid form [90, 291]. It is reported that at 30°C, the conductivity of a vapor equilibrated membrane (λ=14) is 0.066 S/cm while the liquid equilibrated membrane shows higher conductivity which is 0.11 S/cm [90]. There is many experimental data of conductivity vs. membrane water content from 2 to 22, obeying the simple percolation equation [90, 188, 302].

Gebel et al. [305] showed that the membrane conductivity of a liquid equilibrated membrane starts to become constant above a water volume fraction of about 45% until the water volume fraction becomes 80% at which the membrane begins dissolving. The conductivity will reach a maximum value when all the channels are expanded and filled with water and this maximum value is found to be 43% which matches with the value (45%) reported by Gebel et al. [305]. Therefore, it is found that the percolation theory is not valid after the volume fraction of 45% but in the liquid equilibrated mode, still the conductivity is expected to vary with a power of 1.5 with respect to the porosity of the medium, as shown by Bruggeman [257] by considering that medium filled with liquid as the porosity of the membrane [90].

There have been many studies [4, 174, 188, 302, 303] investigating the dependency of the conductivity on the temperature and showing the Arrhenius type dependency. Polymers experience structural changes as the temperature moves toward to the glass-transition temperature and this results in different conductivities in the polymer membranes [90] since the temperature alters the equilibrium constant for the sulfonic acid dissociation and the activation energy for Grotthuss mechanism [90, 296,
At higher temperatures, with the decrease in the activation energy, the conduction transport mechanisms, both vehicle and Grotthuss mechanisms improve[296], especially at liquid equilibrated membranes[90, 306]. The activation energy can also change slightly with the water content but this effect is ignored due to the secondary effect[90, 307]. On the other hand, the temperature increase decreases the water volume fraction; therefore, it shows competing effects on the conductivity[90, 302].

**Water transport properties**

Two other important electrolyte properties for the PEFC system are the water diffusion coefficient and electro-osmotic drag(EOD) coefficient. The determination of water content profile and the calculation of the net water transport across the membrane or shortly the proper water management require accurate descriptions of these parameters in terms of water content.

**Diffusion Coefficient**

Diffusion coefficients associated with both a concentration and a chemical-potential driving force have been estimated using several techniques such as Nuclear Magnetic Resonance (NMR)[58, 188, 290, 301, 308], Transient Sorption Kinetics/Sorption Technique[309-311], Steady State Permeation[271, 294, 312-315] and others[57, 90, 222, 282]. In NMR technique the direct measurement of the self-diffusion coefficient is obtained as a function of the hydration state of the membrane by using an NMR spectrometer which imposes a magnetic field gradient on a membrane sample in different relative humidity environment [312]. The signal strength raised by the molecules is compared with the gradient strength produced by the NMR spectrometer and the self-diffusion coefficients of water are calculated[312]. Since these coefficients don’t account for the chemical potential gradient, Darken factor is used [294, 312]. The Darken factor is computed using the equilibrium water uptake behavior of the membrane as a function of external relative humidity[312].
In Transient Sorption technique, the membrane is placed in a certain relative humidity environment and the weight change over time is observed while steady state water flux across the membrane is measured in Steady State Permeation technique. In the latter technique, in order to create a concentration gradient and driving diffusion, the membrane is exposed to a dry flow of an inert gas on one side and a humidified flow on the other side and then the water content of each stream before and after entering the cell and correspondingly the net water flux through the cell is calculated. While Transient Sorption Technique provides a simple method of measuring the diffusion coefficient directly, Steady State Permeation technique requires a model with well-defined physics to calculate the diffusion coefficient[312].

Yeo and Eisenberg[310] using the transient sorption technique, estimated the interdiffusion/intradiffusion coefficient of water in the membrane over the temperature range 0–99 °C and showed that the diffusion coefficients increase with increasing temperature over the range (1-10) × $10^{-6}$ cm$^2$/s. Zawodzinski et al. [301] using NMR technique, reported that the self-diffusion coefficients of water in Nafion® 117(EW 1100) equilibrated with water vapor decreased by more than an order of magnitude (from roughly $8\times10^{-6}$ cm$^2$/s down to $5\times10^{-7}$ cm$^2$/s) as the water content in the membrane decreased from $\lambda = 14$ to 2. According to the data obtained by Zawodzinski and co-workers [58, 188], the diffusion coefficient of a vapor equilibrated membrane is about $5.5\times10^{-6}$ cm$^2$/s, which is similar to the other experimental values[203, 309].

Zawodzinski et al. [58, 188, 301], Springer et al.[57], Morris and Sun[309], Motupally and co-workers[314, 315] and Ye and LeVan[313] reported that the diffusion coefficient reaches a maximum value at a water content between $\lambda=3$ and 4. Morris and Sun[309] showing that the diffusion coefficient increases with an increase in water content at low water concentration reported a maximum value of about $4\times 10^{-7}$ cm$^2$/s at $\lambda = 4$ at a temperature of 25°C. On the other hand, most of the other
researchers’ results showed a monotonic increase of the diffusion coefficient with water content [58, 90, 188, 271, 301, 316]. Rivin et al.[316] reported a value of $2.62 \times 10^{-6} \text{ cm}^2/\text{s}$ under saturated water vapor conditions at a temperature of 32°C while showing the smooth and continuous increase of diffusion coefficient with concentration. Zawodzinski et al. [58, 188] and Weber and Newman[90] found almost same values at high water content of the membrane ($\lambda>10$) at a temperature of 30°C while Fuller [213] and Ye and LeVan[313] reported higher values. For modeling purposes, while Fuller and Newman[61] suggested a linear relationship for the dependence of the diffusion coefficient on the membrane water content, Zawodzinski et al. [58, 188, 301], Springer et al.[57], Rivin et al.[316], Motupally and co-workers[314, 315], Ye and LeVan[313], Weber and Newman[90], Ge et al.[294] and Ye and Wang[271] proposed more complicated functional formulas.

In summary, the values of the self-diffusion coefficient measured by using NMR techniques, the intradiffusion coefficients reported by using the transient sorption kinetics method and the Fickian diffusion coefficients calculated by using steady state permeation methods and their dependences on the water content in the Nafion® membrane reported in the literature varied significantly from one another[90, 271, 294].

**EOD Coefficient**

The EOD coefficient, $n_d$, sometimes termed as the transport number of water in the membrane, is the number of water molecules carried through the membrane per proton in the absence of a concentration gradient when a protonic current flows through the membrane. It is closely related to the proton conduction mechanisms and is assumed to depend only on temperature and water content, at least macroscopically[90].

The EOD coefficients have been measured for vapor-equilibrated[61, 317] and liquid-equilibrated[90, 203, 261, 301, 306, 315, 318] membranes by various techniques including concentration cell
method[301, 317, 319], electrophoretic NMR technique[261], and streaming potentials[320], etc. Similar to the diffusion coefficient measurements, the EOD coefficients and the dependence on the water content in Nafion® membrane deviate significantly with one another[321].

LaConti et al.[318] have measured $n_d$ in proto-form Nafion® membranes with several different equivalent weights by using the concentration cell method described by Helferrich [322]. In this method, a current is passed through the membrane and the height of a water column is monitored to determine the amount of water transferred per coloumb of charge passed[157]. They reported that $n_d$ of Nafion® membranes linearly increased from 0 at dry state to 4-5 at the fully hydrated state without showing temperature dependence and decreased slightly with a decrease in EW.

Fuller and Newman[61] using the concentration cell method for Nafion® 117 membrane reported that $n_d$ is about 1.4 for a membrane equilibrated with saturated water vapor at 25°C and it decreases slowly as the water content of the membrane decreases but becomes zero as $\lambda$ approaches to 5.

According to the experimental data obtained by Zawodzinski et al. [58, 188] using the same method and equipment, $n_d$ measured for Nafion® 117 membrane other PSFA membranes equilibrated with water vapor Nafion® and other PSFA membranes equilibrated with water vapor over a large range of activities over a large range of activities, is found to be basically 1 being independent from the water content in the range of water content from $\lambda = 1.4$ to 14. On the other hand, below $\lambda = 2$ which is the water content value corresponding to the percolation threshold for the conductivity, the coefficient is ill-defined since there is no protonic current [90]. For mathematical completeness, Weber and Newman[90] proposed that it equals to $\lambda$ below $\lambda = 1$ due to the fact that the coefficient cannot be higher than $\lambda[61, 188]$ while Guvelioglu and Stenger[93] suggested a linear relationship under $\lambda = 5$ as it matches with 1 at $\lambda = 5$. 
Weng et al.[320] measured $n_d$ for Nafion®/H3PO4 membrane electrolyte equilibrated with water vapor at 125°C by designing a cell consisting of a large gas reservoir and a small gas chamber and determining $n_d$ of the membranes from the gas chamber’s partial pressure change[271] and reported that it increased from 0.2 to 0.6 with increasing water activity values from 0.1 to 0.4 while it was found to be zero for phosphoric acid-doped BPI membranes for the water activity values between 0.05 and 0.35 at temperatures above 125°C[271].

The values in Nafion® membrane in contact with liquid water, acid, and methanol solutions are found to be much higher than that in contact with water vapor [188, 261, 301, 306, 315, 319, 323-325]. Zawodzinski et al. [188, 301] reported that $n_d$ increases from 0.9 to 1 and then to 2.5 as the water content increase from11 ($\lambda$=11, dried at 105°C before the measurement) to 14 and then to 22 which is obtained by equilibrating the Nafion® 117 membrane with the liquid water at 30°C, respectively. Ise et al.[261] employed electrophoretic NMR (ENMR) method to measure $n_d$ of Nafion® and polyetheretherketone (PEEK) membranes and reported the values of 2.6 for Nafion® ($\lambda$=20) and 3.1 for PEEK membranes ($\lambda$=40)[32*]. Meier and Eigenberger[324] and Xie and Okada[325] measured $n_d$ for the Nafion® membrane in contact with HCl solution at room temperature by using streaming potential method. Meier and Eigenberger[324] showed that $n_d$ values at $\lambda$= 12.4 and 22.0 are about 1.7 and 2.8, respectively while Xie and Okada[325] reported an $n_d$ value of 2.6. Pivovar et al.[319] indicated that the $n_d$ value can approach to 6 or the membrane in contact with aqueous sulfuric acid solution. Ren et al.[306, 323] developed a measurement for a Nafion® 117 membrane equilibrated with 1.0 M aqueous methanol solution and reported that the value strongly increases with temperature from about 2.0 at 15°C to 5.1 at 130°C. Motupally et al.[315] performed a HCL electrolyzer method by exposing Nafion®
membranes contact with liquid water on one side and with gaseous anhydrous HCl on the other side and showed that \( n_d \) is equal to 3.84 at 80°C and 3.5 at 60°C, respectively.

Figure 2.24[156] demonstrates the EOD coefficient and diffusion coefficient data obtained by [314, 317] respectively, for a Nafion® membrane. As can be seen, EOD coefficient is roughly a constant at unity when \( \lambda < 14 \) and then linearly increases for water content between 14 and 22 while the water diffusion coefficient in the membrane is highly nonlinear and shows a distinctive peak at \( \lambda = 3 \).

![Figure 2.24. Electro-osmotic drag coefficient and water diffusivity as functions of water content in Nafion® membranes [156, 314, 317].](image)

The nonlinearity in membrane transport properties, unfortunately, increases the level of difficulty in numerical solutions[156] since it is hard to describe them in analytical form. Motupally et al.[314] proposed a comparatively simpler relationship for the diffusion coefficient as a function of temperature and water content while Dutta et al.[81] and Fuller [213] proposed a formulation for diffusion coefficient including the EOD coefficient. As a simple relation for the EOD coefficient, Weber and
Newman[90] proposed that it is equal to the value of water content at water contents lower than 1 and it becomes constant and equal to 1 at higher water contents the data obtained by Zawodzinski et al.[317]. A linear relationship for the EOD coefficient is expressed by Springer et al.[57] with a slope of 2.5/22.

Recently, Ge et al.[321] using steady-state permeation along with High Frequency Resistance (HFR) measured EOD coefficients in Nafion® 117 membrane under water vapor and liquid water conditions and proposed the following functional fits of EOD as a function of water content at temperature of 303, 323, and 353 K using the experimental data obtained.

More recently, Ye and Wang[312] presented a measurement method using a hydrogen pumping cell along with a physical model in order to determine the EOD coefficient of Gore-Select membranes and then using the EOD coefficient found to be 1.07 over the wide relative humidity range between 40% and 95%, they determine the water diffusion coefficient of Gore-Select membranes.

2.5.2. Electrokinetic Properties

The most important electrokinetic properties required for fuel cell modeling are the specific interfacial area of the catalyst layer, catalyst loading and the exchange current density of the reactions with transfer coefficients. In order to understand the importance of these parameters, an electrochemistry background related to the reactions will be given.

As mentioned before, in a hydrogen/oxygen fuel cell the anode reaction is oxidation of hydrogen(HOR), in which hydrogen is broken its protons and electrons while the cathode reaction is oxygen reduction (ORR) and water is generated as a product.
In general, an electrochemical reaction involves either oxidation (the loss of electrons or an increase in oxidation state by a molecule, atom, or ion) or reduction (the gain of electrons or a decrease in oxidation state by a molecule, atom, or ion) of the species:

\[
\text{Red} \rightarrow \text{Ox} + ne^-
\]

\[
\text{Ox} + ne^- \rightarrow \text{Red}
\]  \hspace{1cm} (2.17)

The speed at which an electrochemical reaction occurs is the rate at which electrons are released or consumed, basically it represents the electrical current and the current density is described as the current of electrons or protons per unit surface area.

When the oxidation and reduction reactions take place at equal rates, i.e., the release and consumption rate of the electrons are the same, the reaction is defined as to be at equilibrium.

\[
\text{Ox} + ne^- \leftrightarrow \text{Red}
\]  \hspace{1cm} (2.18)

According to the Faraday’s Law, the current density is proportional to the charge transferred and the consumption of reactant per unit area which is directly proportional to their surface concentration with a rate coefficient\[9\]:

\[
i = nFj
\]  \hspace{1cm} (2.19)

Where \(n\) is the number of electrons transferred in the reaction, \(F\) is Faraday’s constant (Coulomb/mol), accordingly \(nF\) is the charge transferred (Coulombs/mol) and \(j\) is the flux of reactant per unit area (mol/s/cm\(^2\)).

The flux for the forward reaction (reduction reaction) and for the backward reaction (oxidation reaction) of equilibrium reaction above are the following expressions, respectively\[9\]:

\[
j_f = k_f C_{\text{Ox}}
\]  \hspace{1cm} (2.20)
\begin{align*}
  j_b &= k_b C_{Rd} \\
  \text{where:} \\
  k_f &= \text{forward reaction (reduction) rate coefficient} \\
  C_{Ox} &= \text{surface concentration of the reacting species} \\
  k_r &= \text{backward reaction (oxidation) rate coefficient} \\
  C_{Rd} &= \text{surface concentration of the reacting species} \\
\end{align*}

The net current generated by these two reactions releasing or consuming electron is the difference between the electrons released and consumed, i.e. the difference between forward and reverse current on the electrode[9]:

\[ i = nF \left( k_f C_{Ox} - k_r C_{Rd} \right) \]  

(2.22)

The measured current or current density by a current-measuring device placed external to the cell is actually the net current.

The rate of an electrochemical reaction involving both a transfer of electrical charge and a change in Gibbs energy[9, 12, 13, 326] is determined by the activation energy that the charge must overcome in moving from proton conductor(electrolyte) to an electron conductor(solid electrode) or vice versa.

According to the Transition State Theory[9, 327], the reaction rate coefficient for a chemical reaction as a function of the Gibbs free energy is given [9, 12, 13, 326]:

\[ k = \frac{k_B T}{h} \exp \left( \frac{-\Delta G}{RT} \right) \]  

(2.23)
Where \( k_B, h, R \) are the Boltzmann’s, Planck’s and universal gas constants; \( T \) is the temperature and \( \Delta G \) is the Gibbs free energy.

The Gibbs free energy, \( \Delta G \), for electrochemical reactions consists of both chemical and electrical terms[9, 327] and formulated for reduction and oxidation reactions, respectively:

\[
\Delta G = \Delta G_{ct} + \alpha_{\text{Rd}}FE \\
\Delta G = \Delta G_{ct} - \alpha_{\text{Ox}}FE
\]

The subscript “ct” represents the chemical component of the Gibbs free energy, \( \alpha \) is a transfer coefficient, and \( E \) is the electrode potential[9].

Mostly, in order to define the reaction rates the symmetry factor, \( \beta \), is used for a single-step reaction involving a single electron transferred \((n=1)\) [9]. Theoretically, the value is between 0 and 1, but for the typical reactions on the metallic surface, it is around 0.5[9]. According to the definition, \( \beta \) requires that the sum of the symmetry factors in anodic and cathodic reactions should be unity; therefore, if it is \( \beta \) for the reduction reaction, it must be \((1-\beta)\) for the reverse, oxidation reaction[9].

Both electrochemical reactions in a PEMFC (HOR and ORR) involve more than 1 step. In that case, the rate of the reaction is determined by the slowest step in the sequence, which is called as the rate-determining step. In order to determine the reaction rate in that multistep process, instead of theoretical \( \beta \), the transfer coefficient, \( \alpha \), which is an experimental parameter is used[9]. \( \alpha_{\text{Rd}} + \alpha_{\text{Ox}} = 1 \) does not necessarily have to be equal to unity. Actually, the following relationship is valid in general[9]:

\[
\alpha_{\text{Rd}} + \alpha_{\text{Ox}} = n/\xi
\]

where \( n \) is the number of electrons transferred in the overall reaction and \( \xi \) is the stoichiometric number defines as the number of times the rate-determining step must occur for the overall reaction to
occur once[9, 210, 328]. The transfer coefficient of a multi-step reaction may change with respect to the temperature, the current or the voltage obtained [127, 329].

The transfer coefficients used for hydrogen PEMFC using Pt catalyst is around 1.0. Larminie and Dicks[330] reported a value of $\alpha=0.5$ for the anode (with 2 electrons involved) and $\alpha=0.1$ to 0.5 for the cathode. Ziegler et al.[127] pointed out the dependency of cathode Tafel Slope at different overpotential on the rate determining step, correspondingly on the transfer coefficient. For moderate overpotential, the number of electrons transferred at the rate determining step is 2 so $\alpha=0.5$ but at higher overpotential, higher current densities, it is assumed that the first electron transfer is the rate determining step[127]. On the other hand, Newman[210] reported that $\alpha$ is in a range between 0.2 to 2.

By using the Transition State Theory and the Gibbs free energy formulation, the forward (reduction) and backward (oxidation) reaction rate coefficients are presented respectively[9]:

\[
\begin{align*}
k_f &= \frac{k_B T}{h} \exp\left[\frac{-\Delta G_{ch} - \alpha_{Rd}FE}{RT}\right] = k_{0,f} \exp\left[\frac{-\alpha_{Rd}FE}{RT}\right] \\
k_b &= \frac{k_B T}{h} \exp\left[\frac{-\Delta G_{ch} + \alpha_{Ox}FE}{RT}\right] = k_{0,b} \exp\left[\frac{\alpha_{Ox}FE}{RT}\right]
\end{align*}
\] (2.26) (2.27)

Then the net current density is obtained as[9]:

\[
i = nF \left\{ k_{0,f} C_{Ox} \exp\left[\frac{-\alpha_{Rd}FE}{RT}\right] - k_{0,b} C_{Rd} \exp\left[\frac{\alpha_{Ox}FE}{RT}\right] \right\}
\] (2.28)

At equilibrium, since the forward and backward reaction rates are equal, the net current is equal to zero, although the reaction happens in both directions simultaneously. The current density and potential occurring at the equilibrium are called the equilibrium or reversible potential, $E_r$, and the exchange current density, $i_0$, respectively [9, 12, 13, 210, 326, 331].
The reversible or equilibrium potential, $E_r$, at the fuel cell anode is 0 by definition of the hydrogen electrode [9, 210, 326, 332] and the theoretical reversible cell potential at the fuel cell cathode is calculated using the Nernst Law[9, 12, 13] in which the thermodynamic data of reaction enthalpy and entropy changes are used originally:

$$
E_r = V_{OC} = 1.229 - 0.9 \times 10^{-3} (T - 298.15) + \frac{RT}{2F} \left( \ln P_{H_2} + \frac{1}{2} \ln P_{O_2} \right)
$$

(2.29)

For a hydrogen fuel cell, the theoretical reversible cell voltage, $E_r$, is 1.229 V at 25°C and atmospheric pressure [9, 12, 13]. At operating fuel cells, the potential at the zero current, open cell voltage or equilibrium potential, $V_{OC}$ or $U_0$, is expected to be the theoretical cell potential given conditions (T,P, concentration of reactants) but due to the different kinds of voltage losses caused by kinetics of the electrochemical reactions, internal electrical and ionic resistance, difficulties in getting the reactants to reaction sites, internal currents, crossover of reactants, this value can be even below 1V. Berger[12] proposed a relation for open cell voltage decreasing with temperature while a relation increasing with temperature is mostly used[36, 93, 95, 333].

The increasing relationship with temperature can be verified by the experimental data obtained by Parthasarathy et al. [329] reporting that the open circuit potential increases with temperature until 80°C while it decreases to 0.7-0.8V at the higher temperatures. Also, it approaches to lower values when the system reaches to SS. The following table[329] indicates the dependency of the open circuit voltage on the temperature after activation and SS.
Table 2.3. Variation of open circuit voltage (o.c.p) with temperature and activation[329]

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>o.c.p. after activation mV</th>
<th>Steady-state o.c.p. mV</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>1005</td>
<td>882</td>
</tr>
<tr>
<td>40</td>
<td>1025</td>
<td>900</td>
</tr>
<tr>
<td>50</td>
<td>1039</td>
<td>916</td>
</tr>
<tr>
<td>60</td>
<td>1083</td>
<td>920</td>
</tr>
<tr>
<td>70</td>
<td>1116</td>
<td>938</td>
</tr>
<tr>
<td>80</td>
<td>1119</td>
<td>962</td>
</tr>
</tbody>
</table>

Since the open circuit voltage is one of the parameters changing the polarization curve obtained by the models significantly, the differences in the formulation would be normal. The theoretical cell voltage decreases with temperature according to the Nernst Law. Meanwhile the reaction rates and consequently the exchange current densities increase with temperature.

By the definition of the exchange current density, the following equation is obtained from Eqn.(2.28) [9]:

\[
i_0 = nFk_{0,r} C_{Ox} \exp \left( -\frac{\alpha_{Rd} F E_r}{RT} \right) = nFk_{0,b} C_{Rd} \exp \left( \frac{\alpha_{Ox} F E_r}{RT} \right) \tag{2.30}
\]

Exchange current density, \(i_0\), in electrochemical reactions is analogous to the rate constant which depends on only the temperature in chemical reactions[9]. As can be seen in the equation above, the exchange current density depends on the concentration of reactants as well as temperature. The current density per unit of electrode geometrical area called as effective current density represents the dependency of the rate of the electrochemical reaction on the electrode catalyst loading and catalyst specific surface area[9, 31].

By combining the equation for exchange current density and net current density, a relationship between current density and potential, Butler-Volmer equation is derived[9, 210, 332]:
\[ i = i_0 \left\{ \exp \left[ -\frac{\alpha_{Rd} F (E - E_r)}{RT} \right] - \exp \left[ \frac{\alpha_{Ox} F (E - E_r)}{RT} \right] \right\} \] (2.31)

The difference between the electrode potential and the reversible potential \( (E - E_r) \) or \( \eta \) is called overpotential or polarization. Although it is also a loss for the fuel cell voltage, it is actually the potential difference required to generate current, i.e. the driving force for the electrochemical reaction.

The surface overall potential for an electrochemical reaction is also demonstrated as:

\[ (E - E_r) = \eta = \Phi_s - \Phi_e - E_r = \Phi_s - \Phi_e - V_{OC} \] (2.32)

where \( \Phi_s \) and \( \Phi_e \) are the electric potential of the electronic(solid) phase and electrolyte, respectively, at the triple-phase interface of the electrode as the charge is moving from electrolyte to the solid electrode.

The Butler-Volmer equation both anode and cathode reaction in a fuel cell are given in the following:

\[ i_a = i_{0,a} \left\{ \exp \left[ -\alpha_{Rd,a} F (E_a - E_{r,a}) \right] - \exp \left[ \frac{\alpha_{Ox,a} F (E_a - E_{r,a})}{RT} \right] \right\} \] (2.33)

\[ i_c = i_{0,c} \left\{ \exp \left[ -\alpha_{Rd,c} F (E_c - E_{r,c}) \right] - \exp \left[ \frac{\alpha_{Ox,c} F (E_c - E_{r,c})}{RT} \right] \right\} \] (2.34)

The overpotential on the anode is positive \((E_a > E_{r,a})\), so the first term of the Butler-Volmer equation is negligible when compared to the second term, meaning that the oxidation current is predominant and the equation may be reduced to[9]:

\[ i_a = -i_{0,a} \exp \left[ \frac{\alpha_{Ox,a} F (E_a - E_{r,a})}{RT} \right] \] (2.35)
Similarly the overpotential on the cathode is negative \((E_c < E_{c,r})\), so the first term of the Butler-Volmer equation is much larger than the second term, meaning that the reduction current is predominant and the equation may be reduced to[9]:

\[
i_c = i_{0,c} \exp\left[\frac{-\alpha_{Rd,a} F (E_c - E_{r,c})}{RT}\right]
\]

The resulting current for the anode has a negative sign, which represents that the electrons are leaving the electrode (net oxidation reaction) while it has a positive sign for the cathode to which the electrons are arriving (net reduction reaction)[9].

Exchange current density can be represented as the eagerness of the electrode carrying out the electrochemical reaction. If the exchange current density is high, the surface of the electrode is more active. The higher the exchange current density, the more active the electrode, the lower the activation energy that the charge must overcome moving from electrolyte to the catalyst surface and vice versa and accordingly, the higher rate of the reaction and the more current generated at any overpotential.

In PEMFCs, the cathode reaction ORR is sluggish while the anode reaction HOR is facile; therefore, the anode overpotential is low while the cathode one is high. In that case, the Butler–Volmer equation can be approximated by the linear kinetic expression and by Tafel kinetics for HOR and ORR, respectively [4, 54, 156]:

\[
i_a = i_{0,a} a_c L_c \left(\frac{C_{H_2}}{C_{H_2}^{\text{ref}}}\right)^{1/2} \left(\frac{a_a + a_c \exp\left(\frac{-a_c}{RT} F \eta\right)}{RT F \eta}\right)
\]

\[
i_c = i_{0,c} a_c L_c \left(\frac{C_{O_2}}{C_{O_2}^{\text{ref}}}\right)^{1/2} \exp\left(\frac{-a_c}{RT} F \eta\right)
\]
Moreover, the cathode exchange current density is several orders of magnitudes lower than the anode exchange current density (\(\sim 10^{-9}\) vs. \(\sim 10^{-4}\) Acm\(^{-2}\)Pt, at 25°C and 1 atm)[9], that’s why the cell potential-current relationship is mostly represented by only by the cathode current density[9]:

\[
i_c = i_{0,c} \exp \left[ -\alpha_{Rd,a} F \left( E_c - E_{r,c} \right) \right] \frac{RT}{}\]

The exchange current density and Tafel slope of ORR have been well documented in references [157, 242, 243, 329, 334, 335]. The local current density is modified by an effectiveness factor in order to account for the effect of diffusion resistance through the electrolyte to the catalyst surface [18, 31, 95], mostly in agglomerate models.

### 2.5.3. Porous Media Properties

The main function of a gas diffusion medium or GDL is to provide a uniform gas distribution of the reactants gases to the CL as well as to conduct electrons from CL to the current collectors or vice versa. Because of these duties, carbon cloth or carbon paper are used as the gas diffusion medium due to their sufficient porosity and electron conductivity. Diffusion medium properties for PEMFCs, such as pore size distribution, porosity, and gas permeability have been recently reviewed by Mathias et al.[254].

Tortuosity of the gas in the pores caused by the merging, branching and curving of the pores is another important transport property of the gas diffusion medium, especially in CL. Tortuosity is defined as the ratio of the average path of the gas flow in the free space to the length of that in the gas diffusion medium. Recently, Suzuki et al.[225] used Monte Carlo Method in order to determine the pore tortuosity in CL computationally. As mentioned before, CL is composed of the distributed nano-size Pt particles with the carbon support intermixed with the polymer electrolyte. The ratio of the carbon, Pt, electrolyte and pores, affects the performance of the electrode so the volume fraction of these
components are also calculated in order to use in the models, especially in homogeneous catalyst models[225].

The GDL also should enable the liquid water transport out of the CL to the gas channels in order to prevent or delay the flooding, that’s why, GDL materials are usually coated with a hydrophobic polymer such as poly(tetrafluoroethylene) (PTFE), Teflon. A micro-porous layer (MPL) might be added to GDL to achieve better water management. There have been many studies studying the effects of PTFE treatment and content in GDLs and their review can be found in Li et al.[161]. In recent years, due to the important role of GDL in water transport, the characterization of the two phase transport properties such as the coefficients of the capillary-induced liquid transport, wettability(contact angle), effective porosity has been the main focus of the GDL characterization studies, Li et al.[161] and Wang[156] presented a review of these studies. Mathias et al.[254] and Lim and Wang[336] performed surface contact angle measurements by using capillary rise method while Lim and Wang[336] showed the dependence of water contact angle on the temperature.

2.5.4. Bipolar Plates Properties

The main purposes of bipolar plates in the PEMFCs are to collect and transport electrons from the cell to the external circuit and to provide accommodation for the flow channels which are small grooves made by engraving or milling the surface of the bipolar plates[31]. For the electron collection and transport, they are made of highly conductive materials such as carbon, graphite and conductive metals. The other important properties, especially for thermal management in the stacks and two phase flow in the channels, are the thermal conductivity and the surface wettability, respectively. These properties for bipolar materials such as graphite and metals are well documented in standard textbooks. The electronic and thermal conductivities of the bipolar plates (>10^5 S/m[156] and >150 W/mK[36]) are
assumed to be very high; therefore, they are not usually included in the FC models, instead, entered as the boundary conditions.

Since the bipolar plates are shaped according to the flow field designs, the configuration of the channels can be considered as another characteristic property of the bipolar plates. In order to provide a uniform distribution of the reactants and to decrease the pumping pressure losses, there have been many flow field designs besides to the conventional ones have been proposed in the literature so far: serpentine, interdigitated, tapered, stepped bio-inspired/ biomimetic such as lung and leave shaped, mesh and porous medium filled.
3. MATHEMATICAL MODEL

3.1. Introduction

In this chapter of the thesis, the mathematical model developed is given with all aspects of modeling in different layers of fuel cell: the governing equations, constitutive relationships, boundary conditions and solution methods. Firstly, an overview of fuel cell modeling is given below and the following sections present the detailed information.

Fuel cell technology is a multi- and interdisciplinary area since many processes including mass, momentum, and heat transport, along with electrochemical reactions take place. Fuel cell modeling aims to describe these processes in the form of mathematical equations and analyze in order to optimize the fuel cell components and operating conditions for the best performance.

Due to the complexity of the mathematical description including the whole phenomena occurring in the fuel cell, it is unavoidable to make assumptions in order to obtain a simpler model but comprehensive enough to analyze the processes concerned. The general approach starts by dividing the system into components such as subsystems or control volumes. For each region, the conservation equations including mass, momentum, species, charge and energy with appropriate source terms are developed. In addition, the equations which deal specifically with the phenomena, such as Darcy’s Law for fluid flow in porous media, Fick’s Law or Stefan-Maxwell equations for diffusion of the gas mixtures, Fourier’s Law for heat conduction, Butler-Volmer equation for reaction kinetics, are furnished. After providing the necessary boundary and initial conditions (or guesses for steady state models), the next step will be the solution of the set of governing equation. Due to the complexity and interconnectivity of the governing equations and constitutive relationships, almost all of the fuel cell models are solved numerically.

A fundamental fuel cell model consists of 5 principles of conservation: mass, momentum, species, charge and thermal energy as mentioned above. These transport equations are then coupled with
electrochemical processes through source terms to describe reaction kinetics and water transport in polymer membrane. Such convection-diffusion-source equation can be summarized in the following form [156]:

$$\frac{\partial (\rho \phi)}{\partial t} + \nabla (\rho \mathbf{u} \phi) = \nabla (\Gamma \nabla \phi) + S$$  \hspace{1cm} (3.1)

where $\phi$ is a general variable to be solved, $\rho$ is the density, $\mathbf{u}$ is the velocity vector, $\Gamma$ is the diffusion coefficient, and $S$ is the source term which includes all terms that cannot be included in the previous terms.

The work presented here incorporates the combined effects of mass and species transfer, momentum conservation, electrical current distribution through the gas channels, the electrodes and the membrane, and the electrochemical kinetics of the reactions in the anode and cathode catalyst layers. The anode feed consists of hydrogen and humidified water vapor whereas humidified air is fed into the cathode channel. The main focus is on the mass and species transfer and water transport through the membrane as well as obtaining the performance of the fuel cell in terms of polarization curves.

The model presented in this study accounts for

- multi-component diffusion and convection of gaseous species through the gas channels, porous anode and cathode as well as effective diffusion in the catalyst layers (CLs) considering the CL structure and water transport in the membrane phase,
- electrochemical reactions including ionic balance in electrodes and membrane, and transport of electrons through solid elements,
- transport of H+ protons through the membrane and polymer phase of the CLs,
• water transport in the membrane governed by diffusion, convection, and electro-osmotic drag (EOD).

The rest of the chapter is composed of 4 sections and gives detailed description of the model presented. First, in the model review section, general assumptions are given and then the component model summary is described according to the assumptions made. In the next sections, the governing conservation equations are given in details as well as the constitutive equations and properties. Finally, the computational models presented in the next chapters separately are described briefly.

3.2. Model Overview

A general mathematical fuel cell model includes 9 separate modeling domains which are:

- Anode Collector Collector (ACC)
- Anode Gas Channels (AGC)
- Anode Gas Diffusion Layer (AGDL)/Backing Layer/Porous Electrode
- Anode Catalyst Layer (ACL)
- Polymer Exchange Membrane (PEM)
- Cathode Catalyst Layer (CCL)
- Cathode Gas Diffusion Layer (CGDL)/Backing Layer/Porous Electrode
- Cathode Gas Channel (CGC)
- Cathode Collector Collector (CCC)

Note that Membrane Electrode Assembly (MEA) consists of anode & cathode GDL, catalyst layers and the polymer membrane, and porous electrode term is sometimes used to present CL while gas diffuser or backing layer is used for GDL. A schematic showing the components of a fuel cell model and the processes is presented in Figure 3.1[157].
PEMFCs shown schematically in Figure 3.1[157] have the following components and functions:

1. **Anode bipolar or collector plate**: Anode collector plate is in contact with the anode gas diffusion layer: Separating different cells in a fuel cell stack, while still maintaining the electrical connectivity between neighboring cells, and feeding the reactant to gas diffusion electrodes are the main duties of collector (bipolar) plates. Reactant flow channels are milled into the plates, which should otherwise be as thin as possible to reduce the weight and volume. Besides, maintaining a good electrical contact between bipolar plate and gas diffusion layers to minimize the electrical contact resistance and hence ohmic losses is also very important in improving fuel cell performance.

![Figure 3.1. Schematic showing fuel cell components and processes[157]: I—convective and diffusive gas flow (2,8); II—gas transport (3,4,6,7); III—electrochemical reaction (4,6); IV—proton transport (4-6); V—electron conduction (1,3,4,6,7,9); VI—water transport (2-9).](image-url)
2. **Anode gas channel** that supplies the fuel cell with reactants: Reactant gases (hydrogen or hydrogen-enriched gases) are transported by convection and diffusion throughout the anode gas channel.

3. **Anode backing layer/gas diffusion layer (GDL)** that transports reactants/products to and from the catalyst layers and conduct electrons from the catalyst layer to the collector plates: Reactant gas mixture components are transported throughout the pores of the gas diffuser via momentum transport, concentration and pressure gradients. Meanwhile, liquid water coming from membrane electrode assembly (MEA) fills the gas diffuser pores. The graphite matrix of the gas diffusers provides a path for the electrons to be transported between the collector plates and the catalyst layers of the MEA. Hydrogen gas from the anode gas channels will be transported through the anode gas diffuser towards the anode catalyst layer.

4. **Anode catalyst layer (CL)** where the electrochemical reactions take place: In the anode catalyst layer, hydrogen gas coming from anode gas diffuser will oxidize. Protons dissolve in the liquid water that impregnates the proton exchange membrane (PEM). Although the catalyst layer is the thinnest part of a PEM fuel cell, it is the key component for fuel cell energy conversion, where fuel and oxidant react electrochemically to produce electrical work. Essentially, the electrochemical reactions in PEM fuel cells occur slowly, especially on the cathode side. In order to increase the reaction rates, catalyst usually consisting of small particles of platinum supported on larger carbon particles, must be coated either on the surfaces of carbon support media or directly on the surfaces of membrane. These carbon particles have to be mixed with some electrolyte material to ensure that protons can migrate towards the reaction site. The composition, morphology, and thickness of catalyst layer are one of the key parameters in optimizing fuel cell performance and reducing costs.
5. **Polymer membrane** that allows the transport of water and protons and separates the reactants H\(_2\) and O\(_2\): The component distinguishing PEMFCs from other type of fuel cells is the proton exchange membrane, a polymer electrolyte. The acidic polymeric membrane, which conducts protons and repels electrons, forces the electrons to travel through the outer circuit providing electrical work. Membrane is characterized by the fixed-charge concentration: a higher fixed-charge concentration can lead to higher proton conductivity. The most commonly used electrolyte material is Nafion® from DuPont. For a PEMFC it is particularly important to maintain appropriate water content in the electrolyte membrane, since the proton conductivity depends directly on water content inside membrane. However, multiple water transport mechanisms co-exist in the membrane, which introduces tremendous challenges to fuel cell engineering, since water balance must be maintained under most complicated operating conditions. The water in the PEM is transported due to convection, diffusion, dispersion, pressure gradients and electro-osmotic forces, being dragged by the moving protons.

6. **Cathode catalyst layer** where the electrochemical reactions take place: In the cathode catalyst layer, oxygen coming from the cathode gas channels dissolves in the liquid water and reacts with the protons coming from the anode through the PEM and with the electrons coming from the anode through an external circuit.

7. **Cathode backing layer/gas diffusion layer** that transports reactants/products to and from the catalyst layer and conduct electrons from the catalyst layer to the collector plate: Reactant gas mixture components are transported throughout the pores of the gas diffuser via momentum transport, concentration and pressure gradients. Meanwhile, liquid water coming from MEA fills the gas diffuser pores. The graphite matrix of the gas diffusers provides a path for the electrons to be transported between the collector plates and the catalyst layers of the MEA. The air
mixture in the cathode gas channels is partially transported through the cathode gas diffuser towards the cathode catalyst layer.

8. **Cathode gas channel** that supplies the fuel cell with reactants: Reactant gases (oxygen only or air) are transported by convection and diffusion throughout the cathode gas channel.

9. **Cathode bipolar or collector plate** that acts as an electron conductor: Cathode collector plate is in contact with the cathode GDL.

### 3.1.1. General Model Assumptions

In order to simplify the complex phenomena occurring in a fuel cell, the following assumptions are presented. Almost all of these assumptions are the common ones used in the fuel cell modeling literature.

1. Steady State: The startup or stop or any transient process of a fuel cell are not considered in the model.

In terms of the validity of the model to real operation conditions, it should be noted that at the average current density of $1.45 \text{ A/cm}^2$, the single fuel cell reaches 80 percent of its final value of current density within the first second[151]. This conclusion makes a steady state model assumption valid.

2. Isothermal: When a single cell is tested, the cell temperature is usually controlled using heating rods and thermocouples; therefore, the operation temperature of a single fuel cell can be kept almost constant in all the regions of the working fuel cell [137, 139]. Since the model validation can be done only by using the experimental test data, isothermal assumption is reasonable. Also, due to their high thermal conductivity, solid parts (membrane and electrodes) are assumed to have uniform and constant temperature[96].
Moreover, according to the thermal management studies, the cell temperature is mostly found to change at most 3 K in different regions of the fuel cell as can be seen in Figure 3.2 and Figure 3.3 presented by Wang[156]. The former one presents the temperature distribution in the middle of the membrane (EW < 1000) for a straight channel PEM fuel cell with a cell voltage of 0.6 V and average current density of 1.42 A/cm² at 80 °C[156] while the latter demonstrates the temperature distribution in-plane direction in a low humidity 50 cm² fuel cell cell with serpentine flow field at 0.6 V or average current density of 0.71 A/cm²[156]. The membrane used in the study is 18 μm thick (EW < 1000) and the anode/cathode feed conditions are the following: pressure=3/3 atm, relative humidity=75%/dry, stoichiometry=1.2/2, and cell temperature=80°C[156]. The in-plane direction can be seen in Figure 3.2[156].

Figure 3.2. Temperature distribution (in K) in the middle of the membrane along the channel[156].

Figure 3.3 gives of the special temperature variation along in-plane direction predicted by the co-simulation of water and heat management in a serpentine fuel cell[156]. The membrane temperature fluctuating between channel and land areas (bipolar plate portions) is higher in the channel area due to
lack of effective cooling, increases along the flow path due to higher current density, and then decreases near the outlet due to decreased current density by oxygen depletion[156].

Figure 3.3. Temperature distribution in a 50 cm² fuel cell with serpentine channels[156].

Figure 3.4. Schematic showing direction definitions used in PEMFC configuration[156].

4. Isotropic and homogeneous electrodes, GDLs, CLs and membrane: This assumption asserts that the porosity is a constant in the whole region of the gas diffusers, and the volume fractions of membrane and Pt/carbon in the catalyst layer are also constant[137].

The other specific assumptions related to each modeling domain if applicable will be given under the corresponding sections.

3.1.2. Model Components Summary

Collector Plates

**Structure:** Non-porous, solid electron conducting plates

**Transported Species:** Electrons

**Function:** Electron Transport from/to the backing layer (GDL) to/from the collectors, distribution of reactants and products to/from MEA.

**Unknowns:** Electrical Current & Potential

Gas Channels

**Structure:** Plain media with series of gas channels running through the collector plates and feeding into the GDLs

**Transported Species:**

- Anode: Gases (Hydrogen & Water)
- Cathode: Gases (Air or Oxygen & Water)

**Function:** Reactant transport to the electrodes & products transport from MEA to out.

**Unknowns:** Density, Flow Velocity Vector, Pressure, Species Concentrations
Assumptions:

✔ Incompressible and Laminar flow of Newtonian fluids: Laminar flow exists everywhere in the gas channels and the flow is fully developed at the exits of the gas channels. The assumption of incompressible laminar flow is based on the low flow velocities (low Reynolds numbers) and the small pressure gradients through a single cell [137, 156, 314]. After the gases flow out of the exits of the gas channels, there are no further chemical reactions, so there are no further changes in the concentration of the gases, such as O₂ or H₂. As a result, the assumption means that, at the exits of the gas channels, the gradients of the gas flow at the outlets are zero [137, 314].

✔ No electrochemical or chemical reaction in the channel and no charged species (electrons or protons) in flow.

Gas Diffusion Layers/Backing Layers/Electrodes

Structure: Porous medium, usually carbon cloth or carbon paper

Transported Species:

➢ Anode: Gases (Hydrogen & Water) & Electrons

➢ Cathode: Gases (Air & Water), & Electrons

Function:

• **Solid (matrix) phase:** Transport of electrons from CL to collector plates in anode side & from collector plates to CL in cathode side.

• **Pores:** Transport of reactants to CL & transport of products into gas channels.

Unknowns: Density, Mass Velocity Vector, Pressure, Electrical Current & Potential
Assumptions:

✓ Momentum equation can be reduced to Darcy’s Law.

Catalyst Layers

Structure: Porous, mixture made from the superposition of the polymer membrane and catalyst particles (generally Pt) with carbon support

Transported Species:

➢ Anode: Gases (Hydrogen & Water) & Electrons & Protons (Hydrogen ions)
➢ Cathode: Gases (Air & Water), & Electrons & Protons (Hydrogen ions)

Function:

• Polymer agglomerates: Proton transport by migration & convection from/to membrane to/from active sites, Electron transport from/to GDL to/from active sites
• Pores: Transport of reactants and products to active sites

Unknowns: Density, Mass Velocity Vector, Pressure, Electrical & Ionic Current, Electrical & Ionic Potential, Species Concentrations

Assumptions:

✓ Protons are transported in the membrane phase of the catalyst layers independently of the other reactants and products present [6, 7] and conductivity has also been shown to be isotropic under normal operation[90].
✓ Superposition of both models for polymer membrane and GDL can be used for the CL since it is composed of pores, carbon support (porous medium which is very similar to GDL), catalyst particles on the carbon support and polymer (membrane material)[6].
The hydration of polymer phase at both interfaces with polymer membrane and CL is in equilibrium with the water activity in the CL [6, 31, 93].

The pressure of the water molecules within the polymer phase is equivalent to that of the gas mixture at the anode and equivalent to that of the liquid water at the cathode [6, 31, 93] if the presence of the liquid water is accounted.

The thickness range of the catalyst layer is assumed to be between 10 μm - 20 μm[225].

**Polymer Membrane**

**Structure:** Porous, interwoven chains of C, F & O atoms with sulfonic acid (SO₃H) groups attached

**Transported Species:** Protons (Hydrogen ions) & Water

**Function:** Transport of protons from anode to cathode, preventing the transport of other reactants

**Unknowns:** Water Concentration, Protonic Potential & Current

**Assumptions:**

- The membrane is considered impermeable for the gas phase which is supported by the findings of an earlier study[48]; therefore, except water there is no flux of any species from the CLs to the membrane and no chemical or electrochemical reactions occur in the membrane.

- Mono-phase flow: Capillary forces are neglected due to the small size of the pores (1nm)[6]; therefore, water in the membrane is not of a particular phase (liquid or gas) but rather simply treated as water molecules.

- Electro-neutrality: The proton concentration in the membrane is assumed to be constant and equal to the concentration of fixed sulfonic acid groups [6, 94]. This means that there is no diffusive force for protons and the flux of protons thus results from a potential gradient, not a
concentration gradient. The transference number of protons in this system is 1 and this greatly reduces the complexity of the governing transport equations.

Equilibrium between ionomer and surrounding fluid (water). This assumption means that the concentration at the boundary of the membrane-catalyst layer is described with the water activity instead of concentration of water in the membrane or catalyst layer which essentially differs [6, 31, 54, 93].

3.3. General Governing Conservation Equations

The model consists of 4 principles of Steady State (SS) conservation: mass, momentum, species, and charge/current excluding the energy conservation equation due to isothermal operation. They are presented below.

3.2.1. Mass, Momentum and Species Conservation

For a SS system, the conservation of mass and momentum are presented with the following equation, respectively:

\[ \nabla \cdot (\rho \mathbf{u}) = S_{ms} \quad (3.2) \]

\[ \frac{1}{\varepsilon^2} \nabla \cdot (\rho \mathbf{u} \mathbf{u}) = -\nabla P + \nabla \cdot (\mu^{\text{eff}} \nabla \mathbf{u}) + S_u \quad (3.3) \]

\( \rho, \mathbf{u}, S_{ms} \) denote the mixture density, the fluid velocity vector and mass source term respectively while \( P, \varepsilon, \mu^{\text{eff}} \), and \( S_u \) denote the pressure, porosity of the porous medium, effective viscosity of the fluid flow and the momentum source term, respectively.

In the mass and momentum equations for both gas channels and porous media, the superficial velocity vector, \( \mathbf{u} = \varepsilon \mathbf{u}_{\text{fluid}} \), which is proportional to the fluid velocity vector by porosity of the porous medium, \( \varepsilon \), is used in order to automatically ensure the normal mass flux continuity at the interface between the
porous GDL and nonporous gas channel\cite{95, 101, 156} that in the gas channel, $\varepsilon$ is unity; therefore, the superficial velocity vector is reduced to the real fluid velocity vector.

For a SS system, the conservation of species $k$, is presented with the following equation:

$$\nabla \cdot (\mathbf{u} C_k) = \nabla \cdot \left( D_k^{\text{eff}} \nabla C_k \right) + S_k$$  \hspace{1cm} (3.4)

where $C_k$, $D_k^{\text{eff}}$ and $S_k$ denote the molar concentration, effective diffusion coefficient and the source term of species $k$, respectively.

Main source terms in the transport equations for a fuel cell model are due to electrochemical reactions taking place in the CL composed of three phases: electronic/solid(s), electrolyte/membrane(m), and gas(g). Electrochemical reactions occurring at the triple-phase boundary is represented according to the following general formula\cite{156}:

$$\sum_k s_k M_k^z = n e^-$$  \hspace{1cm} (3.5)

where the summation is over all species involved in a reaction. $M_k$ is a chemical symbol for species $k$ participating in the electrochemical reaction, $z$ and $s_k$ are charge number and stoichiometric coefficient of the species $k$, and $n$ is the number of electrons transferred in the reaction. The values of $s_k$, $z$ and $n$ can be readily be determined by comparing a specific electrode reaction to this general form.

The anode half reaction, HOR and cathode half reaction (ORR) can be written as, respectively:

$$H_2 - 2H^+ = 2e^-$$  \hspace{1cm} (3.6)

$$2H_2O - O_2 - 4H^+ = 4e^-$$  \hspace{1cm} (3.7)
In summary, for ORR: $s_{H_2O} = 2$, $s_{O_2} = -1$, $s_{H^+} = -4$ and $n = 4$ while for HOR: $s_{H_2O} = 0$, $s_{H_2} = 1$, $s_{H^+} = -2$ and $n = 2$.

The above governing equations are assumed to be applicable for both gas channels and electrodes (Single Domain Approach); therefore, at the interfaces of gas channel-GDL, and GDL-CL, the boundary conditions are not needed. Since the membrane is permeable to the gases and there is only water and proton transport in the membrane, the specific species equation is applied for the membrane and the necessary coupling of CL and membrane for water concentration is built. This approach is called as Mixed Domain Approach [128, 130].

**Water Transport through the Membrane**

The water transport through the membrane, the following conservation equation should be obeyed:

$$\nabla \cdot \mathbf{N}_w = 0 \quad (3.8)$$

where $\mathbf{N}_w$ is the molar flux of water across the membrane. In this study, the net flux of water through the membrane accounts for all mechanisms for transport: electro-osmotic drag, diffusion and convection due to pressure gradient:

$$\mathbf{N}_w = -D_w \nabla C_w - C_w \varepsilon_w \frac{k_p}{\mu_w} \nabla P_m + \frac{\eta_{drag} \mathbf{i}_w}{F} \quad (3.9)$$

$C_w$ is the molar concentration, $D_w$ is the diffusion coefficient of the water in the membrane; the parameters $k_p$, $\mu_w$, $\varepsilon_w$ and $\eta_{drag}$ are the hydraulic permeability of the membrane, water viscosity, the water volume fraction in the membrane and the EOD coefficient, respectively.

The mass flux will become:
\[
N_{w,\text{mass}} = -D_w \nabla c_w - c_w \mu_w \frac{1}{\mu_w} \nabla P_m + \eta_{\text{drag}} \frac{1}{F} M_{\text{H}_2\text{O}} \quad (3.10)
\]

The variation of water volume fraction, \(c_w\), is relatively small and can be considered as a constant as done in almost all of the models presented so far. The proton transport is directly related to the water transport in the membrane and after the molar concentration of water is calculated, the molar concentration of the protons, \(C_p\), can be calculated by using the following relationship[337]:

\[
C_p = \frac{\rho_{\text{m}}^{\text{dry}}}{E W} - b C_w \quad (3.11)
\]

where \(\rho_{\text{m}}^{\text{dry}}, EW\) and \(b\) are the dry density, equivalent weight and experimental swelling coefficient of the membrane, respectively.

The details of the proton transport and the relationship between the water concentration and proton concentration are given in Appendix B.

**3.2.2. Charge/Current Conservation**

Electrochemistry modeling of the fuel cell requires the computation of the rates of the anodic and cathodic reactions. The difference between the phase potential of the solid and the phase potential of the electrolyte/membrane, so-called surface overpotential, is the driving force for these reactions. Therefore, two potential equations are solved in two phases: one potential equation accounting for the electron transport, \(e^-\) through the solid conductive materials (i.e., the current collectors and solid grids of the porous media); the other potential equation representing the protonic/ionic transport of \(H^+\) or \(O^{2-}\). The current in the electrolyte is the ionic current since the transport of current take place through transport of ions while the current in the electrode is the electrical current derived from the fuel cell.
For uniform electrolyte/membrane composition, the sum of the fluxes of all charged species yields the following expression for the current density vector:

\[ \mathbf{i}_m = -\sigma_m \nabla \Phi_m \]  \hspace{1cm} (3.12)

where \( \sigma_m \) denotes the electrolyte/membrane phase conductivity and \( \Phi_m \) is the potential in the electrolyte/membrane phase. The analogous equation is defined by the interfaces for current conduction in the electrodes/solid phases:

\[ \mathbf{i}_s = -\sigma_s \nabla \Phi_s \]  \hspace{1cm} (3.13)

The charge conservation equations (two electrical potential equations by Ohm’s Law) for the electrodes/solid phases and the electrolyte/membrane phase are the following:

\[ \nabla \cdot \left( \sigma_s^{\text{eff}} \nabla \Phi_s \right) = S_{\Phi_s} \]
\[ \nabla \cdot \left( \sigma_m^{\text{eff}} \nabla \Phi_m \right) = S_{\Phi_m} \]  \hspace{1cm} (3.14)

\( \Phi_s, \Phi_m, S_{\Phi_s}, \sigma_s^{\text{eff}} \) and \( \sigma_m^{\text{eff}} \) denote electronic phase potential (subscript s and m represent solid phase and membrane phase, respectively), protonic or membrane phase potential, the source term for charge conservation, effective electronic phase conductivity and membrane phase conductivity, respectively.

### 3.2.3. Source Terms

#### Mass Source Term

If a parameter \( \beta \) is defined to represent the net water transport rate through the membrane per proton[95, 200], it will become:

\[ \beta = \frac{N_w}{\mathbf{i}_m} = \frac{-D_w \nabla C_w - C_w \epsilon \frac{k_p}{\mu_w} \nabla P_m + \eta_{\text{drag}} \frac{\mathbf{i}_m}{F}}{\frac{\mathbf{i}_m}{F}} = \eta_{\text{drag}} - \frac{F}{\mathbf{i}_m} \left( D_w \nabla C_w + C_w \epsilon \frac{k_p}{\mu_w} \nabla P_m \right) \]  \hspace{1cm} (3.15)
The source term, $S_{ms}$, in the continuity equation is caused by mass consumption or production from electrochemical reactions as well as mass loss/gain through phase transformation. In order to account for the effect of water transport through the membrane phase, the mass source term in the ACL and CCL, respectively can be written as:

$$S_{ms} = \begin{cases} -M_{H_2} \frac{j}{2F} - M_{H_2O} \left(2\beta \frac{j}{2F}\right) \\ M_{O_2} \frac{j}{4F} + M_{H_2O} \left[-2 \frac{j}{4F} - 4\beta \frac{j}{4F}\right] \end{cases}$$  \hspace{1cm} (3.16)$$

$j$ is the volumetric transfer current of the reaction.

Note that $D_w$ is the water diffusion coefficient through the membrane phase only.

**Momentum Source Term**

Modified Navier-Stokes equation in which the additional source term, $S_u$, is named as Darcy’s drag. Darcy’s drag $S_u$ is exactly derived using Darcy’s Law\[48] in porous media flow in which an additional force imposed by the pore walls on the fluid within the pores usually results in a significant pressure drop\[95, 156]. Sometimes it is called as the micro-scale viscous term or Darcy’s viscous term, and it is defined as:

$$S_u = -\frac{\mu^{\text{eff}}}{K} u$$  \hspace{1cm} (3.17)$$

where $K$ is a position-dependent permeability in porous electrode:

$$K = \begin{cases} +\infty \quad \text{in gas channel,} \\ K_{PM} \approx 10^{-12} - 10^{-11} \quad \text{in GDL and CL.} \end{cases}$$  \hspace{1cm} (3.18)$$

The definition of $K$ implies that the gas channel is considered as completely permeable, while GDL and CL are present as porous media with small permeability.
Therefore, when $K = \infty$ in gas channel, $S_u = 0$.

By virtue of this additional source term, $S_u$, the momentum balance equation is modified to be valid in both porous media and gas channel, presenting the extended Darcy’s Law for flow in porous GDL with small permeability and exact Navier Stokes equation in gas channel with unit porosity and infinite permeability. This equation (modified Navier-Stokes equation in which the additional source term, $S_u$) is also known as Darcy-Brinkman-Forchheimer model[338].

Note that in a porous medium with a very small permeability, the momentum equation reduces to Darcy’s Law since the pore velocity (superficial velocity) becomes so small causing that the inertia and viscous terms in momentum equation becomes negligible compared to Darcy’s Drag[221].

**Species Source Term**

The volumetric production rate of species $k$ due to electrochemical reaction occurring at the triple-phase boundary (CL) is given by Faraday’s Law:

$$S_k = -\frac{s_ki}{nF}$$

(3.19)

In order to account for the water transport through the membrane phase, the electro-osmotic drag term should be accounted in water species source term in the CLs since the original species conservation equation can’t include this water/membrane phase specific transport. For generality, the source term for species conservation equation becomes[101]:

$$S_k = -\nabla \left( \frac{\eta_{\text{drag}}}{F} \mathbf{i}_m \right) - \left( \frac{s_ki}{nF} \right)$$

(3.20)
Note that the electro-osmotic drag coefficient, $\eta_{\text{drag}}$, is only relevant to the water molecule; thus, its values for other species, $\text{H}_2$, $\text{O}_2$ and $\text{N}_2$ are set to zero. In summary, species source term is 0 except in the CLs.

**Charge/Current Source Term**

The source term in the charge equation is used to describe the transfer current between the electronic and electrolyte phases inside of each anode and cathode catalyst layer.

The transfer currents, or the source terms, are non-zero only inside the catalyst layers and are computed as[95]:

- For the solid phase, $S_\phi = -j$ ($<0$) on the anode side and $S_\phi = +j$ ($>0$) on the cathode side.
- For the membrane phase, $S_\phi = +j$ ($>0$) on the anode side and $S_\phi = -j$ ($<0$) on the cathode side.

Overall, in both side the conservation of charges gives the following relationship:

$$\nabla \cdot i_s = -\nabla \cdot i_m \quad (3.21)$$

$j$ is the volumetric transfer current of the reaction and generally, for electrode reactions it is described by Butler-Volmer equation including $a$, which is the electrochemically active area per unit of electrode volume[9, 210, 332]:

$$j = ai_o \left[ \exp \left( \frac{\alpha_a F}{RT \eta} \right) - \exp \left( -\frac{\alpha_c F}{RT \eta} \right) \right] \quad (3.22)$$

where $i_o$ is the exchange current density, $\alpha_a$ and $\alpha_c$ are the anodic and cathodic transfer coefficients, respectively. $F$ is the Faraday's constant, $R$ is the universal gas constant, and $T$ is the cell temperature.
Thus, the surface overall potential/polarization for an electrochemical reaction, $\eta$, is formulated as:

$$\eta = \Phi_s - \Phi_m - E_r$$  \hspace{1cm} (3.23)

where $\Phi_s$ and $\Phi_m$ are the electric potential of the electronic(solid) phase and electrolyte, respectively, at the triple-phase interface. The last term, $E_r$, is the thermodynamic equilibrium potential of the reaction, which is, in turn, a function of the reactant and product concentrations at the interface as generally expressed by Nernst equation[9, 12, 13]. It is sometimes represented with $V_{OC}$.

The difference between the electrode potential and the reversible potential is called local surface overpotential, $\eta$, also known as the activation loss. It is the potential difference to generate current, i.e., the driving force for the electrochemical reactions occurring. The electrode potential is the difference between the solid and membrane potentials, $\Phi_s$ and $\Phi_m$.

The reversible or equilibrium potential, $E_{rev}$, at the fuel cell anode is 0 V by definition [9, 210, 326, 332] and the reversible potential at the fuel cell cathode is 1.229 V (at 25°C and atmospheric pressure) [9, 12, 13] and it does vary with temperature and pressure.

Theoretically, the thermodynamic equilibrium potential of the reaction, $E_r$, is expected to be equal to open cell voltage, $V_{oc}$, but due to initial losses such as hydrogen crossover and internal currents, $V_{oc}$ becomes smaller than $E_r$.

In PEMFCs, the cathode reaction ORR is slow, i.e., sluggish, while the anode reaction HOR is fast, i.e., facile; therefore, the anode overpotential is low while the cathode one is high. In that case, the Butler–Volmer equation can be approximated by the linear kinetic expression and by Tafel kinetics for HOR and ORR, respectively [4, 54, 156]:
\[ j_a = a_i_{0,a} \left( \frac{\alpha_a + \alpha_c}{RT} F \eta \right) \]  
\[ (3.24) \]

\[ j_c = a_i_{0,c} \exp \left( - \frac{\alpha_c}{RT} F \eta \right) \]  
\[ (3.25) \]

\( i_0, a, \alpha \) are the exchange current density per active surface area, specific active surface area and the transfer coefficient respectively.

The exchange current density for a reaction, \( i_o \), depends strongly on the compositions and temperature at the reaction interface as described in the previous chapter in details.

By using the definition of the exchange current density described in the previous chapter, the Butler-Volmer expressions become:

\[ i_a = i_{0,a}^\text{ref} a_c L_c \left( \frac{C_{H_2}^{\text{ref}}}{C_{H_2}} \right)^{1/2} \left( \frac{\alpha_a + \alpha_c}{RT} F \eta \right) \]  
\[ (3.26) \]

\[ i_c = i_{0,c}^\text{ref} a_c L_c \left( \frac{C_{O_2}^{\text{ref}}}{C_{O_2}} \right)^{1/2} \exp \left( - \frac{\alpha_c}{RT} F \eta \right) \]  
\[ (3.27) \]

\( i_{0}^\text{ref} \) is the reference exchange current density, at reference temperature, \( T_{\text{ref}} \) and pressure, \( P_{\text{r}}^{\text{ref}} \) (typically 298K and 101.25 kPa) per unit catalyst surface area. \( a_c \) is the catalyst specific area and \( L_c \) is the catalyst loading.

Since the total electrical current produced in the anode and the cathode is the same, the following equation for current conservation is valid:

\[ \int_{\text{anode}} j dV = \int_{\text{cathode}} j dV \]  
\[ (3.28) \]
3.4. Constitutive Closure Equations & Properties

In order to solve the conservation equations, due to the complex phenomena occurring in the fuel cells, the transport properties which are usually not a constant and mainly depend on the unknown parameters such as the velocity, the current, etc., should be formulated as well. In this section, the flow transport properties and electrochemical properties will be given as well as the membrane properties.

3.3.1. Flow Transport Properties

Density

To close the equation set for mass, momentum, and species conservation, the Ideal Gas Law is used to describe the gas density varying with its compositions:

\[ \rho = \sum M_k C_k \]  \hfill (3.29)

where \( M_k \) and \( C_k \) are the molecular mass and molar concentration of the species \( k \), respectively.

Species diffusion for multi-component gas mixture can be modeled by Stefan-Maxwell equations[339]. For an ideal gas mixture the diffusive mass flux vector of species \( k \) will be:

\[ \mathbf{J}_k = C^2 \sum_{j=1}^{a} \frac{M_k M_j D_{kj}}{\rho} \nabla x_j \]  \hfill (3.30)

\( C \), \( D_{kj} \), \( x_j \) denote for the molar concentration of gas mixture, binary diffusivity of gas pair \( k-j \) in a multicomponent gas mixture and mole fraction of species \( j \), respectively.

The density of each species \( \rho_k \) is obtained from the perfect gas law relation: \( \rho_k = \frac{P_{op} M_k}{RT} \) in which \( P_{op} \) corresponds to the anode or cathode side pressure, \( T \) is the temperature and \( R \) is the universal gas constant. Accordingly, the density of the mixture of the gases will satisfy the following
relationships while $\omega_k$ is the mass fraction, $x_k$ is the mole fraction and $C_k$ is the molar concentration of species $k$:

$$\rho = \sum_i \frac{1}{\omega_k / \rho_k} \sum \omega_k = 1$$

(3.31)

$$\rho_k = M_k c_k$$

(3.32)

$$x_k = \frac{C_k}{C}$$

(3.33)

Hence the equation of conservation of species takes the following form[115]:

$$\nabla \cdot \left( \rho_k \mathbf{u} + \frac{C^2}{\rho} \sum_{j=1}^{n} M_k M_j D_{kj} \nabla x_j \right) = S_k$$

(3.34)

**Diffusion Coefficients**

The mass fluxes of the species depend on the diffusivities of the species in the medium. The diffusivities of the gases are presented by using the binary diffusivities of the gas pairs. The binary diffusion coefficient of the gas pair $i-j$, $D_{ij}$, can be either experimentally measured or calculated using the Chapman-Enskog equation[156, 339]. The dependence of the diffusion coefficient on temperature and pressure is generally given by[214]:

$$D_{ij}(T,P) = D_{ij}(T_0, P_0) \left( \frac{P}{P_0} \frac{T}{T_0} \right)^{1.5}$$

(3.35)

The binary diffusivities $D_{ij}(T,P)$ are scaled with the temperature and pressure by using the relation presented above with experimentally obtained values of $D_{ij}(T_0, P_0)$ at reference pressure, $P_0$ (usually atmospheric pressure) and reference temperature, $T_0$.

The binary diffusivity of the gas pair i-j, $D_{ij}$, in a multi-component gas mixture is strongly dependent on the mixtures composition, but it can be expressed in terms of the Stefan-Maxwell diffusion coefficient ,
\( D_{ij}^* \), which is independent of composition. For a three-component system, as will be the case in the cathode the relations, the binary diffusion coefficient can be represented as[214]:

\[
D_{ij} = D_{ij}^* \left[ 1 + \frac{x_i \left( M_i / M_j \right) D_{ji}^* - D_{ji}^*}{x_i D_{ji}^* + x_j D_{ji}^* + x_i D_{ji}^*} \right]
\]

(3.36)

In Multicomponent Mixture Model, the species equation can be written in terms of mass fractions, and the following formulation can be used for the gas component \( k \):

\[
\nabla \cdot \left[ -\rho \omega_k \sum_{j=1}^{n} D_{kj} \frac{M}{M_j} \left( \nabla \omega_j + \omega_j \frac{\nabla M}{M} \right) + \rho \omega_k \mathbf{u} \right] = S_k
\]

(3.37)

where \( M \) is the total molar mass of the mixture, and \( M_j \) and \( \omega_j \) are the molar mass and mass fraction of gas \( j \), respectively.

The species diffusivities vary in different mediums of PEMFCs depending on the specific physical phase of component \( k \) and structure of the medium. In flow channels and porous GDLs, species \( k \) exists in the gaseous phase and thus the diffusion coefficient corresponds with that in gas, whereas species \( k \) is dissolved in the membrane phase within the CLs and the membrane. It is known that the values corresponding to dissolved species, are usually a few orders of magnitude lower than that in gas[156]. Therefore, the transport properties of the dissolved species should be corrected.

For multicomponent diffusion in the porous media, the Maxwell–Stephan equations remain the same. However, due to the porous structure, the binary diffusivity terms \( D_{ij} \) need to be corrected for the porosity, \( \varepsilon \), and tortuosity, \( \tau \), of the porous medium, according to the Bruggeman correlation which is a correction factor to account for the non-diffusing space occupied by the solid fragments:

\[
D_{ij}^{\text{eff}} = \frac{\varepsilon}{\tau} D_{ij}
\]

(3.38)
For the low tortuosities and porosities in the range of 0.4-0.5, instead of $\frac{\varepsilon}{\tau}, \varepsilon^{1.5}$ is usually used[340, 341] and the experimental and numerical justification of this simplification can be reviewed in Ref. [340, 341], respectively.

When the pore size becomes comparable to the mean free path of gas, molecule-to-wall collision also becomes important in addition to the molecule-to-molecule collision in ordinary diffusion[156]. The molecule-to-wall collision effect on the diffusion is presented with the Knudsen diffusion[33, 156, 225, 237] which can be computed according to the Kinetic Theory of Gases[214, 339]:

\[
D_{K,k} = \frac{2}{3} \left( \frac{8RT}{\pi M_k} \right)^{1/2} r_p
\]

(3.39)

where $r_p$ is the mean pore radius of the porous medium and $M_k$ is the molecular mass of the diffusing gas while $R$ is the universal gas constant and $T$ is the temperature.

The combined effective diffusivity of species $k$ in gas, due to ordinary and Knudsen diffusion is then calculated from [156, 225]:

\[
D_k = \frac{\varepsilon}{\tau} \left( \frac{1}{D_{K,k}} + \frac{1}{D_{1,k}} \right)^{-1}
\]

(3.40)

In PEMFCs, the mean radii of CLs are of the order of 0.1 µm while they are in order of 10-40 µm for the GDLs [156, 253-255]. The Knudsen diffusion coefficient for O$_2$ and H$_2$O in CL at 80 °C are estimated to be 0.32 and 0.43 cm$^2$/s, respectively[156]. Since these values are comparable to the respective ordinary diffusion coefficients, the rates of oxygen and water transport through the CCL should be predicted by taking the Knudsen diffusion into account[156].
3.3.2. Electrochemical Properties

Electrochemical properties are mostly related to the CL and its structure. Agglomerate CL models are the state-of-art of the CL modeling since they are able to predict the cell performance at entire current density range while pseudo-homogeneous ones fail at high current densities. On the other hand, they require more experimental data of the structure in which this study lacks; therefore, a simpler modified pseudo-homogeneous/agglomerate catalyst layer model is proposed in this thesis.

Exchange Current Density

If a reference exchange current density (at reference temperature and pressure) is defined per actual catalyst surface area, then the effective exchange current density at any temperature and pressure can be estimated by the following equation [9, 342, 343]:

\[
i_0 = i_0^\text{ref} a_c L_c \left( \frac{P_r}{P_r^\text{ref}} \right)^\gamma \exp \left[ - \frac{E_c}{RT} \left( 1 - \frac{T}{T^\text{ref}} \right) \right]
\]

(3.41)

\(i_0^\text{ref}\) is the reference exchange current density, \(\text{Acm}^2\text{Pt}\) at reference temperature, \(T^\text{ref}\) and pressure, \(P_r^\text{ref}\) (typically 298K and 101.25 kPa) per unit catalyst surface area.

\(a_c\) is the catalyst specific area and \(L_c\) is the catalyst loading which are defined on page 187. The theoretical limit of \(a_c\) for Pt catalyst is 2400 cm\(^2\)mg\(^{-1}\), but the state-of-the-art catalyst has about 600-1000 cm\(^2\)mg\(^{-1}\), which is further reduced by incorporation of catalyst in the electrode structures by to 30% while the state-of-art electrodes have 0.3-0.5 mgPtc\(^{-2}\) catalyst loading[9]. Currently, the optimum value of the catalyst loading for PEMFCs is reported to be about 0.4 -0.45 mgPtc\(^{-2}\) [157]. But Wang[54] reported that the novel techniques propose to reduce the value to <0.2mg/cm\(^2\).
The product $a_c L_e$ is also called electrode roughness, meaning the catalyst surface area, cm$^2$, per electrode geometric area, cm$^2$.

$E_c$ is the activation energy (66 kJ mol$^{-1}$ for oxygen reduction on Pt[9, 329, 334, 335, 343]). $P_r$ is the reactant partial pressure, and $\gamma$ is the pressure coefficient (0.5 to 1.2[9, 31, 329, 334, 335]).

In the presence of the liquid water in the catalyst layer, the catalyst surface area decrease with the increase in liquid saturation, $s$, so Wang[54] proposed the following Bruggeman relation in order to account for the liquid water coverage on the decreased or effective catalyst surface area, $a_c^{\text{eff}}$:

$$a_c^{\text{eff}} = (1 - s)^{1.5} a_c \quad (3.42)$$

In the calculation of the exchange current density, a ratio of concentrations at the catalyst surface may be also used instead of the ratio of partial pressures. The oxygen concentration is mostly used as the dissolved oxygen concentration in the electrolyte (at the gas/electrolyte interface), determined by Henry's law[11].

Since the model presented solves mainly for concentration of the reactants and products, the exchange current density is modeled by using the modified equation since it depends on the temperature, overpotential, the reactant concentration, the overall catalyst property in terms of specific reaction surface area per volume of the catalyst layer[9]:

$$i_0 = i_0^{\text{ref}} A_y \left( \frac{C_r^{\text{diss}}}{C_r^{\text{ref}}} \right)^\gamma \exp \left[ -\frac{E_c}{RT} \left( 1 - \frac{T}{T_{\text{ref}}} \right) \right] \quad (3.43)$$
$i_0^{ref}$ is the reference exchange current density per unit catalyst surface area, $A_{cm^2}Pt$ and, $C_r^{ref}$ is the reference concentration value at reference temperature, $T_{ref}$ and pressure, $P_{ref}$ (typically 298K and 101.25 kPa)[9].

$A_r$ is the specific reaction surface area per volume of the catalyst layer and dependent on the platinum loading, $m_{Pt}$, the thickness of the catalyst layer, $t_{CL}$, and the catalyst surface area per unit mass of the catalyst particle, $A_0$ [31, 33, 76]:

$$A_r = A_0 \frac{m_{Pt}}{t_{CL}} \quad (3.44)$$

The catalyst surface area per unit mass of the catalyst particle, $A_0$, is dependent on the size of the Pt particles and on the Pt content of the catalyst particles in the CL. In order to estimate this value, a polynomial fit to the data provided by E-TEK is applied as in [31, 76, 344]:

$$A_0 = 10^8 \left( 4.4198(r_{Pt/C})^9 - 27.691(r_{Pt/C})^8 + 74.206(r_{Pt/C})^7 - 111.06(r_{Pt/C})^6 + 101.43(r_{Pt/C})^5 \right) \left( -57.841(r_{Pt/C})^4 + 20.231(r_{Pt/C})^3 - 4.0809(r_{Pt/C})^2 + 0.39451(r_{Pt/C}) \right) \quad (3.45)$$

where $r_{Pt/C}$ represents the weight ratio of Pt to Carbon content of the CL and $A_0$ is in the units of cm$^2$/g.

The experimental data and the result of this polynomial fit proposed by Song et al.[344] can be seen in Figure 3.5[344].
Figure 3.5. Polynomial fitting of $A_0$ as a function of Pt/C weight percentage in CL by Song et al.[344].

In CL, the volume fraction of the solid phase composed of Pt particles and Carbon support, $\varepsilon_s^{CL}$, and the volume fraction of electrolyte phase, $\varepsilon_m^{CL}$ which is essentially the polymer membrane determine the porosity of the CL, $\varepsilon_{CL}$, enabling the reactant support to/from the CL. The sum of these fractions is simply equal to 1:

$$\varepsilon_s^{CL} + \varepsilon_m^{CL} + \varepsilon_{CL} = 1 \tag{3.46}$$

Solid phase volume fraction is calculated by using the following relation by using Pt and Carbon densities, $\rho_{Pt}$ and $\rho_C$, respectively [31, 33, 344]:

$$\varepsilon_s^{CL} = \left( \frac{1}{\rho_{Pt}} + \frac{1-r_{Pt/C}}{r_{Pt/C} \cdot \rho_C} \right) \frac{m_{Pt}}{t_{CL}} \tag{3.47}$$

Membrane/electrolyte/ionomer phase volume fraction is calculated by using[31]:

$$\varepsilon_m^{CL} = \frac{4}{3} \pi N \left[ r_{agg}^3 \varepsilon_{agg} + \left( r_{agg} + \delta_{agg} \right)^3 - r_{agg}^3 \right] \tag{3.48}$$
\( \delta_{agg} \) is the average thickness of the ionomer/membrane film surrounding the agglomerates, \( r_{agg} \) is the radius of the agglomerates assumed to be spherical shape, \( \varepsilon_{agg} \) is the volume fraction of ionomer inside the agglomerate and \( N \) is the number of agglomerates per unit volume and calculated by[31]:

\[
N = \frac{\varepsilon_{cl}}{4 \pi r_{agg}^3 \left( 1 - \varepsilon_{agg} \right)}
\]

The schematic of the agglomerate structure surrounded with thin film ionomer can be seen in Figure 3.6[31]:

![Figure 3.6. Single catalyst agglomerate with radius \( r_{agg} \) and polymer film thickness, \( \delta_{agg} \)[31].](image)

Even the transport of the reactants are corrected for the porosity of the CL, still it may not give the accurate diffusion transport to the agglomerates since only the fraction of the surface of the agglomerate in contact with gas pore is able to dissolve reactants. In order to account for the effective surface area usable to dissolve the reactants into the agglomerates, a parameter, \( a_{agg} \), is used. \( a_{agg} \) is the ratio between this effective surface area of agglomerate to the catalyst layer volume and can be related to the CL structure by the following relationship[31]:

\[
a_{agg} = N 4 \pi \left( r_{agg} + \delta_{agg} \right)^2 \varepsilon_{cl}
\]
Therefore, this effective area parameter can be used in the mass balance equation source term for oxygen[31].

When the reactants arrive at the catalyst sites inside the agglomerates, they need to dissolve into an infinitesimally thin layer of ionomer which covers the catalyst sites. This layer is assumed to be infinitesimal[31] and the dissolved reactant concentration in membrane phase of the CL, \( C_{r, \text{diss}} \), is calculated by using Henry’s constant, \( H[11, 335] \):

\[
C_{r, \text{diss}} = \frac{C_r}{H}
\]  (3.51)

The dimensionless Henry’s constant for the oxygen gas dissolution in the electrolyte is calculated from the following empirical relation [8, 47, 225, 344]:

\[
H_{O_2} = \frac{1}{RT} \exp \left( \frac{-666}{T} + 14.1 \right)
\]  (3.52)

The experimental data obtained by Parthasarathy et al.[329, 335] was used to correlate the reference exchange current density for ORR on the Pt-electrolyte interface in the following expression as a function of temperature [76, 344]:

\[
i_0^{\text{ref}} = 10^{\left(\frac{3.507 - 4001}{T}\right)}
\]  (3.53)

This expression can be used as the exchange current density with an oxygen reference concentration of \( 0.725 \times 10^9 \) [mol/m\(^3\)]. For dry air at 1 atm and 353 K, it will become \( 2.707 \times 10^{-4} \) [A/m\(^2\)][31].

**Transfer Coefficient**

Parthasarathy et al.[329] reported the rate of change of transfer coefficient with temperature for ORR in Pt/Nafion® system is \( 2.3 \times 10^{-3} \). According to this information and the experimental data[329], the transfer coefficient for ORR as a function of temperature[K] is taken as:
\[ \alpha_c = 0.50 + 2.3 \cdot 10^{-3} (T - 300) \]  \hspace{1cm} (3.54)

**Tafel Slope**

The Tafel slope, \( T_S \), is used when the ORR Butler-Volmer equation is assumed to reduce to Tafel kinetics and it defines the slope in the polarization curve when the natural logarithm of the relationship is taken:

\[ \eta = T_S \ln \left( \frac{i}{i_0} \right) \]  \hspace{1cm} (3.55)

where \( \eta \) is the overpotential, \( i \) is the current density and \( i_0 \) is the exchange current density.

The Tafel slope for ORR depends on on the temperature, the number of electrons transferred in the rate-determining step, \( n_{rds} \) (which is found to be 2 and 1 at low (overpotential<400mV) and high current densities(overpotential>400mV), respectively\[329, 335\]) and the transfer coefficient, \( \alpha_c \):

\[ T_S = -2.303 \frac{RT}{\alpha_c n_{rds} F} \]  \hspace{1cm} (3.56)

The table demonstrating the data for variation of Tafel parameters with temperature for ORR at the Pt/Nafion® interface obtained by Parthasarathy et al.[329] is given below.

For a robust calculation, the value of \( \alpha_a + \alpha_c \) in HOR kinetics is assumed to be equal to 2, while \( \alpha_c = 1 \) in ORR corresponds to a Tafel slope changing between 60-120 mV/decade [42, 156, 329, 345].
Table 3.1. Variation of Tafel parameters with temperature for ORR at the Pt/Nafion® interface [329]

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>$E_r,^\wedge$ mV</th>
<th>Tafel slope $\text{mV/decade}^\circ$</th>
<th>$\log (i_\text{/A/cm}^2)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>1233.4</td>
<td>-65.36</td>
<td>-9.7714</td>
</tr>
<tr>
<td></td>
<td></td>
<td>-123.28</td>
<td>-6.5470</td>
</tr>
<tr>
<td>40</td>
<td>1224.9</td>
<td>-67.60</td>
<td>-9.1347</td>
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<td></td>
<td></td>
<td>-113.86</td>
<td>-6.4880</td>
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<td>1216.6</td>
<td>-68.33</td>
<td>-8.8220</td>
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<td></td>
<td></td>
<td>-119.53</td>
<td>-6.0860</td>
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<tr>
<td>60</td>
<td>1208.2</td>
<td>-69.35</td>
<td>-8.6026</td>
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<td></td>
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<tr>
<td>70</td>
<td>1199.9</td>
<td>-71.24</td>
<td>-8.2566</td>
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<td></td>
<td>-113.76</td>
<td>-5.9600</td>
</tr>
<tr>
<td>80</td>
<td>1191.7</td>
<td>-76.22</td>
<td>-7.7284</td>
</tr>
<tr>
<td></td>
<td></td>
<td>-115.89</td>
<td>-5.8578</td>
</tr>
</tbody>
</table>

$^\wedge$ Reversible potential corrected for temperature and oxygen pressure.

$^\circ$ Calculated for geometric area of the microelectrode (roughness factor of 0.2)

Open Circuit Voltage

Berger [12] proposed the following relation for open cell voltage as a function of temperature:

$$V_{oc} = 1.23 - 0.0009(T - 298)$$  \hspace{1cm} (3.57)

According to the relation above, the equilibrium potential decreases with temperature while the following one used in other references [36, 93, 95, 333] proposes an increase with temperature.

$$V_{oc} = 0.2329 + 0.0025 * T$$  \hspace{1cm} (3.58)

This relationship can be verified by the experimental data obtained by Parthasarathy et al. [329] reporting that the open circuit potential increases with temperature until 80°C while it decreases to 0.7-0.8V at the higher temperatures. Also, it approaches to lower values when the system reaches to SS. The following table [329] indicates the dependency of the open circuit voltage on the temperature after activation and SS.
Since the open circuit voltage is one of the parameters changing the polarization curve obtained by the models significantly, the differences in the formulation would be normal. The theoretical cell voltage decreases with temperature according to the Nernst Law[210]. Meanwhile the reaction rates and consequently the exchange current densities increase with temperature.

Overall, due to the differences in modeling approaches, there are a couple of open circuit voltages relations proposed in the literature and some common ones are given here. The one proposed by Weber et al.[42] may reflect the effect of temperature better when used with the agglomerate model which accounts for the current resistance of the CL structure so it is given in this model description. As a future work, the best relationship can be determined by doing parametric studies with experimental results.

\[
V_{oc} = 4.1868 \cdot \left( \frac{70650 + 8T \cdot \ln T - 92.84T}{2F} \right) \quad (3.59)
\]

For now, the one mostly used in the literature is applied [36, 93, 333]:

\[
V_{oc} = 0.2329 + 0.0025T \quad (3.60)
\]

Effective Protonic Conductivity in CL

In the CL, the effective proton conductivity \( \sigma_{m}^{\text{eff}} \) is modified by Bruggeman factor based on the ionomer content [54, 156, 225]:

**Table 3.2. Variation of open circuit voltage (o.c.p) with temperature and activation[329]**

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>o.c.p. after activation mV</th>
<th>Steady-state o.c.p. mV</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>1005</td>
<td>882</td>
</tr>
<tr>
<td>40</td>
<td>1025</td>
<td>900</td>
</tr>
<tr>
<td>50</td>
<td>1039</td>
<td>916</td>
</tr>
<tr>
<td>60</td>
<td>1083</td>
<td>920</td>
</tr>
<tr>
<td>70</td>
<td>1118</td>
<td>938</td>
</tr>
<tr>
<td>80</td>
<td>1119</td>
<td>962</td>
</tr>
</tbody>
</table>
\[ \sigma^\text{eff}_m = \varepsilon_m^{1.5} \sigma_m \]  

where \( \varepsilon_{\text{ion}} \) is the ionomer volume fraction in CL.

### Effective Electronic Conductivity in GDL

In GDL, the effective electron conductivity \( \sigma^\text{eff}_s \) is modified by Bruggeman factor based on the porosity of the GDL, \( \varepsilon_{GDL} \) [54, 156, 225]:

\[ \sigma^\text{eff}_s = (1 - \varepsilon_{GDL}) \sigma_s \]  

(3.62)

### 3.3.3. Membrane Properties

#### Water content

The water content is formulated by the equation following by using the dry membrane density, \( \rho_m^{\text{dry}} \), the equivalent molecular weight of the membrane, \( EW_m \), the mass concentration of water, \( c_w \), and the molar molecular weight of water, \( M_{H_2O} \) [93, 200]:

\[ \lambda = \frac{EW_m \cdot c_w}{\rho_m^{\text{dry}} \cdot M_{H_2O}} \]  

(3.63)

If the swelling of the membrane is accounted as in Chapter 4, the water content in terms of concentration is represented by the following relationship[57, 337]:

\[ \lambda = \frac{C_w}{\frac{\rho_m}{EW_m} - bC_w} \]  

(3.64)

\( C_w \) is the molar concentration of water in the membrane and \( b \) is an experimentally determined swelling constant coefficient for the membrane.
Both relations are given here since one of the modeling domain (2D MEA) accounts for the swelling of the membrane, the others don’t consider this effect. The modeling domains considered will be given in the next section.

The common used value for a Nafion® membrane is 0.0126[57]. Note that the value of swelling constant is different in different membranes. The common used value for a Nafion® membrane is 0.0126[57].

**Conductivity**

Springer et al. [57] measured the Nafion® 117 conductivity as a function of membrane water content at 30⁰C and corrected with the operating temperature, $T$, as follows:

\[
\sigma_m = \begin{cases} 
\exp \left[ 1268 \left( \frac{1}{303} - \frac{1}{T} \right) \right] \sigma_{30} & \text{for } \lambda > 1 \\
0.1879 & \text{for } \lambda \leq 1
\end{cases}
\]

where $\sigma_{30}$ is the membrane conductivity measured at 30⁰C in units of [S/m] and $T$ is the units of [K]:

\[
\sigma_{30} = 0.5139\lambda - 0.326 \quad \text{for } \lambda > 1
\]

**Water Diffusivity**

The membrane water diffusivity $D_w$ is related to temperature and water content of the membrane with the following relationship of Motupally et al.[314]:

\[
D_w = \begin{cases} 
3.1 \times 10^{-7} \lambda \left[ \exp(0.28\lambda) - 1 \right] \exp(-2346/T), & \lambda \leq 3 \\
4.17 \times 10^{-8} \lambda \left[ 1 + 161 \exp(-\lambda) \right] \exp(-2346/T), & \lambda > 3
\end{cases}
\]

**Electro-osmotic Drag (EOD) Coefficient**

Considering both liquid-equilibrated and vapor-equilibrated membrane conditions, the following relation obtained using the experimental data of Zawodzinski et al.[317] and Springer et al.[57] is used for EOD coefficient[93]:
Viscosity of Water

By using the reference viscosity value, \( \mu_0 = 1.788 \cdot 10^{-3} \text{ kg/(m \cdot s)} \), the viscosity of water as a function of temperature, can be estimated from the empirical relation given in Quan[337]:

\[
\ln \left( \frac{\mu}{\mu_0} \right) = -1.704 - 5.306 \cdot \frac{273}{T} + 7.003 \cdot \left( \frac{273}{T} \right)^2, \quad 273K \leq T \leq 373K
\]

(3.69)

Density of Water

Density of water in the membrane [g/cm³] is calculated as function of temperature[337]:

\[
\rho_w = 1.1603 - 0.0005371 \cdot T
\]

(3.70)

3.3.4. Additional Relations

In order to account for the diffusion through the membrane phase for the reactants in CLs, the diffusivities of the reactants (hydrogen and oxygen, respectively) corrected for the water content, \( \lambda \), of the membrane phase can also be incorporated into the model[346]:

\[
D_{eff, m}^{\text{H}_2} = \varepsilon_m^{CL} \left( 7.16 \cdot 10^{-8} \left( \frac{\lambda}{16.8} \right) \exp \left( -1335/ \frac{1}{T} \right) \right)
\]

(3.71)

\[
D_{eff, m}^{\text{O}_2} = \varepsilon_m^{CL} \left( 2.67 \cdot 10^{-6} \left( \frac{\lambda}{16.8} \right) \exp \left( -2870/ \frac{1}{T} \right) \right)
\]

(3.72)

Moreover, in order to account for the effect of water content in membrane phase of the CLs, an effective water diffusion coefficient in the CLs can be defined [97, 333, 347]:

\[
D_{eff, m}^{\text{H}_2O} = \varepsilon_m^{CL} D_{eff, m}^{\text{H}_2O} + \varepsilon_m^{CL} D_w \frac{RT}{P_{sat}} \frac{d\lambda}{da}
\]

(3.73)
where $D_w$ is the water diffusion coefficient in the membrane phase.

### 3.5. Modeling Domains

The model presented here can be solved in 3D, 2D and 1D with the proper assumptions. Before using the model developed, firstly, an analytical MathCAD analytical model has been developed for a preliminary modeling purpose. Other than the simple MathCAD analytical model, there are two modeling domains considered in this thesis.

The first modeling domain is a 2D MEA model including a novel modified agglomerate/pseudo-homogeneous catalyst layer modeling with consistent treatment of water transport in the MEA. The main objective is to optimize the MEA properties by using this MEA model developed.

The second domain presents a 3D model with different flow field designs. The main objective is to compare the performance between the flow field designs, especially the uniformity of the reactant transport which the first 2D model misses. Moreover, by using ANSYS FLUENT PEMFC Module, the performance of a two-phase straight channel fuel cell will be discussed. The main purpose is to verify the predictive capability of ANSYS FLUENT PEMFC Module for two-phase fuel cell modeling.

The detailed descriptions, boundary conditions (BCs) and results for each model will be given in separate sections or chapters.

**MathCAD Analytical Model**

The analytical model calculates the reversible cell potential at different temperatures and pressures by using the Nernst Equation, then estimates the polarization losses which are activation, ohmic and concentration losses, separately and then subtract them from the reversible voltage obtained. The details of the equations and the properties used in the MathCAD model are given in Appendix C.
In order to investigate the performance prediction of the analytical model, the performances of a Nafion® membrane and a novel composite membrane developed by DOE PEMFC Research Group at UNR are evaluated by using the simulations results compared with the experimental data taken from literature and obtained by the same research group, respectively[348]. The composite membrane was fabricated by using solvent casting technique after mixing specified composition of zirconium sulfate and polymer matrix. The most important advantage of this membrane is the higher temperature range[348]. The membrane electrode assembly (MEA) was fabricated by sandwiching the composite membrane with gas diffusion electrodes (GDEs) which were composed by painting the catalysts on the gas diffusion layer (GDL) [348]. The further details can be found in the DOE report[348]. The performance of the MEA has been tested using single test fuel cell and a polarization curve (I–V curve) has been generated. The operating conditions used in the test are tabulated in Table 3.3.

<table>
<thead>
<tr>
<th>Table 3.3. Physical Properties and Operating Conditions for Experiment with New Membrane</th>
</tr>
</thead>
<tbody>
<tr>
<td>Membrane thickness</td>
</tr>
<tr>
<td>Membrane conductivity</td>
</tr>
<tr>
<td>Equivalent Weight</td>
</tr>
<tr>
<td>Back pressure</td>
</tr>
<tr>
<td>Temperature</td>
</tr>
<tr>
<td>MEA area</td>
</tr>
</tbody>
</table>

The polarization curves obtained by analytical model are compared with the experimental data as given in Figure 3.7. Even if the analytical model doesn’t account for the geometry of the fuel cell, calculation of the polarization losses separately estimates the fuel cell performance in a correct order without wasting any time. Therefore, it can be used for robust prediction of the cell performance at different operating conditions such as temperature and pressure, and the electrochemical properties such as the catalyst loading, the exchange current density and the diffusion coefficients of the reactants.
Figure 3.7. Comparison: Polarizations curves obtained by analytical simulation results for a novel composite membrane and Nafion® membrane and experimental data[295].

This simple model is also useful in investigating the degree of the different polarization losses and the effects of primary model properties on the performance. As can be seen in Figure 3.8, the fuel cell with the new membrane suffers from the ohmic losses due to the low conductivity of the membrane (3.2 S/m) while a Nafion® membrane has an average conductivity about 11 S/m. This figure also shows that
the activation and concentration losses at the cathode are much higher than the ones at the anode. These results agree with the predictions presented in the literature[9].

![Polarization Losses-Composite Membrane](image1)

![Polarization Losses-Nafion® Membrane](image2)

**Figure 3.8.** Comparison of activation, concentration and ohmic losses.
4. 2D MEA MODEL

4.1. Objective and Motivation

The first modeling domain used in this study is a 2D MEA model. The main objective was to develop a fundamental 2D MEA model accounting for treatment of water transport in the MEA. And optimize the MEA properties by using this MEA model developed. The 2D MEA model includes a novel modified agglomerate/pseudo-homogeneous catalyst layer modeling with consistent treatment of water transport in the MEA. For a straight channel fuel cell as shown in Figure 4.1[108], taking advantage of geometric symmetry, the computational domain includes only half of the gas channel and half of the current collector and MEA between two sides of the fuel cell (Section C).

![Figure 4.1. 3D Schematic of a PEMFC with multiple parallel and single straight channels[108].](image)
Section C which is rotated 90° in clockwise direction is shown in Figure 4.2. Using this symmetric section reduces computational requirements for this complex problem.

Figure 4.2. Schematic showing computational domain for 2D MEA Model with dimensions in [mm].

The present study differs from earlier studies in transport modeling, especially in the CL and the membrane. The CL model developed here proposes a novel approach considering the agglomerate structure while using the comparatively more robust and simpler pseudo-homogeneous modeling for CL. Also the water transport through the membrane is accounted by considering the swelling effect and the convection transport which are mostly neglected in the previous models.
4.2. Boundary Conditions

The computational domain for 2D MEA Model is formed by using only half of the gas channel and half of the current collector due to the symmetry of the geometry, as seen in the Figure 4.2. The boundaries and the related BCs are presented below.

Gas channels-GDL interfaces

Since the model geometry doesn’t include the channel domain and the direction of the flow velocity is perpendicular to the MEA model domain considered in the model; the composition of the fluid at gas channel boundaries are taken to be equal to the one in gas channel, therefore; they are defined by using the mole fractions, $x$, and pressure, $P$:

Anode gas channel at $x = 0$, $y = \left[ 0, \frac{W_{ch}}{2} \right]$:

$$
x_{H_2} = x_{H_2}^0 = \left( 1 - x_{H_2}^{0_{H_2O_a}} \right)
$$

$$
P = P_{a}^0
$$

Cathode gas channel at $x = t_{GDL}^a + t_{CL}^a + t_m + t_{GDL}^c + t_{CL}^c$, $y = \left[ 0, \frac{W_{ch}}{2} \right]$:

$$
x_{H_2} = x_{H_2}^0 = \left( 1 - x_{H_2}^{0_{H_2O_a}} \right)
$$

$$
x_{O_2} = x_{O_2}^0
$$

$$
x_{N_2} = x_{N_2}^0 = \left( 1 - x_{O_2} - x_{H_2O_c} \right)
$$

$$
P = P_{c}^0
$$
**Current Collector-GDL Interface**

For the charge conservation, the boundary conditions are constructed either by giving the current density values or potential values on both anode and cathode current collector. The model presented here uses the latter one and in order to have a cell potential \( V_{cell} \) which is essentially the difference of the potential between the cathode and anode size, the potential at the cathode is assigned as \( V_{cell} \) while anode current collector boundary is used as ground potential, 0.

**Anode current collector at** \( x = 0, y = \left[ W_{ch} / 2, W_{ch} / 2 + W_{cc} / 2 \right] \) : \( \Phi_s = 0 \)

**Cathode current collector at**

\[
x = t_{GDL}^a + t_{CL}^a + t_m + t_{GDL}^c + t_{CL}^c, \quad y = \left[ W_{ch} / 2, W_{ch} / 2 + W_{cc} / 2 \right] \quad \Phi_s = V_{cell}
\]

The mass and momentum transport boundary conditions between the bipolar plate shoulders and the gas distribution electrodes are all insulation.

**Symmetry conditions are applied at symmetric boundaries:**

\[
x = \left[ 0, t_{GDL}^a + t_{CL}^a + t_m + t_{GDL}^c + t_{CL}^c \right], \quad y = 0
\]

\[
x = \left[ 0, t_{GDL}^a + t_{CL}^a + t_m + t_{GDL}^c + t_{CL}^c \right], \quad y = \left[ W_{ch} / 2, W_{ch} / 2 + W_{cc} / 2 \right]
\]

**GDL-CL Interfaces**

Since a single-domain approach is used in the solution of the model, the interfaces between the GDL and CL don’t require BCs in order to solve the mass, momentum, species and charge conservation equations. By entering the porous material properties affecting the flow and charge conservation for each layer, a smooth transition is obtained at these interfaces.
CL-Membrane Interfaces

While the gas mixtures on both sides are transported in GDL and CL, due to impermeability assumption of the membrane against the reactant gases, only water is transported in the membrane so only water can enter from the anode and cathode membrane-CL interfaces. The momentum equation still does not need a BC since the pressures at these boundaries are set to be solved for the anode and cathode pressures; however, the BC for the water concentration is required. By considering the hydrophobic nature of the membrane and Schroeder’s paradox and by assuming the water is in equilibrium, equivalent boundary conditions for water content are used. In this approach, in order to calculate the water content at the membrane-CL boundaries, i.e. in order to couple the water concentration in CL-membrane interfaces, the experimental fit between the water content sorbed by the membrane and the water activity in the gas mixture, obtained by Springer et al. [57] is used:

\[ \lambda = \begin{cases} 
0.043 + 17.81a - 39.85a^2 + 36.0a^3 & 0 \leq a \leq 1 \\
14.0 + 1.4(a - 1) & 1 \leq a \leq 3 \\
16.8 & a \geq 3 
\end{cases} \quad (4.1) \]

\( a \) is the water vapor activity given by:

\[ a = \frac{x_w P}{P_w^{\text{sat}}} \quad (4.2) \]

where \( x_w \) is the mole fraction of water, \( P \) is the pressure and \( P_w^{\text{sat}} \) is the saturation pressure at the operating temperature, \( T \).

\( P_w^{\text{sat}} \) is calculated in the units of atm by[57]:

\[ \log_{10} P_w^{\text{sat}} = -2.1794 + 0.02953(T - 273.17) - 9.1837 \times 10^{-5}(T - 273.17)^2 + 1.4454 \times 10^{-7}(T - 273.17)^3 \quad (4.3) \]

The derivative of water content with respect to the water activity which is used to calculate the water diffusivity in membrane phase of CL will be:
\[
\frac{d\lambda}{da} = \begin{cases}
17.81 - 79.70a + 108a^2 & 0 \leq a \leq 1 \\
1.4a & 1 \leq a \leq 3 \\
0 & a \geq 3
\end{cases}
\] (4.4)

4.3. Solution Technique

One of the most significant challenges in fuel cell modeling is to find the appropriate numerical methods to solve the large sets of differential and algebraic equations that are highly nonlinear, complex and stiff. Finite difference, finite element, and finite volume are the methods commonly used in these problems. Commercial computational fluid dynamics packages are also options to run the simulation.

A multiphysics solution package, COMSOL Multiphysics 4.2 along with the Fuel Cell and Batteries Module was used to build 2D MEA Model and solve the non-linear system of equations. COMSOL Multiphysics software uses Finite Element Method (FEM) for computation. The following physics application modes so-called physics interfaces in COMSOL Multiphysics and Fuel Cell and Batteries Module were used for solving the dependent variables given in parentheses:

- Darcy's Law for pressure in the porous GDEs and membrane (p);
- Transport of Concentrated Species along with Maxwell–Stefan multi-component diffusion and convection for mass fraction of oxygen and water at the cathode gas channels and GDE (wO2 and wH2Oc); and mass fraction of hydrogen at the anode gas channels and GDE (wH2);
- Secondary Current distribution interface for charge balance in GDE and membranes (φs,phis and φm,phis);
- General PDE form for water concentration in the membrane (cw).

Please refer to COMSOL Multiphysics and Fuel Cell and Batteries Module documentations [349, 350] for further information about the physics interfaces used.

COMSOL Multiphysics package allows for different mesh elements. 10400 quad elements were used in order to have a grid independent convergent solution with a minimum $10^{-4}$ relative error tolerance for
the base case geometry. A stationary non-linear solver was used together with Direct linear system solver.

Polarization curves were obtained by varying the cell voltage/potential, i.e., $V_{\text{cell}}$: starting with a voltage value close to open cell voltage and decrease the voltage values with a 0.05 V steps. The cell voltage is simply the electrical potential difference between anode and cathode. The anode is generally taken as 0 V and the electrical potential for the cathode gives the cell voltage.

The model mesh was updated when the current mesh was not enough for the convergence of the model, especially in low potentials ($V_{\text{cell}} < 0.7$ V). The 2D simulation for each operating cell potential converged in 200–1500 s, the larger being for the high current density and limiting reactant cases. The majority of the runs were completed under 600 s on an i7 Intel processor with 2.8 GHz CPU with 8GB of DDR2 ram.

4.4. Model Validation

To date, the model validation has been conducted mostly against the cell global polarization (or $I$-$V$) curve, which is an overall performance outcome of many interacting phenomena in the fuel cell. An excellent match with the polarization curve between the simulation and experimental results can be really hard due to the lack of the experimental data of the model parameters when a literature test has been used. Even it is accomplished, the agreement with the current or species distribution may remain unsatisfactory; thus, the validation against global polarization curve may be insufficient and often misleading[156]. Therefore, the current state of experimental validation is to validate comprehensive models against distribution data of multiple parameters, such as current and species distributions[156].
Table 4.1. Geometric Parameters

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas channel width</td>
<td>1 [mm]</td>
</tr>
<tr>
<td>Collector shoulder width</td>
<td>1 [mm]</td>
</tr>
<tr>
<td>Electrode thickness</td>
<td>260 [μm]</td>
</tr>
<tr>
<td>Membrane thickness</td>
<td>230 [μm]</td>
</tr>
<tr>
<td>Electrode porosity</td>
<td>0.6</td>
</tr>
</tbody>
</table>

In order to validate the 2D MEA model, polarization curves with average current densities obtained are compared with the experimental data provided by Ticianelli et al.[295], using the same input parameters. The fuel cell dimensions and operating conditions are tabulated in Table 4.1 and Table 4.2, respectively. As can be seen in Figure 4.3, the model matches with the experimental data for low and moderate current densities. However, since the 2D model does not account for the reactant flow along the channel and the effect of the reactant concentrations decreased along the channel on the performance, and it assumes a constant mole fraction of reactants in the GDL-channel interface, there is a significant difference with the experimental data at high current densities. Note that high current-density performance of a PEMFC is mass transport limited.

Table 4.2. Operating Conditions

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cell Temperature</td>
<td>348[K]</td>
</tr>
<tr>
<td>Anode Pressure</td>
<td>3[atm]</td>
</tr>
<tr>
<td>Cathode Pressure</td>
<td>5[atm]</td>
</tr>
<tr>
<td>Open Circuit Voltage</td>
<td>1.1[V]</td>
</tr>
<tr>
<td>Anode RH</td>
<td>100%</td>
</tr>
<tr>
<td>Cathode RH</td>
<td>100%</td>
</tr>
</tbody>
</table>

According to Secanell[31], for 2D through-the-channel models, like presented here, only experiments performed at very high stoichiometric values for both oxygen and hydrogen can be used for the validation so the commonly used experimental polarization curves at low stoichiometries obtained by Ticianelli et al.[295] cannot be used. However, the experimental curves at high stoichiometries are seldom published, an experimental data from a fuel cell with a serpentine flow field or segmented flow
field can be used for validation since these flow fields provide comparatively more uniform flow along the channels. For this validation, the experimental data obtained by Bender et al. [351] has been used.

![Polarization Curve](image)

**Figure 4.3. Comparison of model performance with experimental results by Ticianelli et al.[295].**

As it can be seen in Figure 4.4, the experimental data obtained in a more uniform flow matches better with the modeling results when the water transport effects on the membrane conductivity and performance are considered. Moreover, the model still seems to predict the performance at lower and medium current density values better when compared to higher current densities. Overall, the 2D MEA model developed is considered satisfactory to predict the fuel cell performance and can be used for parametric study.
4.5. Parametric Study

Before using the model developed here, COMSOL Multiphysics code is first used to model a 2D steady-state cell with two adjacent flow channels of different pressures, which may occur in a cell with serpentine channels or in interdigitated flow field design. This model is directly taken form COMSOL Model Library and modified. It has been shown that among the other catalyst models including interface models and pseudo-homogeneous film models[31], the agglomerate model gives better predictions especially at high current densities, where mass transport limitations become dominant over activation and ohmic losses[18, 75]. However, they require more empirically determined parameters such as agglomerate radius, characteristic length, macroscopic and microscopic porosity inside and between agglomerates, electrolyte (polymer) volume fraction in the catalyst, etc. A parametric study showed that fuel cell performance increases significantly with decreasing agglomerate radius (Figure 4.5).
The main objective of fuel cell research is to increase the performance by developing new technologies or optimizing the performance fuel cell with the current operating conditions [31]. Since the fuel cell performance is usually presented in terms of polarization curve, the performance can be improved or optimized either at a single operating point (either voltage or current density) or for a specified range of operating conditions so-called multi-point optimization [31]. Multi-point optimization, being very challenging due to the complexity of fuel cell modeling and capabilities of the computing environment, is an active area of research.

By using a 2D MEA model, the performance of the MEA, especially the membrane, can be optimized by considering the current density values at fixed voltage values. Therefore, the design variables may be selected regarding the properties of the MEA that can be controlled such as membrane thickness, membrane EW, catalyst loading, GDL porosity, the ionomer/polymer or carbon content of the CL and
the operating conditions affecting the performance significantly like temperature, humidity of the reactant streams and the flow field designs.

In this thesis, the main objective is to optimize the membrane properties, and the selected parameter is membrane conductivity by varying temperature and water content as shown in Table 4.3.

Table 4.3. 2D MEA Model Parametric Study Physical Parameters

<table>
<thead>
<tr>
<th>Physical Parameter</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cell Temperature, T</td>
<td>333/343/353/363[K]</td>
</tr>
<tr>
<td>Anode Pressure</td>
<td>3 atm</td>
</tr>
<tr>
<td>Cathode Pressure</td>
<td>5 atm</td>
</tr>
<tr>
<td>Open Circuit Voltage</td>
<td>(0.2329+0.0025T)[V]</td>
</tr>
<tr>
<td>Anode RH</td>
<td>100%</td>
</tr>
<tr>
<td>Cathode RH</td>
<td>100%</td>
</tr>
<tr>
<td>EW</td>
<td>1.5/2/2.5/3[kg/mol]</td>
</tr>
</tbody>
</table>

4.6. Results & Discussion

4.5.1. Temperature and Water Content Effect on Conductivity and Performance

According to the literature, the cell performance increases with the cell temperature (0-60°C)[9]. The cell performance is computed at different cell temperatures while the membrane conductivity is taken constant (11[S/m]). As can be seen in Figure 4.6, the cell performance slightly increases with temperature (60-90°C).

On the other hand, when the transport of the water and its effect on the membrane conductivity are considered, the trend significantly changes after 70 °C as demonstrated in Figure 4.7.
Figure 4.6. Cell performances at different temperatures with constant membrane conductivity.

Figure 4.7. Cell performances at different temperatures with variable membrane conductivity.
The reason for the significant decrease in the performance at higher temperatures is that the drying/dehydration of the membrane occur on the anode side. As the cell temperature increases, the water activity in the gas phase, the water content in the membrane and accordingly the membrane conductivity decrease and this decreasing trend becomes more significant at higher temperatures (>80°C) since the water content values at the anode side approaches around 5 while it is around 15 at 333 K as seen in Figure 4.8.

Figure 4.8. Water content distributions in MEA at 363 K & 0.5 V and MEA at 333 K & 0.5V.
Figure 4.9[164, 285] explains the reason for the effect of the water content on membrane conductivity. The dramatic increase in the proton conductivity of Nafion® as $\lambda$ approaches 5-6 can be seen in Figure 4.9[164, 285] which depicts the proton conductivity of Nafion® and a sulfonated polyaromatic membrane at room temperature as a function of water content[285].

Figure 4.9. Experimental data for membrane conductivity of Nafion® and sulfonated-polyaromatic membrane as a function of water content, $n$ [285].
5. 3D MODELS with STRAIGHT, STEPPED and TAPERED FLOW FIELDS

5.1. Objective and Motivation

This chapter presents a 3D model with different flow field designs including straight, tapered and stepped. The main objective is to compare the performance between the flow field designs, especially the uniformity of the reactant transport along the channel which the first 2D model lacks. The cross sections of tapered[107, 108] and stepped[114] flow field designs can be seen in Figure 5.1.

![Figure 5.1. Schematic showing 2D views of fuel cell with stepped and tapered channels [108, 114].](image)

In this study, recently proposed flow field designs, tapered and stepped, are compared for the first time. Also, the study reported for the stepped flow field design[114] doesn’t account for some of the modeling elements, such as water transport through the membrane as well the dependencies of membrane conductivity and transport properties on water content, the transport effects of CL structure, etc. which are considered here.

The common physical properties and operating conditions for the models considered are given in Table 5.1 and Table 5.2, respectively. The only difference between the models is the channel design with the
same inlet area and conditions. The outlet height is the half of the inlet height in tapered and stepped flow field designs while it remains the same in a straight channel. According to Min[114], the performance of the stepped flow field does not change significantly after 1 step reduction in the height of the flow channel; therefore, in order to decrease the complexity, here stepped flow field with 1 step reduction is considered and compared with the other flow field designs.

Table 5.1. 3D Model Physical Properties

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cell length</td>
<td>0.02 [m]</td>
</tr>
<tr>
<td>Channel inlet height</td>
<td>0.001 [m]</td>
</tr>
<tr>
<td>Inlet cross section area of channel</td>
<td>0.0002 [m²]</td>
</tr>
<tr>
<td>Outlet area of tapered and stepped gas channel</td>
<td>0.0001 [m²]</td>
</tr>
<tr>
<td>Channel width</td>
<td>0.7874 [mm]</td>
</tr>
<tr>
<td>Rib width</td>
<td>0.90932 [mm]</td>
</tr>
<tr>
<td>GDL thickness</td>
<td>380 [μm]</td>
</tr>
<tr>
<td>Electrode thickness</td>
<td>50 [μm]</td>
</tr>
<tr>
<td>Membrane thickness</td>
<td>100 [μm]</td>
</tr>
<tr>
<td>GDL porosity</td>
<td>0.4</td>
</tr>
<tr>
<td>CL porosity</td>
<td>0.3</td>
</tr>
<tr>
<td>CL membrane content</td>
<td>0.3</td>
</tr>
<tr>
<td>GDL permeability</td>
<td>1.18e-11 [m²]</td>
</tr>
<tr>
<td>CL Permeability</td>
<td>0.59e-10 [m²]</td>
</tr>
<tr>
<td>GDL electronic conductivity</td>
<td>222 [S/m]</td>
</tr>
<tr>
<td>Membrane conductivity</td>
<td>9.825 [S/m]</td>
</tr>
</tbody>
</table>

Table 5.2. 3D Model Operating Conditions

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cell temperature</td>
<td>453 [K]</td>
</tr>
<tr>
<td>Anode inlet flow velocity</td>
<td>0.2 [m/s]</td>
</tr>
<tr>
<td>Cathode inlet flow velocity</td>
<td>0.5 [m/s]</td>
</tr>
<tr>
<td>Anode/Cathode viscosity</td>
<td>1.19/2.46e-5 [Pa s]</td>
</tr>
<tr>
<td>Anode inlet H₂ mass fraction</td>
<td>0.743</td>
</tr>
<tr>
<td>Cathode inlet O₂ mass fraction</td>
<td>0.228</td>
</tr>
<tr>
<td>Cathode inlet H₂O mass fraction</td>
<td>0.023</td>
</tr>
</tbody>
</table>


5.2. Boundary Conditions

The boundary conditions (BCs) used is the same with the ones used in 2D Model except the flow inlet and outlet conditions. The inlet conditions are defined as inlet velocities, \( \mathbf{u}_{\text{in}} \), expressed by using the stoichiometric ratios, \( \xi \) defined at average current density, \( I_{\text{ave}} \):

\[
\left( \begin{array}{c}
\mathbf{u}_{\text{in},a} \\
\mathbf{u}_{\text{in},c}
\end{array} \right)_{\text{inlet}} = \frac{I_{\text{ave}} A_m}{F} \left( \begin{array}{c}
\frac{\xi_a}{2C_{\text{H}_2}A_a} \\
\frac{\xi_c}{4C_{\text{O}_2}A_c}
\end{array} \right)_{\text{inlet}}
\] (5.1)

The \( A_a, A_c \), and \( A_m \) stands for the flow cross sectional areas of the anode and cathode gas channels and the membrane area, respectively while \( C \) is the inlet molar concentration of the reactants, determined by the inlet pressure and humidity according to the Ideal Gas Law.

5.3. Solution Technique

For 3D computations are also obtained by using COMSOL Multiphysics 4.2a along with the Fuel Cell and Batteries Module. The following physics interfaces were used for solving the dependent variables given in parentheses for 3D models:

- Free and Porous Flow Interfaces for pressure and velocity vector at anode and cathode gas channels, GDLs and CLs (\( p, \mathbf{u} \) and \( p_2, \mathbf{u}_2 \), respectively).

- Darcy’s Law for pressure in the membrane (\( p_3 \));

- Transport of Concentrated Species along with Maxwell–Stefan multi-component diffusion and convection for mass fraction of oxygen and water at the cathode gas channels and GDE (\( w_{\text{O}_2} \) and \( w_{\text{H}_2\text{O}_c} \)); and mass fraction of hydrogen at the anode gas channels and GDE (\( w_{\text{H}_2} \));

- Transport of Diluted Species for water concentration in the membrane(\( c_{\text{H}_2\text{O}_m} \));
Secondary Current distribution interface for charge balance in GDE and membranes ($\phi_s$, $\phi_{is}$ and $\phi_m$, $\phi_{im}$).

Please refer to COMSOL Multiphysics and Fuel Cell and Batteries Module documentations[349, 350] for further information about the physics interfaces used.

For 3D models, more than 200000 hexahedral elements were used in order to have a grid independent convergent solution with a minimum $10^{-4}$ relative error tolerance for the base case geometry. A stationary non-linear solver was used together with Direct linear system solver.

Polarization curves were obtained by varying the cell voltage/potential with a 0.05 V steps. The model mesh was updated when the current mesh was not enough for the convergence of the model, especially in low potentials. The 3D simulation for each operating cell potential converged in 300–4000 s, the larger being for the high current density and limiting reactant cases. The majority of the runs were completed under 1500 s on an i7 Intel processor with 2.8 GHz CPU with 16 GB of DDR2 ram.

**5.4. Model Validation**

A 3D model is developed to investigate the transport of reactants and water in the flow channels, GDLs, electrodes and polymer membrane at high temperatures (between 100 °C and 150°C). Water management in PEMFCs plays important role for the design of materials and operating conditions to produce sufficient liquid water to fully hydrate the membrane without flooding. This makes the fuel cell modeling more challenging since it includes multiphase mass transport in catalyst sites, gas diffusion layers and flow channels besides the solution of fundamental equations which consist of conservation of mass, momentum, species and charge coupled with electrochemical processes through source terms to describe reaction kinetics and water transport in polymer electrolyte. Since the Nafion® membrane can actually not be used at temperatures higher than 70 °C, the dependence of membrane conductivity on the water transport is not known; the current model uses a constant conductivity, electro-osmotic drag coefficient, diffusivity coefficient of water for the polymer membrane which actually depends on the
water content in the membrane but the results are satisfactory so far. The polarization curve obtained with different membrane thicknesses is shown in Table 5.2. As expected the performance decreases with increasing membrane thickness and the polarization curve becomes more linear since the ohmic resistance becomes dominant.

![Polarization Plot](image)

**Figure 5.2.** Polarization curve with different membrane thicknesses.

The model defined above was actually a COMSOL Model Library model and it is modified for predictions of different flow field designs at the same physical and operating conditions.

### 5.5. Comparison of Flow Field Designs: Results & Discussion

As mentioned, in this chapter, the performances of the fuel cells with different flow field designs will be compared by predicting the polarization curves and mass transport along the channels. In Figure 5.3, the
polarization curves obtained for 3D, single-phase fuel cell models with straight, tapered and stepped flow field designs are presented.

Figure 5.3. Predicted polarization curves for different flow field designs.

As can be seen in the figure, while the performances are approximately the same for high cell voltages (>0.6 V), a difference in the polarization losses arises at higher current densities or at lower cell voltages; and this difference is significant with stepped flow field design. As can be seen in Table 5.3, at a cell voltage of 0.5 V, the current density value in tapered flow field increases 2% while it increases much more, 18%, in stepped flow field compared to the one obtained in straight flow field design.
Table 5.3. Fuel cell performance comparison of flow fields at cell voltage value of 0.5 V

<table>
<thead>
<tr>
<th>Flow Field</th>
<th>Cell Voltage (V)</th>
<th>Current Density (A/cm²)</th>
<th>Power Density (W/cm²)</th>
<th>Increase in Current (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Straight</td>
<td>0.5</td>
<td>0.615</td>
<td>0.308</td>
<td>–</td>
</tr>
<tr>
<td>Tapered</td>
<td>0.5</td>
<td>0.629</td>
<td>0.314</td>
<td>2.13</td>
</tr>
<tr>
<td>Stepped</td>
<td>0.5</td>
<td>0.726</td>
<td>0.363</td>
<td>18.0</td>
</tr>
</tbody>
</table>

When the power density values predicted are compared, the performance improvement with the stepped flow field becomes more significant. As can be seen in Table 5.4, while the maximum power density occurs at a voltage value of 0.35 V in straight and tapered flow fields, this value occurs at a lower cell voltage value of 0.3 V giving much higher current density. The relative increase of power density becomes around 3% when tapered flow field is used instead of straight flow field, and this value reaches to 20.4 % for stepped flow field design.

Table 5.4. Cell performance comparison of flow fields at their maximum power density obtained

<table>
<thead>
<tr>
<th>Flow Field</th>
<th>Cell Voltage (V)</th>
<th>Current Density (A/cm²)</th>
<th>Maximum Power Density (W/cm²)</th>
<th>Increase in Power (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Straight</td>
<td>0.35</td>
<td>1.065</td>
<td>0.373</td>
<td>–</td>
</tr>
<tr>
<td>Tapered</td>
<td>0.35</td>
<td>1.093</td>
<td>0.383</td>
<td>2.60</td>
</tr>
<tr>
<td>Stepped</td>
<td>0.30</td>
<td>1.562</td>
<td>0.469</td>
<td>20.4</td>
</tr>
</tbody>
</table>

According to the studies done with tapered [107, 108] and stepped [114] flow fields, these flow fields are beneficial in improving the gas flow, local current density distribution, water management and cell performance with an inevitable penalty of pressure losses. On the other hand, the pressure losses obtained in tapered and stepped flow fields, respectively, were found to be approximately 2[107, 108] to 1.5 [114] times of a typical pressure loss in a straight channel for a geometry of which the exit area is half of the inlet area. Unfortunately, none of these studies have compared the cell performance
quantitatively by using the polarization curves obtained with straight flow field design. Therefore, a well-established comparison of the simulations results obtained in this study with the literature values is not possible except the pressure loss. The pressure loss is found to be around 8 Pa, 29 Pa and 23.5 Pa in the simulations done with straight, tapered and stepped flow fields, respectively and these values agree with the literature in terms of order of magnitude. It should be noted that the channel lengths used in these studies (0.0762 m in tapered[107, 108] and 0.06 m in stepped[114]) are 3 to 4 times of the one used in this study (0.2 m); therefore, a direct comparison is not possible.

In summary, according to the simulation results (Figure 5.3), the stepped flow field demonstrates a better performance at the higher current densities compared to the straight and tapered flow fields. Since the polarization losses are mainly caused by mass transport limitations at higher current densities, this difference is thought to be caused by the mass transport enhancement with the stepped flow field design. The enhancement obtained with the tapered flow field may not be as significant as the stepped flow field since the flow field channel length used in the model is not long enough. In addition to the polarization performance, stepped flow field design also gives a lower pressure drop compared to the tapered flow field.

In order to investigate the difference in the mass transport, the reactant concentrations at the active areas along the channels can be analyzed. On the other hand, a longer gas channel length than the used one in the model presented is to be used in the simulations in order to explore the enhancement to be obtained with the tapered flow field.
Figure 5.4. Schematic showing the molar concentration of oxygen at a low voltage, 0.10825 V, in the fuel cell with tapered channel flow field design.

As seen in Figure 5.3, the current density for voltages lower than 0.15 V has not been displayed for straight and tapered flow fields. The reason behind this is that the fuel cell reactants (especially oxygen) are depleted in the active areas due to the high consumptions at high current densities. This situation can be demonstrated in Figure 5.4 and Figure 5.5. Along the channel, the molar concentration of oxygen is almost zero at the cathode GD and CL. The current cannot be produced without at least one of the reactants and this prevents the convergence of the computation. Although, there is enough oxygen fed into the channels, due to the nonuniform distribution of the reactants, the polarization caused by the mass transport limitations and parasitic currents increases and this decreases the cell voltage.
Figure 5.5. Schematic showing the molar concentration of oxygen at a low voltage, 0.11025 V, in the fuel cell with straight channel flow field design.

On the contrary, the oxygen distribution is more uniform in the stepped flow field design as can be seen in Figure 5.6 and accordingly, the cell performance is higher at the current density values where the other two flow field designs face mass limitation problems.

On the other hand, the reason not having convergent current density values at the cell voltage values lower than 0.3 V in the polarization curve is considered to be fluid dynamic related rather than mass limitation. Due to the possible flow instability created by the steps, the convergence of the simulations cannot be obtained unless the exact reason behind this and its solution are found. The studies investigating the reason of divergence and instability are in progress.
Figure 5.6. Schematic showing the molar concentration of oxygen at voltage of 0.3 V, in the fuel cell with stepped channel flow field design.

The comparison of the performances of these three flow field designs can be improved by using longer gas channel length and simulating the reactant distributions with different properties in order to understand the combined effects of the physical and geometric properties on the fuel cell performance.
6. TWO-PHASE STUDY using ANSYS FLUENT FUEL CELL MODULE

6.1. Objective and Motivation

A 2-phase version of the 3D model with the straight flow field is computed by using ANSYS FLUENT PEMFC Module which is defined below. ANSYS FLUENT PEMFC Module is well-established package with a robust calculation; however, it is not fully validated, especially for two-phase modeling in fuel cells. The main purpose is to verify the predictive capability of ANSYS FLUENT PEMFC Module for two-phase fuel cell modeling.

6.2. Introduction to ANSYS FLUENT PEMFC Module

The PEMFC Module is an add-on module based on FLUENT CFD package using Finite Difference Method (FDM) for computations. While the basic governing equations related to the mass, momentum and energy transport are solved by FLUENT CFD solver as usual, the other constitutive relations unique to fuel cell application, related to electric potential and current as well as electrochemical reactions are computed with additional equations coming with the add-on module. For additional details, it can be referred to ANSYS FLUENT Fuel Cells Modules Manual[352]. Although the governing equations used in the module are very similar to the ones presented in this thesis, there are important differences, especially in the constitutive relationships. Main differences are given in Table 6.1.

Table 6.1. ANSYS FLUENT PEMFC Module vs. COMSOL Multiphysics and Fuel Cell Module

<table>
<thead>
<tr>
<th>FLUENT vs. COMSOL</th>
<th>ANSYS FLUENT PEMFC Module</th>
<th>COMSOL Multiphysics &amp; Batteries and Fuel Cell Module</th>
</tr>
</thead>
<tbody>
<tr>
<td>Computation Method</td>
<td>Finite Difference Method (FDM)</td>
<td>Finite Element Method (FEM)</td>
</tr>
<tr>
<td>Mesh and Geometry Creation</td>
<td>Complex and comprehensive</td>
<td>Simple but limited</td>
</tr>
<tr>
<td>Flexibility in FC Modeling</td>
<td>Only for modeling PEMFCs</td>
<td>All types of FCs (PEMFC in this study)</td>
</tr>
<tr>
<td>Catalyst Layer Modeling</td>
<td>Pseudo-homogenous model</td>
<td>Any kind of model (modified agglomerate/ pseudohomogeneous in this study)</td>
</tr>
<tr>
<td>Membrane modeling</td>
<td>Springer's model (modifications can be done by using User Defined Functions(UDFs))</td>
<td>Any kind of model(Springer's model in this study)</td>
</tr>
</tbody>
</table>
The additional feature of the module is that the two phase effects can be accounted by the saturation model based on Nam and Kaviany[129] and Nguyen[353] used in order to model the formation and transport of liquid water. In this approach, the liquid water formation and transport is governed by the following conservation equation for the volume fraction of liquid water, \( s \), or the water saturation[352]:

\[
\frac{\partial (\varepsilon \rho_l s)}{\partial t} + \nabla \cdot \left( \rho_l V_l s \right) = r_w \tag{6.1}
\]

where the subscript \( l \) stands for liquid water.

\( \varepsilon \) and \( \rho_l \) represent the porosity and the density liquid water, respectively. \( r_w \) is the condensation rate and it is modeled as[352]:

\[
r_w = c_r \max \left[ \left( 1 - s \right) \frac{P_{wv} - P_{sat}}{RT} M_{w,H,\rho}, -s \rho_l \right] \tag{6.2}
\]

\(-r_w\) is added to the water vapor equation, as well as the pressure correction (mass source) while it is not applied inside the membrane[352]. \( c_r \) is the condensation rate constant with a default value of 100s\(^{-1}\). \( P_{wv} \) and \( P_{sat} \) stand for the local water vapor pressure and the saturation pressure of water at temperature \( T \), respectively. It is assumed that the liquid velocity, \( V_l \), is equivalent to the gas velocity inside the gas channel (i.e., a fine mist) [352].

Inside the porous zones which are GDL and CL, the convective term in the Eqn.(6.1), is replaced by the use of the capillary diffusion term and Eqn.(6.1) takes the following form[352]:

\[
\frac{\partial (\varepsilon \rho_l s)}{\partial t} + \nabla \cdot \left( \rho_l \frac{K_{s^3}}{\mu_l} \frac{dP}{ds} \nabla s \right) = r_w \tag{6.3}
\]

\( K \) is the absolute permeability of the porous medium while \( K_{s^3} \) term represents the relative permeability of the liquid phase as described in Section 2.4. \( \mu_l \) is the viscosity of liquid water.
Depending on the wetting properties of the porous medium, i.e. hydrophobicity and hydrophilicity, the capillary pressure, $P_c$, is computed as a function of the wetting phase saturation by the use of Leverett-J function[352]:

$$P_c(s) = \sigma \cos \theta_c \left\{ \begin{array}{ll}
(1.417(1-s) - 2.120(1-s)^2 + 1.263(1-s)^3) & \text{if } \theta_c < 90^\circ \\
(1.417s - 2.120s^2 + 1.263s^3) & \text{if } \theta_c > 90^\circ 
\end{array} \right. \left( \frac{K/\varepsilon}{(K/\varepsilon)^{1/2}} \right)$$

(6.4)

where $\sigma$ and $\theta_c$ represent the surface tension [N/m²] and the contact angle, respectively.

In addition to the processes such as vapor condensation, water vaporization, capillary diffusion and surface tension modeled by using the approach explained above, the clogging of the porous media and the flooding of the reaction surface are modeled by multiplying the porosity and the active surface area by $(1 - s)$ which is the volume fraction remained for gas transport[352].

### 6.3. Preliminary Modeling Studies

For the preliminary modeling studies, FLUENT software has been used for solver and post processing and GAMBIT for geometry creation and mesh generation as a preprocessor. FLUENT has implemented an add-on module called PEMFC which is used for polymer electrolyte membrane fuel cell modeling. After the geometry and mesh are generated in GAMBIT, the relevant zones for the modeling domains which are current collectors, flow channels, gas diffusion layers, catalyst layers and membrane can be identified easily by using this module. The input for the module is either the cell voltage or the average current density. The cell voltage is simply the electrical potential difference between anode and cathode. The anode is generally taken as 0 V and the electrical potential for the cathode gives the cell voltage. In addition, the flow rates and conditions at the inlet are given as well as the boundary conditions at the outside walls. The default membrane for the module is Nafion®TM.
In order to verify the PEMFC module developed by FLUENT, firstly, a simple 3D model single straight channel counter-flow PEM fuel cell- was developed by using a tutorial published by ANSYS FLUENT and the results obtained were examined. 3D view of the geometry and 2D view of the mesh generated can be seen in Figure 6.1.

The default model parameters with their descriptions are given in Appendix D.

![Figure 6.1. a) 3D View of Geometry, b) 2D View of Mesh for Straight-Channel PEMFC.](image)

The physical validity of the model was aimed to be tested through comparison with experimental data of polarization curve. The input for the model is the cell voltage and consequently, the result obtained is the average current density. The open circuit voltage is 0.95 V. In order to obtain a polarization curve, electrical potential for the cathode should be varied by starting from a voltage near the open circuit voltage and gradually decreasing it while the program converge a solution for the average current density for each cell voltage. The polarization and power curves obtained for cell voltages varying between 0.95 V and 0 V can be seen in Figure 6.2. Comparisons of the computed result with the experimental data in literature indicate agreement in the overall polarization curve with the exception of the limiting current density and the maximum power amount which are higher than the ones in all
experimental test data obtained in the literature. The reason for these is proposed to be the exchange
current density values; they are larger than the values published in the literature.

![Figure 6.2. PEMFC Polarization and Power Curves for Straight-Channel PEMFC.](image)

6.4. Model Validation

In order to verify the validation of the model developed in FLUENT PEMFC Module, firstly, a steady state
fuel cell model with a straight channel geometry is developed with the properties taken from Siegel et
al. model[18].

![Figure 6.3. PEMFC with single straight channel geometry built in ANSYS Design Modeler.](image)
The geometry creation and mesh generation of fuel cell with single-straight channel have been completed by using ANSYS Design Modeler and Meshing (Figure 6.3). There are a number of methods for measuring mesh element quality. The most important ones are skewness and aspect ratio. The skewness is a measure of the relative distortion of an element compared to its ideal shape and is scaled from 0 (Excellent) to 1 (Unacceptable)[95]. The "aspect ratio" is a measure of the stretching of a cell, and is defined as the ratio of the maximum distance between the cell centroid and face centroids to the minimum distance between the nodes of the cell[80]. For CFD calculations, the aspect ratio should be smaller than 100. The meshes generated are acceptable since the maximum skewness is not more than 0.4 and the maximum aspect ratio is at around 6.

Table 6.2. Physical parameters and physical conditions used in FLUENT Model[18]

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas channel length (mm)</td>
<td>66</td>
</tr>
<tr>
<td>Gas channel width (mm)</td>
<td>2.0</td>
</tr>
<tr>
<td>Gas channel height (mm)</td>
<td>2.0</td>
</tr>
<tr>
<td>GDL thickness (mm)</td>
<td>0.175</td>
</tr>
<tr>
<td>Membrane thickness (mm)</td>
<td>0.127</td>
</tr>
<tr>
<td>Catalyst layer thickness (mm)</td>
<td>0.1</td>
</tr>
<tr>
<td>Collector thickness (mm)</td>
<td>3.0</td>
</tr>
<tr>
<td>GDL porosity (-)</td>
<td>0.5</td>
</tr>
<tr>
<td>Catalyst layer porosity (-)</td>
<td>0.09</td>
</tr>
<tr>
<td>Specific area of catalyst layer (1/mm)</td>
<td>8000</td>
</tr>
<tr>
<td>Ref. anode exchange current density (A/m²)</td>
<td>5.0</td>
</tr>
<tr>
<td>Ref. cathode exchange current density (A/m²)</td>
<td>6.00E-04</td>
</tr>
<tr>
<td>Oxygen reference concentration (mol/m³)</td>
<td>4.55</td>
</tr>
<tr>
<td>Hydrogen reference concentration (mol/m³)</td>
<td>21.7</td>
</tr>
<tr>
<td>Open circuit voltage (V)</td>
<td>1</td>
</tr>
<tr>
<td>Permeability of GDL (1/m²)</td>
<td>5.68E+10</td>
</tr>
<tr>
<td>Permeability of catalyst layer (1/m²) [36]</td>
<td>1.00E+14</td>
</tr>
<tr>
<td>Anode inlet pressure (psig)</td>
<td>24.9</td>
</tr>
<tr>
<td>Cathode inlet pressure (psig)</td>
<td>25.5</td>
</tr>
<tr>
<td>Anode flow rate (SLPM)</td>
<td>2.5</td>
</tr>
<tr>
<td>Cathode flow rate (SLPM)</td>
<td>50</td>
</tr>
<tr>
<td>Anode Relative Humidity (%)</td>
<td>65</td>
</tr>
<tr>
<td>Cathode Relative Humidity (%)</td>
<td>50</td>
</tr>
<tr>
<td>Cell temperature (K)</td>
<td>348</td>
</tr>
</tbody>
</table>
Predictions of the model are compared with the published results by Siegel et al.[18] accounting for species transport, electrochemical kinetics, current distribution and water uptake with a similar geometry and well-defined properties matching with the module input properties. With the exception the permeability value of catalyst layer[36] which is not a model parameter in the work of Siegel et al.[18], the geometry, physical parameters and conditions used in the model presented in this work are matched. The physical parameters and physical conditions used in the model are tabulated in Table 6.2.

First the model predictions are compared for two different catalyst porosity values at cell voltage of 0.5V. Current densities predicted by the presented model are slightly higher than the values reported by Siegel et al. [18], 1.1% for 0.09 porosity and 4.4% for 0.04 porosity (Table 6.3). The difference can be attributed mainly to the different domain approaches of two models. The compared model uses single domain consisting of all computational domains while 3-D governing equations are solved separately in FLUENT. In addition, compared model is two dimensional and uses only 35 x 147 elements whereas our model is three dimensional and is divided into 1420000 elements.

<table>
<thead>
<tr>
<th>Catalyst Porosity (-)</th>
<th>Cell Voltage (V)</th>
<th>Current Density Computed (A/cm²)</th>
<th>Current Density Compared (A/cm²)</th>
<th>Relative Error (%)</th>
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</thead>
<tbody>
<tr>
<td>0.09</td>
<td>0.5</td>
<td>0.363</td>
<td>0.367</td>
<td>1.0899</td>
</tr>
<tr>
<td>0.04</td>
<td>0.5</td>
<td>0.348</td>
<td>0.364</td>
<td>4.3956</td>
</tr>
</tbody>
</table>

The polarization curve predicted by the model and its comparison with the test results is shown in Figure 6.4. The model matches with the test results, especially at the lower current densities (<0.3 A/cm²) or higher cell voltages (>0.65 V).
The discrepancy to be seen at the lower cell voltages, in other words at the higher current densities may be due to different approaches in catalyst layer modeling. The compared model [18] uses agglomerate model for the CL, the heart of the chemical reactions that seriously affects the polarization, while the FLUENT PEMFC Module models it as a diffusing medium without considering its micro-geometry rather than a reactive boundary, similar to pseudo-homogenous CL modeling. It’s well known that the utilization of catalyst particles is very important since CL can become current limiting at high current densities due to its low intrinsic porosity. Catalyst layer can become further limited by a liquid drop in porosity due to flooding at the cathode. In the present model the liquid water is taken as a parameter, liquid water saturation, which describes as the ratio of the liquid volume to the pore volume of the porous medium. This approach can account for the liquid saturation effects to some degree but cannot fully demonstrate the flooding at the cathode; therefore, it probably cannot fully reveal the effect of
liquid water on PEMFC performance and overestimates the fuel cell performance. Also the FLUENT PEMFC Module uses permeability as a parameter for the catalyst layer which is hard to define and determine. As it can be seen FLUENT PEMFC Module creates approximately linear profile for the polarization curve implying that it cannot take into considerations of mainly transport/concentration limitations correctly which mainly depend on catalyst structure, accordingly modeling approach. This also explains the similarity of the results obtained at the voltage above 0.5 V where the ohmic losses are dominant.

Since the agglomerate model cannot be incorporated into the FLUENT PEMFC Module settings, as a future work, the model validation may be done with an experimental data not affected by the catalyst geometry that much. On the other hand, since ANSYS FLUENT PEMFC Module provides a well-defined two phase modeling for PEMFCs at low current densities, the two-phase modeling capabilities of the module can be used by having parametric studies affecting the two-phase flow such as relative humidity (RH) values of the reactant feeds especially air or oxygen RH.
7. GENERAL DISCUSSION, CONCLUSION AND FUTURE WORK

7.1. Discussion

PEMFCs are one of the most promising energy conversion systems in many applications due to their high efficiency, low emissions, fuel flexibility, reliability, low maintenance need and cogeneration capability. The performance of a fuel cell is generally expressed by the polarization curve which gives the relationship between the current density and cell voltage and it is known that it is highly affected by reactant distribution, water and heat management and electrochemical properties mainly determined by the catalyst layer and membrane properties. Therefore, fuel cell research mainly focuses on developing new materials for catalyst layers and membranes, improving the reactant transport towards the active areas where the electrochemical reactions occur and managing the heat and water produced. Fuel cell modeling plays a very significant role in determining the way the new materials developed, the best configuration for the reactant transport and the optimum operating conditions of the fuel cell.

While being very important and necessary in fuel cell research and design, fuel cell modeling is not an easy task since there are different operating conditions and physical parameters affecting the overall cell performance in a non-linear manner and there is a strong need for a multidisciplinary knowledge, interaction and integration due to complex phenomena occurring in the fuel cell.

In this thesis, a general representation of CFD model of PEMFC accounting for the mass transport, momentum transport, and electrochemical processes occurring in the membrane electrolyte and catalyst layers as well as water transport through the membrane has been developed. The main objective was to develop a comprehensive, computational model which can be a used as a design tool while being robust and efficient. To some degree, this objective is fulfilled by developing a 2D MEA model with a novel agglomerate/pseudo-homogenous CL model that can be used to optimize MEA properties. 3D models with different flow field designs are developed to investigate the mass transport
mechanisms and their effects on the performance. Finally, a two phase model was used to explore the operating conditions for enhanced water and heat management.

The model descriptions used in the computational models (1D, 2D and 3D), are different from each other. Therefore, among them, the results obtained cannot be directly compared. In 3D models, the computational challenges prevented the use of complex modeling employed in 2D model. For instance, the membrane model used in 2D model accounts for the convection mechanism of water transport and swelling effect of membrane material which are not considered in 3D models. Similarly, the comparison between 3D single phase model (COMSOL model) and 3D two phase model (FLUENT model) was not possible due to the different modeling approaches used as summarized in Table 6.1.

Among the many MEA properties, the membrane conductivity has been selected and their effects on the fuel cell performance have been investigated by using the 2D MEA model. The results showed that the membrane conductivity is strongly dependent on the water transport and temperature. Sufficient water content is necessary not only for a high value of membrane conductivity but also for more uniform ionic and electronic current conduction. It should be noted that a nonuniform ionic or electronic current conduction may cause parasite currents through the fuel cell components and thus, deteriorate the overall performance. Temperature plays an important role for the saturation of water which affects the water activity and water content in the membrane and changes the membrane conductivity drastically, especially at low water contents.

CL is the most complex component of the fuel cell since it is a three-phase boundary medium accomplishing two important tasks: enabling the electrochemical reactions with catalyst particle and reactants diffused through its pores while transporting the ions and electrons to opposite directions with the agglomerates formed by polymer and carbon pellets. The ratios of catalyst particles, polymer (essentially the membrane) and carbon composing the CL and the remaining pores needed for reactant
transport have an important effect on the performance and these components of CL should have an optimum combination for an optimum performance. The simulations can be performed by using the 2D MEA Model in order to determine the optimum ratio of polymer content in the CL.

Different flow field designs have been investigated in order to have a uniform reactant distribution and accordingly decrease the mass transport related polarization losses. The reactant depletion along the flow channel is unavoidable; however, the negative effect of this decrease can be minimized by making the reactant flow more uniform. Serpentine flow field was proposed for this purpose but due to the high pressure losses and pumping power, the research of new flow field designs such as stepped and tapered flow fields have continued. According to the results, these flow fields provide better transport of reactants towards the active areas and increase the cell performance at the higher current densities where the concentration losses become dominant. The stepped flow field having higher current density and higher power density was found to improve the performance better due to more uniform reactant distribution along the channel and also gives lower pressure drop compared to the tapered flow field. On the other hand, it is inevitable to have higher pressure losses for both flow field designs when compared to straight flow field design. On the other hand, the lack of the modeling studies with different flow fields is that the model results with either tapered or stepped flow field designs have not been validated by experimental results yet. Therefore, the results can be better analyzed after a validation study. Moreover, the comparison of the performances of these three flow field designs can be improved by using longer gas channel length and simulating the reactant distributions with different properties in order to understand the combined effects of the physical and geometric properties on the fuel cell performance.

Two phase model developed by using ANSYS FLUENT PEMFC Module are validated for lower current densities but there is an increasing difference in the predicted performance at higher current density
values. This may be caused by the catalyst model approach and the incapability of the two phase modeling approach in the FLUENT PEMFC Module.

### 7.2. Conclusion

The main conclusions obtained by the modeling studies presented in this thesis are summarized below:

- The presented 2D MEA model can be used to optimize MEA properties in order to have an enhanced fuel cell performance.
- Temperature plays an important role in fuel cell performance by significantly affecting the membrane conduction capability as well as the reaction kinetics.
- Uniform reactant distribution is very significant for the fuel cell performance at the higher current densities where the mass transport limitations are dominant and the flow field design can be very effective in improving the reactant transport and performance.
- ANSYS FLUENT PEMFC Module is not capable of predicting at higher current densities and a well-established two-phase flow model is necessary in order to predict the entire fuel cell polarization curve.

### 7.3. Future Work

The aim of computational fuel cell modeling is making it possible to investigate complex geometries and different situations in less time with less effort than the experimental investigations; however, the model developed requires validation based on the experimental data. Available experimental data and mathematical models have been obtained for very restricted and idealized situations. Therefore, there is still a need for both experimental and numerical studies to be conducted and compared with each other in order to describe complete fuel cell system.

Especially for transport modeling within the membrane, the following tasks should be accomplished:
Measurement of more conductivity data over a range of temperatures and as a function of water content,

Experimental investigation of the membrane water transport properties such as diffusion coefficient and EOD coefficient as well as the detailed validation of Electro-Neutrality assumption in the membrane,

A more sophisticated membrane model such as the binary friction model [164] by having more experimental data on related transport properties of water and the reactants,

Data collection for different operating conditions.

As a future work, the next step in improving the current model will be to include the water transport in the membrane using conductivity, electro-osmotic drag coefficient and diffusion coefficient as a function of water content in a new membrane synthesized for high temperature applications. Thus, in order to predict the fuel cell behavior with the new membrane better, the transport properties of the new membrane such as electro-osmotic drag coefficient and water diffusion coefficient will be determined by using a hydrogen pumping cell method proposed by Ye and Wang [271]. The constant membrane conductivity given in the Table 3.3 has been determined by the DOE research group by using HFR method.

In addition to the water transport properties, the effect of the following properties can be investigated with the parametric studies using the presented model in order to optimize the MEA performance:

- Membrane swelling coefficient,
- Membrane density,
- Equivalent weight,
- Polymer, carbon and catalyst weight ratios in CL,
- Effective conductivity of CL,
- GDL porosity and permeability.

A comprehensive and sophisticated fuel cell model accounting for all of the phenomena occurring in an operating fuel cell, is not easy to be computed, since the performance depends on these coupled phenomena and is controlled by a large number of parameters having competing effects on different physical phenomena. For instance, increasing temperature enhances the reaction kinetics; on the other hand, it may deteriorate the performance of membrane by decreasing the water content in the membrane. Therefore, in order to have an optimum design, all design parameters are altered simultaneously by using parametric studies for one or two design parameter. However, when the number of design parameters increases, it becomes almost impossible. Therefore, more robust and effective optimization techniques should be developed.

In addition to the optimization techniques, the convergence and instability issues should be investigated more deeply in order to take advantage of the modeling more efficiently.

In this study, the main focus is on developing a well-defined fuel cell model accounting for most of the phenomena occurring in the fuel cell. Therefore, the investigation of the effect of parameters used in the modeling should be more broadened. More parametric studies on operating conditions such as temperature, pressure, humidity, flow rates, velocity; and geometric properties such as channel length, height, width, rib length, bipolar plate thickness, porous media thickness should be performed. It should be noted that the further validation of model requires the test data collection on different operating conditions and geometric parameters.

The 2D MEA model presented here is based on an agglomerate/pseudo homogeneous CL model and a semi-empirical membrane model mostly based on the model of Springer et al.[57] which is the most widely used one. Reaction kinetics mostly relies on the CL modeling which requires a large number of experimental parameters. Most of these parameters heavily depend on operating conditions and may
change with a slight modification of membrane or GDL material. Therefore, for a better CL model depicting the reaction kinetics, more experimental data should be collected for different catalyst layer configurations at different operating conditions.

The COMSOL models developed is single–phase which does not take the water transport and possible flooding in the fuel cell components into account. ANSYS FLUENT PEMFC Module is not good enough since it lacks agglomerate catalyst layer model and a well-established two-phase flow model. Therefore, the models presented in this thesis are capable of predicting the fuel cell performance at low and medium current densities and SS operation; however, they are not satisfactory enough at high current densities and they don’t account for the transient effects at all. Therefore, two phase modeling and transient modeling can be implemented into the current model developed as a future work.
APPENDICES
## APPENDIX A

### Summary of Models Presented

<table>
<thead>
<tr>
<th>Year</th>
<th>Type</th>
<th>Phase</th>
<th>Temperature</th>
<th>Description</th>
<th>Page</th>
</tr>
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<tbody>
<tr>
<td>1990</td>
<td>1D</td>
<td>SS</td>
<td>Single-phase</td>
<td>Isothermal</td>
<td>Cathode Membrane &amp; GDL</td>
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<td>1991</td>
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<td>Membrane, Anode &amp; Cathode (both, as only one domain)</td>
</tr>
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<td>1992</td>
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<td>Membrane, Cathode CL &amp; GDL, Anode CL</td>
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<td>1992</td>
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<td>SS</td>
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<td>Non-isothermal</td>
<td>Membrane, Cathode CL &amp; GDL, Anode CL &amp; GDL</td>
</tr>
<tr>
<td>1993</td>
<td>2D</td>
<td>SS</td>
<td>Single-phase</td>
<td>Isothermal</td>
<td>Membrane with electrode layers with gas channels</td>
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<td>1995</td>
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<td>Isothermal</td>
<td>Membrane, Cathode CL &amp; GDL, Anode CL &amp; GDL</td>
</tr>
<tr>
<td>1998</td>
<td>2D</td>
<td>SS</td>
<td>Single-phase</td>
<td>Non-isothermal</td>
<td>Whole fuel cell</td>
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<tr>
<td>1998</td>
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<td>SS</td>
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<td>Membrane &amp; Electrodes (anode &amp; cathode)</td>
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<td>Microscopic model of catalyst layer</td>
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<td>SS</td>
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<td>Isothermal</td>
<td>Cathode Electrode &amp; Cathode interdigitated gas channels</td>
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<td>1999</td>
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<td>Cathode Electrode &amp; Cathode gas channels (interdigitated)</td>
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<td>Cathode GDL, Cathode CL</td>
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<td>Isothermal</td>
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<tr>
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<td>2D</td>
<td>Transient</td>
<td>Two-phase</td>
<td>Isothermal</td>
<td>Cathode, Cathode gas channel &amp; Cathode bipolar plate</td>
</tr>
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<td>Single-phase</td>
<td>Isothermal</td>
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<tr>
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<td>Cathode CL, GDL and Gas channel</td>
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<td>Whole fuel cell with parallel straight-flow gas channels</td>
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<td>Whole fuel cell with bipolar plates</td>
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<tr>
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### Summary of Models Presented Cont’d.

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<td>[99]</td>
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<td>Isothermal Whole fuel cell</td>
<td>[126]</td>
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<td>[137, 138]</td>
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<td>[101]</td>
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<td>[139]</td>
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<td>[92]</td>
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<td>Isothermal Membrane, Cathode CL &amp; GDL, Anode CL &amp; GDL</td>
<td>[127]</td>
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<td>Isothermal Whole fuel cell with bipolar plates</td>
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<td>[112]</td>
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APPENDIX B

Proton Transport in the Membrane

Similar to water transport, proton transport in the membrane also obeys the following mass conservation principle:

$$\nabla \cdot \mathbf{N}_p = 0$$  \hspace{1cm} (A. 1)

where $\mathbf{N}_p$ is the molar flux of proton across the membrane.

In order to describe the proton transport in the membrane Nernst-Planck equation is used. Nernst-Planck accounts for the migration due to an electric potential, diffusion due to concentration and convection due to the velocity of water in the membrane [8, 67, 337]:

$$\mathbf{N}_p = -z_p u_{m,p} FC_p \nabla \Phi_m - D_p \nabla C_p + C_p \mathbf{U}_i$$  \hspace{1cm} (A. 2)

where $z_p$ is the charge of proton (=$1$), $D_p$ is the proton diffusion coefficient, $C_p$ is the molar concentration of protons and $\mathbf{U}_i$ is the convective velocity of liquid water estimated by Schlogl equation[67, 337]:

$$\mathbf{U}_i = E_w \left( \frac{k_\Phi}{\mu_i} z_f C_f \nabla \Phi_m - \frac{k_p}{\mu_i} \nabla P \right)$$  \hspace{1cm} (A. 3)

Where $k_\Phi$ and $k_p$ denote the electric and hydraulic permeabilities, respectively; $z_f$ is the charge number of the fixed charges (sulfonic acid groups)(=$1$); $C_f$ is the fixed charge concentration in the membrane and $\mu_i$ is the liquid water viscosity.

This equation considers two different water mechanisms: the electro-osmotic drag, whereby protons migrating through the membrane drag water molecules with them, and pressure driven flux, which is usually directed from the cathode side to anode side. Strictly speaking, a diffusive term should be accounted for as well, however, comparing with the migration and pressure gradient effects, this term is neglected to simplify the model formulation. In addition, one should note that under SS[337]:

$$\nabla \cdot \mathbf{U}_i = 0$$  \hspace{1cm} (A. 4)

Mobility of the protons, $u_{m,p}$, can be written as[337]:

$$u_{m,p} = \frac{D_p}{RT}$$  \hspace{1cm} (A. 5)

Membrane conductivity is defined as[337]:

...
\[ \kappa = \frac{F^2}{RT} D_p C_p \]  

(A. 6)

Electro-Neutrality Condition is assumed:

\[ z_f C_f + z_p C_p = 0 \Rightarrow C_f = C_p \]  

(A. 7)

Thus, the molar concentration of the protons is equal to the molar concentration of the fixed charges so it is a constant.

The proton concentration varies with the variation of the hydration in the membrane and the functional relation between them:

\[ C_p = \frac{\rho_m^{\text{dry}}}{b \lambda + 1} \Rightarrow C_p = \frac{\rho_m^{\text{dry}}}{EW} - bC_w = C_f = C_{\text{SO}_4^{2-}} \]  

(A. 8)

The electrical potential expression in terms of water molar concentration in the membrane:

\[ -\nabla^2 \Phi = \frac{1}{\kappa} \frac{b}{\frac{\rho_m^{\text{dry}}}{EW} - bC_w} (\nabla C_w \cdot \mathbf{i}) - \frac{RT}{F} \frac{b}{\frac{\rho_m^{\text{dry}}}{EW} - bC_w} \nabla^2 C_w - \frac{RT}{F} \left( \frac{b}{\frac{\rho_m^{\text{dry}}}{EW} - bC_w} \right)^2 (\nabla C_w \cdot \nabla C_w) \]  

(A. 9)
APPENDIX C

Calculation of Reversible Cell Potential by Nernst Equation

UNITS:
\( kJ = 1000 \cdot J \quad kmol = 1000 \cdot mol \quad \mu m = 10^{-6} \cdot m \quad bar = 100 \cdot kPa \quad mill = 1 \cdot 10^{-3} \cdot in = 0.025 \cdot mm \)

CONSTANTS:
Reference T and P: \( P_{ref} = 100 \cdot kPa \quad T_{ref} = 298 \cdot K \)
Universal Gas Constant: \( R_{gas} = 8.314 \frac{kJ}{kmol \cdot K} \)
Faraday Constant: \( F = 96485 \frac{C}{mol} \)

Nernst Law for Thermodynamic Reversible Cell Potential at 1 atm & 323 K:
The enthalpy, \( h \), and entropy, \( s \), values of each reactant and product in the fuel cell reactions, at any temperature and pressure can be calculated by using the reference values at a reference temperature and pressure. The specific heat values are taken as a constant. These reference values and constant can be found in any thermodynamics or heat transfer textbook.

**H₂O (vapor):**

\[
h_{f\_H₂O\_g} = -241826 \frac{kJ}{kmol} \quad s_{f\_H₂O\_g} = 188.835 \frac{kJ}{kmol \cdot K} \]

\[
c_{p\_H₂O\_g} = 33.696 \frac{kJ}{kmol \cdot K} \]

\[
h_{H₂O\_g} = h_{f\_H₂O\_g} + \int_{T_{ref}}^{T_{FC}} c_{p\_H₂O\_g} d\theta_{FC} \]

**H₂O (liquid):**

\[
h_{f\_H₂O\_l} = -285830 \frac{kJ}{kmol} \quad s_{f\_H₂O\_l} = 69.950 \frac{kJ}{kmol \cdot K} \]

\[
c_{p\_H₂O\_l} = 75.24 \frac{kJ}{kmol \cdot K} \]

\[
h_{H₂O\_l} = h_{f\_H₂O\_l} + \int_{T_{ref}}^{T_{FC}} c_{p\_H₂O\_l} d\theta_{FC} \]

**O₂:**

\[
h_{f\_O₂} = 0 \frac{kJ}{kmol} \quad s_{f\_O₂} = 205.148 \frac{kJ}{kmol \cdot K} \]

\[
c_{p\_O₂} = 29.504 \frac{kJ}{kmol \cdot K} \]

\[
h_{O₂} = h_{f\_O₂} + \int_{T_{ref}}^{T_{FC}} c_{p\_O₂} d\theta_{FC} \]

**H₂:**

\[
h_{f\_H₂} = 0 \frac{kJ}{kmol} \quad s_{f\_H₂} = 130.678 \frac{kJ}{kmol \cdot K} \]

\[
c_{p\_H₂} = 28.418 \frac{kJ}{kmol \cdot K} \]

\[
h_{H₂} = h_{f\_H₂} + \int_{T_{ref}}^{T_{FC}} c_{p\_H₂} d\theta_{FC} \]
The total enthalpy change for overall reaction is calculated by:

\[ \Delta H = -1 \cdot (h_{H_2} + 0.5 \cdot h_{O_2} - h_{H_2O_g}) \]

**Operating Conditions:**

**Fuel Cell Temperature and Saturation Temperature:**

\[ T_{FC} = 323 \cdot K \quad T_{sat} = 323 \]

**Water Saturation Pressure:**

\[
\begin{align*}
P_{sat} & = 10^{-2} \cdot 1.234 \times 10^4 \text{ Pa} \\
& = \left[-2.1794 + 0.02953 \left( T_{sat} - 273 \right) - 9.1837 \cdot 10^{-5} \left( T_{sat} - 273 \right)^2 + 1.4454 \cdot 10^{-7} \left( T_{sat} - 273 \right)^3\right] \times 1.234 \times 10^4 \text{ Pa}
\end{align*}
\]

\[ P_{H_2O_sat} = P_{sat \cdot atm} = 1.234 \times 10^4 \text{ Pa} \]

**Anode and Cathode Pressures and Relative Humidities:**

\[ P_{anode} = 1 \text{ atm} + 5 \text{ psi} = 1.358 \times 10^5 \text{ Pa} \quad RH_a = 1
\]

\[ P_{cathode} = 1 \text{ atm} + 5 \text{ psi} = 1.358 \times 10^5 \text{ Pa} \quad RH_c = 1
\]

At the anode and cathode pressure given above, \( H_2O \) is assumed to be in vapor phase and the pressure of water vapor is taken as the saturation pressure at the fuel cell temperature.

**Water pressure:**

\[ P_{H_2O} = P_{H_2O_sat} \]

**Hydrogen pressure:**

\[ P_{H_2} = (P_{anode} - RH_a \cdot P_{H_2O_sat}) \]

**Oxygen pressure:**

\[ P_{O_2} = (P_{cathode} - RH_c \cdot P_{H_2O_sat}) \left[ \frac{1}{(1 + 3.76)} \right] = 2.594 \times 10^4 \text{ Pa} \]

In order to account for the change in the pressure from the reference pressure, a pressure ratio/fraction is used:

\[ f_{H_2O} = \frac{P_{H_2O}}{P_{ref}} \quad f_{H_2} = \frac{P_{H_2}}{P_{ref}} \quad f_{O_2} = \frac{P_{O_2}}{P_{ref}} \]

While the enthalpies are modified by only temperature, the entropy changes depend on both temperature and pressure:

\[
\begin{align*}
\mathcal{s}_{H_2O} &= \mathcal{s}^{f}_{H_2O_g} + \int_{T_{ref}}^{T_{FC}} \left( \frac{c_{p_{H_2O_g}}}{T_{FC}} \right) \mathcal{d}T_{FC} - R_{gas} \ln(f_{H_2O}) \\
\mathcal{s}_{H_2} &= \mathcal{s}^{f}_{H_2} + \int_{T_{ref}}^{T_{FC}} \left( \frac{c_{p_{H_2}}}{T_{FC}} \right) \mathcal{d}T_{FC} - R_{gas} \ln(f_{H_2})
\end{align*}
\]
The total entropy change for the reaction is calculated by:

\[
\Delta S = -T_{\text{FC}} \left( \frac{s_{\text{O}_2} - 0.5s_{\text{H}_2} - s_{\text{H}_2O}}{T_{\text{ref}}} \right) - R_{\text{gas}} \ln \left( f_{\text{O}_2} \right)
\]

The Gibbs free energy for a reaction is calculated by subtracting the total entropy change from the total enthalpy change:

\[
\Delta G = \Delta H - T_{\text{FC}} \Delta S
\]

The electrical work done by the system will be equal to the Gibbs free energy:

\[
W_e = -\Delta G
\]

The efficiency of the system will be the ratio of the electrical work done and the enthalpy change of the reaction.

\[
\eta = \frac{W_e}{\Delta H}
\]

The electrical work needed for the transport of electrons in a reaction is calculated by Faraday's Law:

\[
n = 2 \quad \text{for PEMFC} \quad q = n \cdot F
\]

The reversible fuel cell potential is calculated by using the change in Gibbs free energy, in other words, the electrical work done and the work needed for the state change of reactants and products.

\[
E_{\text{reversible}} = \left( \frac{-\Delta G}{q} \right) - \left( \frac{R_{\text{gas}} \cdot T_{\text{FC}}}{q} \right) \ln \left( \frac{f_{\text{H}_2O}}{f_{\text{H}_2} \left( f_{\text{O}_2} \right)^{0.5}} \right)
\]

\[
W_e = 2.318 \times 10^5 \quad \text{kJ/kmol} \quad \eta = 0.958 \quad E_{\text{reversible}} = 1.224 \text{V}
\]

\[
E_{\text{rev}} = 1.224 \text{V}
\]
**Calculation of Polarization Losses, Cell potential and Current**

**Electrolyte Characteristics:**

Reference current density loss: \( i_{\text{loss,ref}} := 4 \cdot \frac{mA}{cm^2} \)

The new membrane properties are estimated by using the Nafion® 117 membrane properties.

Nafion® membrane properties:

Membrane thickness: \( d_m = 7\text{ mill} = 0.178\text{ mm} \)

The total ohmic resistance in a fuel cell is composed of the ionic, electronic and contact resistances between the fuel cell components. Since the backing layers are the same, the electronic resistance will be the same.

\[
R_{i_b} := 0.30 \cdot \Omega \cdot cm^2 \\
R_{i_i} := \frac{2 \cdot R_{i_b}}{3} \\
R_{i_i} := 0.2 \cdot \Omega \cdot cm^2 \\
R_{i_e,c} := R_{i_b} - R_{i_i} = 0.1 \cdot \Omega \cdot cm^2 \\
\]

New membrane thickness: \( d_{m_{\text{new}}} := 26.95 \cdot 10^{-4} \text{ m} \)

\[
R_{i_i} := \frac{d_{m_{\text{new}}}}{d_m} = 3.031 \cdot \Omega \cdot cm^2 \\
R_{i_{\text{t}}} := R_{i_i} + R_{i_e,c} = 3.131 \cdot \Omega \cdot cm^2 \\
\]

The new membrane conductivity is determined by using HFR:

\[ \kappa := 0.031 \text{ S/cm} \]

The new membrane ionic resistance:

\[
R_{i_{\text{new}}} := \frac{d_{m_{\text{new}}}}{\kappa} = 8.694 \cdot \Omega \cdot cm^2 \\
\]

Total resistance of the fuel cell with the new membrane:

\[ R_i := R_{i_{\text{new}}} + R_{i_e,c} = 8.794 \cdot \Omega \cdot cm^2 \]

**Electrode Characteristics:**

Reference Exchange Current Densities:

\[ i_{o_{A_{\text{ref}}}} := 5 \cdot 10^{-6} \cdot \frac{A}{cm^2} \]

\[ i_{o_{C_{\text{ref}}}} := 5 \cdot 10^{-6} \cdot \frac{A}{cm^2} \]

Catalyst surface area per mg of catalyst:

\[ a_{c_{\text{pt}}} := 600 \cdot \frac{cm^2}{mg} \]

Catalyst loading:

\[ l_{c_{\text{pt}}} := 0.35 \cdot \frac{mg}{cm^2} \]

**Anode Characteristics:**

Diffusion media thickness:

\[ \delta_A := 3000 \cdot \mu m \]

Transfer coefficient:

\[ \alpha_A := 0.5 \]

Number of electrons:

\[ n_A := 4 \]
Hydrogen diffusion coefficient:

\[ D_{H2} := 0.915 \cdot 10^{-4} \cdot 0.3^{1.5} \cdot \frac{P_{H2}}{P_{ref}^{307.1 \cdot K}} \cdot m^2/s \]

Hydrogen molar concentration at the inlet:

\[ C_{H2} := \frac{P_{H2}}{R_{gas} \cdot T_{FC}} \]

Reference hydrogen molar concentration:

\[ C_{H2\_ref} := 56.4 \text{ mol/m}^3 \]

Exchange current density:

\[ i_{o\_A} := i_{o\_A\_ref} \cdot a_{c\_pt} \cdot I_{c\_pt} \cdot \left( \frac{C_{H2}}{C_{H2\_ref}} \right) = 8.559 \frac{A}{m^2} \]

Limiting current density:

\[ i_{L\_A} := \frac{\left( n_A \cdot F \cdot D_{H2} \cdot C_{H2} \right)}{\delta_A} \quad i_{L\_A} = 11.547 \frac{A}{cm^2} \]

**Cathode Characteristics:**

Diffusion media thickness:

\[ \delta_C := 3000 \mu m \]

Transfer coefficient:

\[ \alpha_C := 0.5 \]

Number of electrons:

\[ n_C := 2 \]

Oxygen diffusion coefficient:

\[ D_{O2} := 2.2 \cdot 10^{-5} \cdot 0.4^{1.5} \cdot \frac{P_{cat\_hode}}{P_{ref}^{291.3 \cdot K}} \cdot m^2/s \]

Oxygen molar concentration at the inlet:

\[ C_{O2} := \frac{P_{O2}}{R_{gas} \cdot T_{FC}} \quad C_{O2} = 9.658 \text{ mol/m}^3 \]

Henry's constant for oxygen:

\[ H_{O2} := 2 \cdot 10^5 \text{ atm/cm}^3 \text{ mol/mol} \]

Oxygen molar concentration dissolved in membrane:

\[ C_{O2\_diss} := R_{gas} \cdot T_{FC} \cdot C_{O2} \cdot H_{O2} = 1.28 \frac{mol}{m^3} \]

Reference hydrogen molar concentration:

\[ C_{O2\_ref} := 40.8 \frac{mol}{m^3} \]

Exchange current density:

\[ i_{o\_C} := i_{o\_C\_ref} \cdot a_{c\_pt} \cdot I_{c\_pt} \cdot \left( \frac{C_{O2\_diss}}{C_{O2\_ref}} \right) = 0.329 \frac{A}{m^2} \]

Limiting current density:

\[ i_{L\_C} := \frac{\left( n_C \cdot F \cdot D_{O2} \cdot C_{O2} \right)}{\delta_C} \quad i_{L\_C} = 0.521 \frac{A}{cm^2} \]
Fuel cell limiting current density is equal to the cathode limiting current density since it is lower than the anode limiting current density:

\[ i_L = i_{L_C} = 0.521 \frac{A}{cm^2} \]

The current density of the fuel cell is described in terms of limiting current density:

\[
i := \begin{bmatrix} 0.01 \cdot i_L \\ 0.03 \cdot i_L \\ 0.1 \cdot i_L \\ 0.2 \cdot i_L \\ 0.4 \cdot i_L \\ 0.6 \cdot i_L \\ 0.7 \cdot i_L \\ 0.8 \cdot i_L \\ 0.9 \cdot i_L \\ 0.99 \cdot i_L \\ (1 - 10^{-15}) \cdot i_L \end{bmatrix}
\]

Polarization Losses:

\[ j = 0..10 \]

**Anode and Cathode Activation Losses:**

\[
\Delta V_{act_Aj} := \frac{(R_{gas \cdot T_{FC}})}{\alpha_A \cdot F} \cdot \ln \left( \frac{i_j}{i_{o_A}} \right) \\
\Delta V_{act_Cj} := \frac{(R_{gas \cdot T_{FC}})}{\alpha_C \cdot F} \cdot \ln \left( \frac{i_j}{i_{o_C}} \right)
\]

**Anode and Cathode Concentration Losses:**

\[
\Delta V_{conc_Aj} := \frac{(R_{gas \cdot T_{FC}})}{n_A \cdot F} \cdot \ln \left( \frac{i_{L_A}}{i_{L_A} - i_j} \right) \\
\Delta V_{conc_Cj} := \frac{(R_{gas \cdot T_{FC}})}{n_C \cdot F} \cdot \ln \left( \frac{i_{L_C}}{i_{L_C} - i_j} \right)
\]

**Ohmic Losses:**

\[ \Delta V_{ohm_j} := i_j \cdot R_i \]
The current density produced by the fuel cell is the sum of the external current density obtained by the external circuit and the current density losses. Therefore, the external current density and current density loss are obtained by iteration.

\[
i_{\text{loss}}(i_{\text{ext}}) := \frac{i_{\text{ext}} - i_{\text{ext}}}{i_{\text{ext}} + i_{\text{loss}}}
\]

\[
i_{\text{ext}}(i_{\text{ext}}) := i - i_{\text{loss}}(i_{\text{ext}})
\]

Given

\[
i = i_{\text{ext}} + i_{\text{loss}}(i_{\text{ext}})
\]

\[
i_{\text{ext.iterate}}(i, i_{\text{ext}}) := \text{Find}(i_{\text{ext}})
\]

\[
i_{\text{ext}} := i_{\text{ext.iterate}}(i, i_{\text{ext}})
\]

\[
i_{\text{loss}} := i - i_{\text{ext}}
\]
The cell voltage is obtained by subtracting the polarization losses from the reversible fuel cell potential.

\[ E_{\text{FC.1}} = E_{\text{rev}} - \Delta V_{\text{act_A}} \]
\[ E_{\text{FC.2}} = E_{\text{rev}} - \Delta V_{\text{act_A}} - \Delta V_{\text{act_C}} \]
\[ E_{\text{FC.3}} = E_{\text{rev}} - \Delta V_{\text{act_A}} - \Delta V_{\text{act_C}} - \Delta V_{\text{ohm}} \]
\[ E_{\text{FC.4}} = E_{\text{rev}} - \Delta V_{\text{act_A}} - \Delta V_{\text{act_C}} - \Delta V_{\text{ohm}} - \Delta V_{\text{conc_A}} \]
\[ E_{\text{FC}} = E_{\text{rev}} - \Delta V_{\text{act_A}} - \Delta V_{\text{act_C}} - \Delta V_{\text{ohm}} - \Delta V_{\text{conc_A}} - \Delta V_{\text{conc_C}} \]
<table>
<thead>
<tr>
<th>$E_{\text{rev}}$</th>
<th>$E_{\text{FC.1}}$</th>
<th>$E_{\text{FC.2}}$</th>
<th>$E_{\text{FC.3}}$</th>
<th>$E_{\text{FC.4}}$</th>
<th>$E_{\text{FC}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>V 1.224</td>
<td>V 1.123</td>
<td>V 0.842</td>
<td>V 0.796</td>
<td>V 0.796</td>
<td>V 0.796</td>
</tr>
<tr>
<td>1.224</td>
<td>1.062</td>
<td>0.719</td>
<td>0.582</td>
<td>0.582</td>
<td>0.582</td>
</tr>
<tr>
<td>1.224</td>
<td>0.995</td>
<td>0.585</td>
<td>0.127</td>
<td>0.127</td>
<td>0.127</td>
</tr>
<tr>
<td>1.224</td>
<td>0.957</td>
<td>0.508</td>
<td>-0.408</td>
<td>-0.408</td>
<td>-0.411</td>
</tr>
<tr>
<td>1.224</td>
<td>0.918</td>
<td>0.431</td>
<td>-1.4</td>
<td>-1.4</td>
<td>-1.4</td>
</tr>
<tr>
<td>1.224</td>
<td>0.896</td>
<td>0.386</td>
<td>-2.361</td>
<td>-2.361</td>
<td>-2.374</td>
</tr>
<tr>
<td>1.224</td>
<td>0.887</td>
<td>0.369</td>
<td>-2.836</td>
<td>-2.836</td>
<td>-2.853</td>
</tr>
<tr>
<td>1.224</td>
<td>0.88</td>
<td>0.354</td>
<td>-3.309</td>
<td>-3.309</td>
<td>-3.332</td>
</tr>
<tr>
<td>1.224</td>
<td>0.873</td>
<td>0.341</td>
<td>-3.78</td>
<td>-3.78</td>
<td>-3.812</td>
</tr>
<tr>
<td>1.224</td>
<td>0.868</td>
<td>0.33</td>
<td>-4.202</td>
<td>-4.203</td>
<td>-4.267</td>
</tr>
<tr>
<td>1.224</td>
<td>0.867</td>
<td>0.329</td>
<td>-4.249</td>
<td>-4.25</td>
<td>-4.73</td>
</tr>
</tbody>
</table>

**Cell Voltage/Potential vs. External Current Density**

- $E_{\text{rev}}$
- $E_{\text{FC.1}}$
- $E_{\text{FC.2}}$
- $E_{\text{FC.3}}$
- $E_{\text{FC.4}}$
- $E_{\text{FC}}$

ΔV
- ΔV

Internal Current Density (A/cm²)

**External Current Density (A/cm²)**

- $i_{\text{ext}}$

- $\frac{i_{\text{ext}}}{10000}$
APPENDIX D

Default Properties and Values Used in ANSYS FLUENT PEMFC Module

<table>
<thead>
<tr>
<th>Parameter Name</th>
<th>Symbol in Literature</th>
<th>Unit</th>
<th>Description</th>
<th>Common Value in Literature</th>
<th>Default Value in Module</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Electrochemistry</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Open Circuit Voltage</strong></td>
<td>$V_{OC}$, $OC$, $E_0$</td>
<td>V</td>
<td>It is voltage where is no current (electrical circuit is not closed, at zero current) if the cell is supplied with reactant gases. It is expected to be theoretical cell potential for given conditions(T,P,concentration of reactants) but due to losses even when no current is generated[9].</td>
<td>~1.0</td>
<td>0.95</td>
</tr>
<tr>
<td><strong>Specific Leakage Current</strong></td>
<td>$I_{\text{leak}}$</td>
<td>A/m³</td>
<td>It models the effect of species cross-over from one electrode to another across electrolyte(cross-over current). It can be also specified by UDF.</td>
<td>Not Applicable</td>
<td>0</td>
</tr>
<tr>
<td><strong>Anode</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Reference Current Density</strong></td>
<td>$j_{\text{ref,an}}$, $j_{0,\text{anode}}$, $i_{0,a}$</td>
<td>A/m²</td>
<td>At the equilibrium potential there is no net current flowing through the electrode. However, the equilibrium is a dynamic one, that is, the electrode reaction proceeds at &quot;equal rates&quot; both in the forward and in the reverse direction, resulting in a zero &quot;net&quot; reaction rate and a zero &quot;net&quot; current. The rate of the electrode reaction can be expressed as an equivalent current density and the &quot;exchange current density&quot; of a reaction is the current density flowing &quot;equally&quot; in both directions in equilibrium.</td>
<td>$0.5\times10^{-4}$ A/m²Pt</td>
<td>1.50E+09</td>
</tr>
<tr>
<td><strong>Reference Concentration</strong></td>
<td>$[A]<em>{\text{ref}}, C</em>{\text{ref, H2}}$</td>
<td>kmol/m³</td>
<td>Molar concentration of the species(H₂) at the interface of GDL&amp;gas channel, inlet concentration at reference temperature and pressure.</td>
<td>~5.0$\times10^{-2}$</td>
<td>1</td>
</tr>
<tr>
<td><strong>Concentration Exponent</strong></td>
<td>$\gamma$</td>
<td>–</td>
<td>Concentration or pressure dependence.</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td><strong>Exchange Coefficient</strong></td>
<td>$\alpha_{\text{anode}}$, $k$</td>
<td>–</td>
<td>Transfer coefficient.</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td><strong>Cathode</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Reference Current Density</strong></td>
<td>$j_{\text{ref,cat}}$, $j_{0,\text{cathode}}$, $i_{0,c}$</td>
<td>A/m²</td>
<td>Exchange current density is a measure of an electrode’s readiness to proceed with the electrochemical reaction. A large exchange current density indicates a fast reaction, while a small exchange current density indicates a slow reaction. Reference exchange current density &quot;at reference temperature &amp;pressure&quot;(typically 25 °C &amp; 101.25kPa per unit catalyst surface area)[9].</td>
<td>$10^{-5}$ A/m²Pt</td>
<td>4.00E+06</td>
</tr>
<tr>
<td><strong>Reference Concentration</strong></td>
<td>$C_{\text{ref, O2}}$, $[C]<em>{\text{ref, O2}}$, $C</em>{\text{ref}}$</td>
<td>kmol/m³</td>
<td>Depends on concentration, temperature, pressure, electrode catalyst loading and specific surface area.</td>
<td>~4$\times10^{-3}$</td>
<td>1</td>
</tr>
<tr>
<td><strong>Concentration Exponent</strong></td>
<td>–</td>
<td>–</td>
<td>Concentration or pressure dependence.</td>
<td>0.5</td>
<td>1</td>
</tr>
<tr>
<td><strong>Exchange Coefficient</strong></td>
<td>$\alpha_{\text{cat}}$, $\alpha_{\text{cathode}}$, $k$</td>
<td>–</td>
<td>Transfer coefficient.</td>
<td>2</td>
<td>2</td>
</tr>
</tbody>
</table>
### Default Properties and Values Used in ANSYS FLUENT PEMFC Module Cont’d.

<table>
<thead>
<tr>
<th>Zones</th>
<th>Anode</th>
<th>Cathode</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td><strong>Porosity</strong> ε</td>
<td><strong>Porosity</strong> ε,τ</td>
</tr>
<tr>
<td>Electrode(GDL)</td>
<td>A measure of the void spaces in a material, and is a fraction of the volume of voids over the total volume, between 0–1, or as a percentage between 0–100%.</td>
<td>Void space fraction in gas diffusion layer.</td>
</tr>
<tr>
<td>Electrode Viscous Resistance 1/m²</td>
<td>1/Permeability.</td>
<td>1/Permeability.</td>
</tr>
<tr>
<td>Electrode Zone Contact Angle θc degree</td>
<td>Contact angle is a quantitative measure of the wetting of a solid by a liquid. It is defined geometrically as the angle formed by a liquid at the three phase boundary where a liquid, gas and solid intersect. It is used for multiphase FC calculations.</td>
<td>Effective contact angle of gas diffusion layer for multiphase FC calculations.</td>
</tr>
<tr>
<td>Catalyst Layer Porosity ε</td>
<td>Void space fraction in catalyst layer.</td>
<td>Void space fraction in catalyst layer.</td>
</tr>
<tr>
<td>Catalyst Viscous Resistance 1/m²</td>
<td>1/Permeability.</td>
<td>1/Permeability.</td>
</tr>
<tr>
<td>Catalyst Zone Contact Angle θc degree</td>
<td>Effective contact angle of catalyst layer for multiphase FC calculations.</td>
<td>Not Applicable</td>
</tr>
<tr>
<td>Catalyst Zone Surface to Volume Ratio C_an 1/m</td>
<td>Specific reaction surface area per unit volume of the catalyst layer.</td>
<td>Specific reaction surface area per unit volume of the catalyst layer.</td>
</tr>
</tbody>
</table>

### Electrolyte/ Membrane

<table>
<thead>
<tr>
<th>Zones</th>
<th>Electrolyte/ Membrane</th>
</tr>
</thead>
<tbody>
<tr>
<td>Equivalent Weight M_m, EW kg/kmol in the module but in general g/eq is used</td>
<td>A characteristic weight of a substance relating to a specific reaction the substance participates. In electrochemical reactions, the molecular weight or atomic weight divided by the number of electrons transferred during the reaction. Consequently, the equivalent weight of a substance can be different for different reactions.</td>
</tr>
<tr>
<td>Protonic Conduction Coefficient β</td>
<td>These two coefficients are defined for generality in the equation used in order to calculate membrane conductivity in the module; the original equation is the one developed for Nafion 117 by Springer et al.[57] and these values are 1 in this equation.</td>
</tr>
<tr>
<td>Protonic Conduction Exponent α</td>
<td></td>
</tr>
</tbody>
</table>

**Values:**

- Electrode(GDL) Porosity ε: 0.5, 0.5
- Electrode Viscous Resistance: 1/m², ~10⁻¹¹, 1.00E+12
- Electrode Zone Contact Angle θc: 110°, 110
- Catalyst Layer Porosity ε: ~0.25, 0.5
- Catalyst Viscous Resistance: 1/m², ~10⁻¹⁴, 1.00E+12
- Catalyst Zone Contact Angle θc: Not Applicable, 110
- Catalyst Zone Surface to Volume Ratio C_an: 1/m, ~10⁻⁷, 200000
- Catalyst Viscous Resistance: 1/m², ~10⁻¹⁴, 1.00E+12
- Catalyst Zone Contact Angle θc: Not Applicable, 110
- Catalyst Zone Surface to Volume Ratio C_cat: 1/m, ~10⁻⁷, 200000
- Electrode(GDL) Porosity ε,τ: 0.5, 0.5
- Electrode Viscous Resistance: 1/m², ~10⁻¹¹, 1.00E+12
- Electrode Zone Contact Angle θc: 110°, 110
- Catalyst Layer Porosity ε,τ: ~0.15, 0.5
- Catalyst Viscous Resistance: 1/m², ~10⁻¹⁴, 1.00E+12
- Catalyst Zone Contact Angle θc: Not Applicable, 110
- Catalyst Zone Surface to Volume Ratio C_cat: 1/m, ~10⁻⁷, 200000
- Equivalent Weight M_m, EW: 1100, 1100
- Protonic Conduction Coefficient β: 1, 1
- Protonic Conduction Exponent α: 1, 1
### Reference Diffusivity

<table>
<thead>
<tr>
<th>Species</th>
<th>$D_0$</th>
<th>$m^2/s$</th>
<th>Value</th>
<th>Application</th>
</tr>
</thead>
<tbody>
<tr>
<td>H2</td>
<td>$D^0_{H2}$</td>
<td>$m^2/s$</td>
<td>$10^{-6}$</td>
<td>$3.00E-05$</td>
</tr>
<tr>
<td>O2</td>
<td>$D^0_{O2}$</td>
<td>$m^2/s$</td>
<td>$10^{-6}$</td>
<td>$3.00E-05$</td>
</tr>
<tr>
<td>H2O</td>
<td>$D^0_{H2O}$</td>
<td>$m^2/s$</td>
<td>$10^{-6}$</td>
<td>$3.00E-05$</td>
</tr>
<tr>
<td>Other Species</td>
<td>$D^0_i$</td>
<td>$m^2/s$</td>
<td>Not Applicable</td>
<td>$3.00E-05$</td>
</tr>
</tbody>
</table>

### Multiphase

<table>
<thead>
<tr>
<th>Saturation Exponent for Pore Blockage</th>
<th>$r_s$</th>
<th>$\gamma_t$</th>
<th>$\gamma_p$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.5</td>
<td>2.5</td>
</tr>
</tbody>
</table>

The liquid saturation restricts the gas diffusion by reducing the diffusion area and creating tortuous diffusion path, and this is commonly modeled by a normalized function $g(s) = (1-s)^m$ ($m = r_s$) if the pore structure does not change with water saturation, $m = 1.5$ from prediction of the effective medium theory [129].

### Default Material Properties Defined in Module

<table>
<thead>
<tr>
<th>Zone</th>
<th>Material Name in Module</th>
<th>Type</th>
<th>Density ($kg/m^3$)</th>
<th>$C_p$, Specific heat constant ($J/kg-K$)</th>
<th>Thermal Conductivity ($W/m-K$)</th>
<th>$\sigma$, Electrical Conductivity (1/ohm-m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anode Current Collector</td>
<td>collector-default</td>
<td>solid</td>
<td>2719</td>
<td>871</td>
<td>8</td>
<td>1000000</td>
</tr>
<tr>
<td>Anode Catalyst Layer</td>
<td>catalyst-default</td>
<td>fluid</td>
<td>2719</td>
<td>871</td>
<td>8</td>
<td>5000</td>
</tr>
<tr>
<td>Anode GDL (Porous Electrode)</td>
<td>difflayer-default</td>
<td>fluid</td>
<td>2719</td>
<td>871</td>
<td>8</td>
<td>5000</td>
</tr>
<tr>
<td>Cathode Current Collector</td>
<td>collector-default</td>
<td>solid</td>
<td>2719</td>
<td>871</td>
<td>8</td>
<td>1000000</td>
</tr>
<tr>
<td>Cathode Catalyst Layer</td>
<td>catalyst-default</td>
<td>fluid</td>
<td>2719</td>
<td>871</td>
<td>8</td>
<td>5000</td>
</tr>
<tr>
<td>Cathode GDL (Porous Electrode)</td>
<td>difflayer-default</td>
<td>fluid</td>
<td>2719</td>
<td>871</td>
<td>8</td>
<td>5000</td>
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<td>Electrolyte/Membrane</td>
<td>membrane-default</td>
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<td>1980</td>
<td>2000</td>
<td>2</td>
<td>1.00E-16</td>
</tr>
</tbody>
</table>
BIBLIOGRAPHY

[16] SERİNCAN, M. F., 2005, "DYNAMICAL MODELING OF WATER TRANSPORT IN POLYMER ELECTROLYTE MEMBRANE FUEL CELL (PEMFC) DESIGNS," Master of Science, SABANCI UNIVERSITY, SABANCI UNIVERSITY.


