The Pennsylvania State University

The Graduate School

Department of Mechanical and Nuclear Engineering

FUNDAMENTAL CHARACTERIZATION OF MULTI-PHASE TRANSPORT IN
THIN-FILM FUEL CELL DIFFUSION MEDIA

A Thesis in
Mechanical Engineering

by

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ABSTRACT

Proper tailoring of the water transport mechanism in the reactant flow channel and the porous diffusion media (DM) of a polymer electrolyte fuel cell (PEFC) is of great importance to significantly increase stack power density, durability and performance stability under normal and cold-start operations. This study is motivated by the need to establish a fundamental understanding of the water transport mechanism on and through the thin-film fuel cell DM. In the first phase of this study, the liquid water droplet behavior and instability in the reactant flow channel of a PEFC are investigated. The critical conditions leading to the droplet removal are determined, and an empirical correlation relating the surface tension and DM PTFE content is developed. The results indicate that operational conditions, droplet size, channel geometry and level of surface hydrophobicity of the DM directly affect the droplet instability.

In the second part of this study, the capillary water transport mechanism through the minute pores of the fuel cell DM is investigated. Direct measurements of capillary pressure-saturation benchmark data are generated over a wide range of conditions to develop a validated transport model for multi-phase flow in these materials. The effects of hydrophobicity, compression and operating temperature on the capillary transport characteristics of a DM are elucidated. Based on the extensive database, a modified Leverett approach applicable to fuel cell DM has been constructed. The salient feature of the new approach is that it includes the non-uniform wettability characteristics of the thin-film DM and incorporates the subsequent changes in capillary transport characteristics of the DM over a wide range of operating conditions.
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### NOMENCLATURE

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$b$</td>
<td>Half width of the channel above the droplet, m</td>
</tr>
<tr>
<td>$c$</td>
<td>Chord length of droplet, m</td>
</tr>
<tr>
<td>$d_c$</td>
<td>Hydraulic diameter of the channel, m</td>
</tr>
<tr>
<td>$h$</td>
<td>Droplet height, m</td>
</tr>
<tr>
<td>$i$</td>
<td>Current density, A/cm$^2$</td>
</tr>
<tr>
<td>$i_L$</td>
<td>The limiting current density, A/cm$^2$</td>
</tr>
<tr>
<td>$i_0$</td>
<td>Exchange current density, A/cm$^2$</td>
</tr>
<tr>
<td>$k$</td>
<td>Permeability, m$^2$</td>
</tr>
<tr>
<td>$k_{hyd}$</td>
<td>The hydraulic permeability coefficient, unitless</td>
</tr>
<tr>
<td>$k_r$</td>
<td>Relative permeability, unitless</td>
</tr>
<tr>
<td>$j$</td>
<td>Molar flux, mole/l</td>
</tr>
<tr>
<td>$n$</td>
<td>Number of electrons equivalent per mole reactant, unitless</td>
</tr>
<tr>
<td>$m$</td>
<td>Fitting parameter, unitless</td>
</tr>
<tr>
<td>$r$</td>
<td>Radius of the droplet, m</td>
</tr>
<tr>
<td>$r_p$</td>
<td>Pore radius, m</td>
</tr>
<tr>
<td>$s$</td>
<td>Saturation, unitless</td>
</tr>
<tr>
<td>$s_{TR}$</td>
<td>Compressive strain, unitless</td>
</tr>
<tr>
<td>$u$</td>
<td>Phase velocity in x direction, m s$^{-1}$</td>
</tr>
<tr>
<td>$u'$</td>
<td>Average velocity above the droplet, m/s</td>
</tr>
<tr>
<td>$y'$</td>
<td>Centerline of the $FF'$ plane</td>
</tr>
</tbody>
</table>
\( \nu \)    Phase viscosity, m s\(^{-1}\)
\( \chi \)    Local distance from catalyst layer, m
\( B \)    Half width of the channel, m
\( C \)    Compression pressure, MPa
\( D \)    Diffusion coefficient of species, cm\(^2\)/s
\( F \)    Faraday constant, 96,485 C/eq-mol
\( F \)    Force, N
\( E \)    Potential, V
\( F_{\text{Drag}} \)    Drag force, N
\( F_P \)    Pressure force, N
\( F_{\text{Shear}} \)    Shear force, N
\( F_{\text{ST}} \)    Surface tension force, N
\( H \)    Enthalpy, kJ/kg
\( I \)    Current density, A cm\(^{-2}\)
\( L \)    Total length of the material, m
\( MW \)    Molecular weight, g mol\(^{-1}\)
\( N \)    Mole flux, mol/cm\(^2\) s
\( P_A, P_B \)    Pressure at \( AA' \) and \( BB' \) planes, Pascal
\( P_C \)    Capillary pressure, Pascal
\( P_e \)    Pore entry pressure, Pascal
\( Ra \)    Roughness parameter, unitless
\( Re \)    Reynolds number, unitless
The universal gas constant, 8.314 J/mol K

Resistance of the electrolyte membrane and fuel cell components, Ω

Total resistance of fuel cell, Ω

Temperature, °C

Average velocity in unobstructed channel, m/s

Volume, m³

**Abbreviations**

Al  Aluminum

Au  Gold

DM  Diffusion Media

e⁻  Electron

H⁺  Hydrogen ion

H₂  Diatomic hydrogen gas molecule

H₂O  Water

J(s)  Leverett function

K(s)  Modified Leverett function

MPL  Micro-porous layer

MSP  Method of Standard Porosimetry

MMP  Method of Mercury Porosimetry

PEFC  Polymer electrolyte fuel cell

PTFE  Polytetraflouroethylene (Teflon®)

O₂  Diatomic oxygen gas molecule
Subscripts

\( a \)  Anode
\( c \)  Cathode
\( c \)  Compressed
\( C \)  Capillary
\( e \)  Effective
\( g \)  Gas
\( l \)  Liquid
\( o \)  Uncompressed
\( w \)  Water
\( w \)  Wetting phase
\( act \)  Activation
\( conc \)  Concentration polarization
\( diff \)  Diffusion
\( ele-osm \)  Electro-osmotic
\( hyd \)  Hydraulic permeation
\( int \)  Interface
\( irr \)  irreducible
\( nw \)  Non-wetting phase
\( ohm \)  Ohmic
Greek

$\alpha$  Azimuth angle at droplet surface, radian

$\alpha_A$  Anodic transfer coefficient, unitless

$\alpha_C$  Cathodic transfer coefficient, unitless

$\varepsilon$  Porosity, unitless

$\rho$  Density, kg m$^{-3}$

$\eta$  Overpotential, V

$\lambda$  Water content, mol H$_2$O/mol(SO$_3$H$^-$)

$\lambda$  Pore distribution index, unitless

$\tau$  Shear stress, N/m$^2$

$\phi$  Relative humidity, unitless

$\xi$  Electro-osmotic drag coefficient, unitless

$\zeta$  Stoichiometry, unitless

$\theta$  Contact angle, degree

$\theta_A, \theta_R$  Advancing and receding contact angles, radian

$\Delta$  Difference between advancing and receding angle, $\theta_A - \theta_R$, radians

$\gamma$  Surface tension of water-air, N m$^{-1}$

$\gamma_{sl}, \gamma_{sv}, \gamma_{lv}$  Interfacial tension, (solid-liquid, solid-vapor, liquid-vapor), N/m

$\mu$  Viscosity of the air, kg/m s

$\%wt.$  Weight percentage of hydrophobic additive, unitless
ACKNOWLEDGEMENTS

This is an impossible task to list the people that have helped me to achieve this success. I am going to try anyway, and if your name is not listed, rest assured that my gratitude is not less than for those listed below. Before I start to write this brief note, I need to mention that I am very appreciative to GOD for everything I have achieved so far. I hope he walks with me all the time and blesses me through all my life.

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Chapter 1
INTRODUCTION

This chapter explains the fundamentals and operating principles of a polymer electrolyte fuel cell (PEFC). Topics covered in this chapter include: fuel cell types and operation, component design and materials specifications, performance efficiency, and water management.

1.1 Background and History

A fuel cell is a unique device that can continuously convert the chemical energy of a fuel and oxidizer directly into electrical energy through an electrochemical reaction. Unlike a battery, a fuel cell will produce electricity as long as the reactants are continuously supplied. Hydrogen (H₂), the most typically used fuel in PEFCs, is the most abundant element in the universe, and therefore is considered to be a potential long-term energy source for the fuel cell engines. With the potential for high power density and efficiency, fuel cells hold the most promise for powering future portable, automotive and stationary.

Although the concept of reversing the electrolysis of water was discovered in 1839, it was more than 120 years later before this technology was put into practical use. The lawyer and scientist William Robert Grove discovered the reverse electrolysis process of water [1]. The research and development of the fuel cell remained minimal
until the late 1950s. In the early 1960s, due to the special requirements of compact and
efficient power generation device in space applications, fuel cells were considered to be
the potential power sources for space applications. For that reason, NASA had initiated
fuel cell research program focusing on the integration of these alternative power
producing devices into space applications.

In 1955 Willard Thomas Grubb, a chemist at General Electric (GE), invented the
sulphonated polystyrene ion-exchange membrane, which was used as the electrolyte of
PEFC. Three years later, Leonard Niedrach, another GE chemist, developed a technique
to deposit platinum onto the membrane, which greatly improved the power density of
PEFC [1]. In the middle 1980s, research on PEFCs became active again because of
breakthroughs in electrolyte material and catalyst technology. Developments of proton
exchange membranes based on stable sulphonated fluoropolymers (commonly known as
fluoroethylene) greatly lengthened the lifetime of PEFCs. In the early 1990s, the carbon
supported platinum catalyst was invented by a group at Los Alamos National Laboratory.
The invention of such a novel catalyst resulted in a considerable reduction in the platinum
loading requirements from 28 mg/cm² to 0.4 mg/cm² [2]. These improvements caused the
resurgence of the use of PEFC systems and created new research areas regarding the non-
hydrocarbon electrolyte development for terrestrial applications. Today, the PEFC has
become an emerging type of fuel cell, and is considered to be the primary alternative to
the internal-combustion engine in future automotive applications.
1.2 Operating Principles of a PEFC

1.2.1 Advantages of a PEFC

Fuel cells provide unique advantages over the traditional power-producing devices such as batteries and internal combustion engines. The major advantages of fuel cells are listed as follows [2]:

1. Fuel cells have potential for a high operating efficiency, which is not a strong function of system size. Fuel cell systems can approach an overall system efficiency of 50-60%, while traditional internal combustion engines can operate with maximum efficiency of 35%.

2. Fuel cells have zero or near-zero greenhouse gas emissions, providing environmentally friendly operations. Pollutants such as nitrous oxides and particulate matter are eliminated entirely, while carbon dioxide and carbon monoxide are reduced to near zero. The only chemical product of fuel cell using hydrogen as a fuel is pure water.

3. Fuel cells have no moving parts, providing vibration-free and highly reliable operations. Although there are pumps, compressors and valves involved in the entire fuel cell system, the fuel cell stack itself contains no moving parts. Thus, fuel cells are inherently silent and vibration free.

4. Fuel cells can be easily scaled up to different size depending upon the power requirements. There is no size limitation on fuel cells unlike heat engines (i.e. thermal efficiency does not vary with size).
5. Fuel cells have nearly instantaneous recharge capability compared to batteries. The main difference between a battery and a fuel cell is that fuel cells do not require extensive recharging periods. Conversely, batteries require recharging.

There are several types of fuel cells used for different applications. Fuel cells are characterized according to their electrolytes. They all have different structures, electrode reactions, power capacities and applications. The operating principles and fundamentals are same, however. The five main types of fuel cells are: i) polymer electrolyte membrane fuel cell (also called proton exchange membrane fuel cell-PEFC), ii) phosphoric acid (PAFC), iii) alkaline (AFC), iv) molten carbonate fuel cell (MCFC), and v) solid oxide fuel cell (SOFC). Table 1-1 [4] compares different types of fuel cells in terms of their electrolytes, operating temperatures performance characteristics and possible application areas.

Among the fuel cell types, the PEFC has drawn serious attention due to its high operating efficiencies and low emissions. Currently, there is great interest in using PEFC systems in portable applications and residential power generation devices. Especially, PEFC systems exhibit favorable characteristics for automotive applications compared to other fuel cell types. PEFCs can operate on either pure hydrogen gas, or on a liquid hydrocarbon-carrier fuel such as methanol or formic acid.
1.2.2 Components of a PEFC

A polymer electrolyte fuel cell consists of a polymer based electrolyte, anode and cathode porous diffusion media, catalyst layers, and bi-polar plates (current collector plates). Figure 1-1 shows the typical components of a PEFC.

An ion conducting solid polymer membrane (polyperfluorosulfonic acid membrane) is typically used as the electrolyte in PEFC systems. Development of the perfluorosulfonic-acid (PFSA) membranes is one of the major improvements in PEFC technology. The main features of this type of ionomer include: chemical resistance due to C-F bonds, high mechanical strength and suitable proton conductivity. PFSA membranes are more stable than the hydrocarbon-based polymer membranes used earlier in PEFCs [4]. DuPont® produces the industry’s most widely used membrane, Nafion®, although other similar products exist. Figure 1-2 shows the structural composition of Nafion®, which is typically composed of a polytetraflouroethylene (PTFE or Teflon®) backbone and perfluorinated-vinyl-polyether side chains with sulfonic acid groups [5]. When the membrane is humidified, highly hydrophilic sulphonic acid groups will absorb water and ionize. This enables the mobility of $H^+$ ions, providing the desired proton conductivity. The Teflon side chains allow hydronium ions ($H_3O^+$) to move freely from one side chain to the other when the membrane is hydrated. The mobility or conductivity of protons is highly dependent on the water content of the membrane. For a Nafion® membrane, a conductivity as high as 0.1 S cm$^{-1}$ can be achieved with full hydration at 80 °C. The ionic conductivity of Nafion® 117 as a function of water content is shown in Fig. 1-3 [6].
The diffusion media (DM) is a thin layer of carbon cloth or paper with a thickness ranging from 180 µm to 450 µm. The DM serves to transport the reactants from the flow channels to the catalyst sites, and it also removes the reaction products from the catalyst layer (reaction sites) to flow channels. Additionally, it conducts the electrons from the catalyst layer to the current collecting land, while mechanically supporting the electrolyte. DMs have a relatively low density (around 0.3 kg/m³), and they are reasonably easy to manufacture. Naturally hydrophilic DM is commonly coated with the hydrophobic agent PTFE (Teflon®) to provide the hydrophobicity necessary for effective water removal.

The catalyst layer is the power-producing component of a PEFC. It is made of platinum on carbon support, Nafion® ionomer and Teflon. The Nafion® ionic phase provides the ionic conductivity or pathways for the protons to migrate to and from the membrane electrolyte. On the other hand, Teflon® creates the hydrophobic gas region for reactant gas transport. Most importantly, the water is generated through an electrochemical reaction in the catalyst layer. The catalyst layer consists of a platinum (Pt) powder (~2 nm in diameter) usually supported by larger carbon particles with a diameter of 45 to 90 nm. An average loading of 0.5 mg/cm² of platinum catalyst is used on both anode and cathode for enhancing the electrochemical reaction [3]. Pt particles are heterogeneously coated on the surface to increase the active surface area required for electrochemical reactions. The membrane, diffusion media and catalyst layers assembly is often referred to as the membrane electrode assembly (MEA).

The final component is the bi-polar plates or so called current collector plates. The bi-polar plate includes gas flow channels, which are machined through one side of
the bi-polar plate. The bi-polar plates are made of an electrically conductive material, usually graphite or aluminum with an average thickness of 2 cm, and they serve to distribute the reactants through the overall assembly and transport the electrons from anode to cathode, while providing robustness and support for the overall cell assembly.

1.2.3 Performance Analysis of a PEFC

A fuel cell operates much like a standard battery. A fuel cell has an anode side and a cathode side. The difference in activity of the reactants creates a potential difference across the two sides (anode and cathode). In a PEFC, hydrogen gas or fuel is supplied to the anode side through the flow channels, while an oxidizer such as oxygen or air enters the cathode side in the same manner. The flow channel is open to the DM, so the reactant gas can diffuse to the catalyst electrode surfaces (active electrochemical sites) through the DM in both electrodes to meet with the Pt particles for electrochemical reactions.

At the anode, hydrogen is split by an electrochemical oxidation reaction into hydrogen ions, $H^+$ and electrons, $e^-$. The semi-permeable polymer membrane is conductive to ions ($H^+$), but it does not allow electrons to pass through. The electrons must flow through an external circuit, producing useful current. The electrons passing through the external circuit reunite with $H^+$ ions and O$_2$ molecules to participate in the electrochemical reduction reaction at the cathode catalyst layer. As a result, water and waste heat are generated at the end of overall reaction.
Anode Reaction:

\[ 2H_2 \rightarrow 4H^+ + 4e^- \] \[1.1\]

Cathode Reaction:

\[ O_2 + 4e^- + 4H^+ \rightarrow 2H_2O \] \[1.2\]

Overall Reaction:

\[ H_2 + 1/2O_2 \rightarrow H_2O \] \[1.3\]

The performance of a PEFC is characterized by four kinds of losses. These are i) activation polarization, ii) ohmic polarization, iii) concentration (mass transfer) polarization, and iv) fuel cross-over polarization. The typical performance curve of a PEFC and the current density regions, where each loss dominates are as shown in Fig. 1-4.

The activation polarization represents the rate of an electrochemical reaction controlled by sluggish electrode kinetics in the low current density region. Similar to chemical reactions, electrochemical reactions in fuel cells also involve an activation energy that must be overcome by the reacting species. In other words, electronic barriers must be overcome prior to current generation and ion transport. Activation overpotential can be described by the Butler-Volmer equation for an electrode [3]:

\[ i = i_0 \left[ \exp \left( \frac{\alpha nF}{RT} \eta_{act} \right) - \exp \left( - \frac{\alpha nF}{RT} \eta_{act} \right) \right] \] \[1.4\]
where \( i \) represents the current density (A/m\(^2\)), \( F \) is Faraday’s constant which is 96,485 (C/mole-eq), \( i_0 \) is the exchange current density (A/m\(^2\)), \( \eta_{act} \) is the activation overpotential, \( n \) is the number of electrons transferred in the elementary electrode reaction charge-transfer sites, \( \alpha_a \) is the anodic transfer coefficient, and finally \( \alpha_c \) is the cathodic transfer coefficient.

Ohmic polarization is caused by the limited ionic conductivity of the membrane, the electrical resistance of the porous DM and the current collector plates. In addition, due to the small length scales of fuel cell components, the inherent contact resistance at the interface of the current collector plates and DM also contributes to the ohmic polarization. The ohmic polarization (loss) is a strong function of the current density, and tends to increase with an increase in high current densities. As shown in Fig. 1-4, the ohmic losses are more pronounced at moderate current density region, and are strongly affected by the hydration level of the membrane. Therefore, the hydration of the membrane is essential to reduce ohmic loss of the membrane. The ohmic losses can be expressed by Ohm’s law:

\[
\eta_{ohm} = i R_{total} \quad [1.5]
\]

where \( R_{total} \) is the total resistance of a fuel cell including the contact resistance and the ionic resistance, and \( i \) is the current density.

Concentration polarization represents the mass transport limitations of the reactant gases to the reaction sites at high current densities. At high current density operations, the amount of generated water vapor increases. Due to the low operating temperature (~80°C) and humidification of reactant gases, the generated water condenses,
and blocks the available pores of the DM. As a result, the reactant gas fluxes can not diffuse to the active reaction sites in the catalyst layer. The diffusive limitation in the DM results in a concentration difference between the catalyst surface and the DM, and subsequently causes a reduced electrode potential. According to the Nernst equation, the concentration polarization from thermodynamic activity loss can be expressed as [3]:

$$\eta_{\text{con}} = \frac{RT}{nF} \ln \left( 1 - \frac{i}{i_L} \right)$$  \hspace{1cm} [1.6]

where $i_L$ is the limiting current density, indicating the maximum rate at which a reactant can be supplied to an electrode and $T$ is temperature.

The final type of loss occurring in the fuel cell is the fuel cross-over loss. In a PEFC, hydrogen can be easily transferred from anode to cathode through the membrane due to the high concentration gradient across the electrodes. Such crossed-over fuel does not release its electrons, which normally go through the external circuit, but instead reacts with oxygen at the cathode catalyst layer directly. This leads to a reduction in electrochemical reaction rate, therefore decreasing the cell efficiency [8].

1.3 Water Transport Mechanism across the Membrane

Membrane hydration is essential for effective proton conduction. In PEFC operations, water is generally carried into the fuel cell by pre-humidified reactant gas streams. Some water passes through the DM, and reaches the membrane in the form of vapor, which in turn, increases the hydration level of the membrane. In addition to the
input streams, the water vapor is also generated in the cathode catalyst layer by the electrode reaction. Water transport across the membrane originates from the imbalance in water concentration and static pressure across the membrane. Therefore, the water transport mechanism across the membrane is a controlling factor that determines the level of membrane hydration. The water is transported through the membrane via three modes: electro-osmotic drag, diffusion and hydraulic permeation. Figure 1-5 schematically summarizes the water transport mechanism across the membrane of an operating PEFC.

1.3.1 Electro-osmotic Drag

When $H^+$ ions migrate from the anode to the cathode, they tend to attract and drag water molecules along with them across the electrolyte. This phenomenon is referred to as electro-osmotic drag. The number of water molecules transported per hydrogen proton ($H^+$) is called the drag coefficient ($\xi$). The drag coefficient commonly ranges from 1 to 2.5 for Nafion® membranes, as reported by Janssen and Overvelde [10]. Ren and Gottesfeld [11] have reported the drag coefficients as high as $5 \frac{H_2O}{H^+}$ for fully hydrated Nafion® 117 membranes, and they observed that the drag coefficient is a linearly increasing function of temperature within the range of 20 to 120 °C. The water flux driven by electro-osmotic drag ($j_{w, ele-osm}$) is proportional to the proton flux under a given condition (hydration level, temperature, etc.), and is described as:

$$j_{w, ele-osm} = \frac{i \cdot \xi(\lambda)}{F} \quad [1.7]$$
where \( i \) is the local current density, \( F \) is Faraday’s constant and \( \lambda \) is the water content of membrane, which indicates the number of water molecules adsorbed by each sulfonic acid group. \( \xi \) is a proportional constant termed as “electro-osmotic drag coefficient”, which physically indicates the number of water molecules dragged by each proton. The drag coefficient strongly depends on the water content of the membrane (\( \lambda \)) since the membrane exhibits the structural changes in various states of hydration. The rate of electro-osmotic drag from the anode to the cathode is directly proportional to the operating current density. Especially at high current densities, the electro-osmotic drag increases, causing the cell to dry the anode side, while flooding the cathode side.

1.3.2 Diffusion

The diffusion of water between the electrodes is caused by a water concentration gradient (\( \Delta C_{c-a} \)) across the membrane during operation. The diffusion rate depends on the membrane thickness (\( \Delta x \)) and the concentration gradient [4]. The water diffusive flux \( (j_{w,diff}) \) can be represented by Fick’s Law given as [3]:

\[
j_{w,diff} = -D_w(\lambda) \cdot \frac{da_w}{dx}
\]  

[1.8]

where \( D_w \) is the diffusion coefficient (a function of local water content of the membrane, \( \lambda \)), and \( da_w/dx \) is the water activity gradient across the membrane.

Water can diffuse across the membrane in either direction. However, water concentration is usually higher at the cathode due to the water generation in the cathode.
As a result, in conventional fuel cell operations, water generally tends to diffuse toward the anode side. The water transport from cathode to anode is called back-diffusion. Bidirectional water diffusion driven by an activity gradient plays an important role in maintaining the water balance of PEFCs. In an operating PEFC, the anode tends to dry-out because water is transported to the cathode by electro-osmotic drag, and the cathode tends to be flooded because both electro-osmotic drag and water production causes to accumulate an excess amount of water to the cathode side. Back-diffusion of water from cathode to anode compensates the water loss of the anode, and tends to flatten the water activity profile across the membrane, therefore preventing the anode dry-out and reducing the cathode flooding phenomena.

1.3.3 Hydraulic Permeation

Water may also be transported through the membrane by hydraulic permeation, which is caused by the differences in the pressures of the gas reactants across the membrane. The rate of hydraulic permeation depends on the characteristics of the membrane such as the membrane thickness ($\Delta x$), the current density, the operating temperature and the magnitude of the difference in pressures ($\Delta P$). For operating conditions when both reactant gas pressures (anode and cathode) are relatively equal, as is a common practice in PEFCs, the hydraulic permeation rate approaches to zero, and thus can be neglected. Water flux transported by hydraulic permeation ($j_{w,hyd}$) is directly related to the pressure gradient across the membrane, and can be described as:
where \( k_{\text{hyd}} \) is the hydraulic permeability coefficient of the electrolyte membrane (function of membrane water content, \( \lambda \)), and \( \frac{dP}{dx} \) represents the pressure gradient across the membrane.

\[
j_{w,\text{hyd}} = -k_{\text{hyd}}(\lambda) \cdot \frac{dP}{dx} \tag{1.9}
\]

### 1.4 Water Management

Current state of fuel cell technology faces a number of technical challenges that must be surmounted in order to successfully compete against internal combustion engines and batteries. Among those, water management is the bottleneck issue not only to efficient fuel cell operation, but also to prolonging operational lifetime. A delicate balance between membrane hydration and cathode flooding avoidance must be established for reliable and efficient operation.

Adequate water in the membrane electrolyte is a necessity for achieving high performance, since membrane proton conductivity strictly depends on water content of the membrane. There are two main water sources to humidify the membrane: \( i \) humidification of the inlet reactant gas flows, and \( ii \) water generation at the cathode due to the electrochemical reaction. However, achieving the delicate water balance is complicated due to the different modes of internal water transport. Electro-osmotic drag tends to dehydrate the anode, but humidification of the hydrogen gas flow at the inlet can assist in maintaining the hydration level of the membrane. Water production along with electro-osmotic drag generally results in a greater water concentration at the cathode, but
humidification of the reactants in cathode gas stream is still required to some extent. For instance, at lower current densities, the water generation in the catalyst layer and the electro-osmotic drag may not be sufficient to maintain a fully hydrated membrane. Thus, additional water must be introduced to the system from an external source via humidifying the cathode inlet flow.

Water management on the cathode DM is also of paramount importance and highly complicated because of the complex internal architecture of the porous DM. Water is produced from the oxidation-reduction reaction (ORR) at the cathode. The generated water is in the form of vapor, and can be defined by Faraday’s law:

\[
j_{w,\text{production}} = \frac{iA}{2F}
\]  

[1.10]

where \(j_{w,\text{production}}, i, A, F\) represent the water generation rate, the current density, the active surface area and Faraday’s constant, respectively. However, due to the lower operating temperature and the utilization of external humidification of the reactant gases, water vapor may condense. The excess liquid water in the catalyst layer may migrate (via capillary action) towards the DM surfaces, and consequently block or seal the surface pores, hindering the oxygen transport towards the active electrochemical sites. This phenomenon is referred to as “flooding” of the electrode, and it significantly limits the fuel cell performance. Therefore, removal of the excess liquid water from the porous DM is required to reduce the mass transport loss and maintain a global water balance within the fuel cell.
1.5 Objective of the Present Study

The porous fuel cell diffusion media (DM) represents the key component that governs the water transport mechanism within the cathode side of the PEFC. However, the inherent complexity of multiphase flow and the marked heterogeneity of the thin-film DM yield a difficult set of problems that can be resolved by proper tailoring of the multi-phase transport characteristics of the DM. This involves a number of material-dependent parameters, including the capillary pressure, phase saturation, surface wettability characteristics and relative orientation of the pores. This challenging issue is, however, highly multifaceted because of the extremely anisotropic internal architecture of the thin-film DM, minute length scales involved, complex bi-modal pore configuration and strong interaction of the transport properties with the mixed wettability characteristics of the pore network.

To date, state-of-the-art models of multiphase flow in the thin-film porous DM rely on traditional transport relationships borrowed from soil science, where vastly different length scales, surface to volume ratios, pore size and wettability distributions exist. Often, as a simplification, a generic Leverett approach applicable for homogenous soil beds with uniform wettability is employed to describe the capillary transport mechanism in these mixed wettability DMs. The use of the traditional Leverett relationship without true validation limits the effectiveness of the multi-phase transport models, and hinders reliable guidance for assessing component design criteria required to achieve effective water management in PEFC operations.
This combined experimental and analytical study is motivated by the need to develop a fundamental understanding of the liquid water transport mechanism on and through the thin-film fuel cell porous media tailored with mixed wettability. The objectives of the present research are to:

1. Investigate the liquid droplet behavior and instability in the reactant flow channel to identify the critical conditions leading to droplet removal for achieving effective water purging in the flow channel.

2. Experimentally determine the precise capillary pressure-saturation relationship over a wide range of realistic fuel cell operating conditions, including, different compressions and operating temperatures.

3. Elucidate the effects of compression, temperature and the degree of hydrophobicity loading on the capillary transport characteristics of fuel cell DM.

4. Evaluate the effectiveness of the standard Leverett approach commonly employed in fuel cell models to describe the water transport behavior of the fuel cell DM.

5. Based on the analysis in Item-4, develop a modified Leverett approach applicable to fuel cell DMs that can precisely correlate the capillary pressure as a function of hydrophobicity of the DM, compression pressure, operating temperature and other relevant transport properties.

6. Develop a physical capillary transport model describing the modes of the water transport in different regions of a fuel cell DM.
This study provides a fundamental understanding required for establishing an accurate physical theory to describe the multi-phase transport characteristics of the fuel cell DM. This understanding will provide useful guidance for engineering new DM materials necessary to satisfy the requirements for empowering micro-fluidic management for next-generation fuel cell systems.

1.6 Bibliography


Table 1-1: Overview of common fuel cell types [3].

<table>
<thead>
<tr>
<th>Fuel Cell</th>
<th>Electrolyte</th>
<th>Operating Temp.</th>
<th>System Efficiency</th>
<th>Application</th>
</tr>
</thead>
<tbody>
<tr>
<td>AFC</td>
<td>KOH</td>
<td>60-120 °C</td>
<td>35-55 %</td>
<td>Military, Space</td>
</tr>
<tr>
<td>PEFC</td>
<td>Nafion®</td>
<td>50-100 °C</td>
<td>50-60%</td>
<td>Automotive, Portable, Stationary</td>
</tr>
<tr>
<td>PAFC</td>
<td>Phosphoric Acid</td>
<td>~220 °C</td>
<td>40%</td>
<td>Stationary (200kW)</td>
</tr>
<tr>
<td>MCFC</td>
<td>Potassium Carbonate</td>
<td>~650 °C</td>
<td>&gt;50%</td>
<td>Stationary (200-1000 kW)</td>
</tr>
<tr>
<td>SOFC</td>
<td>Zirconia</td>
<td>~1000 °C</td>
<td>&gt;50%</td>
<td>Stationary (200-1000 kW)</td>
</tr>
</tbody>
</table>
Figure 1-1: Schematic view of basic components of a PEFC.
Figure 1-2: Schematic view of the structure of Nafion® [12].
Figure 1-3: Ionic conductivity of Nafion® 117 as a function of water content [6].
Figure 1-4: Typical polarization curve of a PEFC [7].
Figure 1-5: Schematic summary of water transport modes across PEFC membrane [8].
Chapter 2

TWO-PHASE FLOW AND CAPILLARY TRANSPORT IN A POLYMER ELECTROLYTE FUEL CELL

2.1 Introduction

Membrane hydration and electrode flooding avoidance are essential criteria for high cell performance [1-3]. During the operation of PEFCs, the membrane electrode assembly (MEA) should be well-humidified in all circumstances to reduce the ohmic resistance and additional losses. Furthermore, the liquid water formed by the condensation restricts the transport of the oxidant (oxygen) to the electro-active sites, consequently reducing the cell performance. Such a limiting factor in PEFC cathode electrode is a major bottleneck for maintaining the delicate water balance in PEFC. Therefore, understanding the multi-phase flow within the pores of the fuel cell DM is of paramount importance and represents an important step towards achieving the favorable micro-fluidic management in PEFC.

This chapter serves to provide a detailed description of the fundamentals of two-phase transport in an operating PEFC. The definitions of basic two-phase flow parameters and the different modes of flooding phenomena are explained in detail. Finally, an extensive literature survey regarding the multi-phase transport and water management in PEFC is given to serve as a fundamental background for the present study.
2.2 Thin-Film Fuel Cell Diffusion Media

Proper tailoring of the fuel cell components is of great importance for resolving the conflicting water management requirements. For that aspect, the thin-film porous DM represents a vital component of concern to fully understand and characterize the nebulously defined flooding phenomenon, since the most promising improvement of PEFC performance is based on minimization of the transport losses occurring in the cathode porous DM.

The porous DM is an essential component of a PEFC, serving as a support for the polymer electrolyte membrane. Ideally, a DM serves to provide an efficient pathway for the gas reactants to active catalyst sites for electrochemical reaction, and it also ensures proper and rapid transport of product water, electrons, and excess heat of the reaction without inhibiting the gas transport [4].

2.2.1 Structure of the Diffusion Media

The thin-film porous media is constructed from a sheet of electrically conductive macro-porous substrate with varying degree of mixed wettability. Carbon-fiber based products, such as non-woven papers and woven cloths are commonly preferred in fuel cell applications due to their high porosity, better electrical conductivity, high stiffness, high strength and light weight [4]. Both carbon paper and cloth DM substrates have complex and heterogeneous structure with pore size ranging from a few microns to tens of microns. The porosities range from 40 to 90%, whereas they are available in thicknesses between 90 and 500 µm [5]. Pores are randomly distributed and pore size
ranges from a few microns to tens of microns in cloth, whereas carbon paper substrates have pore size about 40-60 µm.

In terms of the structural difference, carbon cloth and paper DMs have different characteristics of spatial uniformity and degree of anisotropy. Carbon cloth DM has a spatially heterogeneous woven structure, resulting in three degrees of macroscopic anisotropy. In contrast, carbon paper DM is relatively more homogenous due to its random lacing, yielding two degrees of anisotropy [5]. Carbon paper DM is usually made thinner than carbon cloth DM. Carbon paper substrates are specially designed for low or high temperatures in both ambient and pressurized gas conditions, especially preferred for moderate-to-high humidity conditions [6]. On the other hand, carbon cloth is more compressible and flexible, providing a higher porosity (>70%) and liquid permeability compared to rigid carbon paper. However, due to its structural flexibility, carbon cloths tend to intrude into flow channels, resulting in increased reactant flow-field pressure drop.

Additional thin micro-porous layer (MPL) of carbon black mixed with polytetraflouroethylene (PTFE) is also coated to one side of the DM substrate to provide better electrical contact and lower cathode DM flooding [7,8]. Generally, micro-porous layers have a pore size of 100 to 500 nm. This compact layer acts as a diffusion barrier, hindering the accumulation of condensed liquid water to the pores of DM substrate. Figure 2-1 depicts the scanning electron microscopy (SEM) images of a carbon paper, carbon cloth and micro-porous layer.
2.2.2 Hydrophobic Coating

The naturally hydrophilic DM substrates are typically tailored by addition of hydrophobic agent called Teflon (polytetraflouroethylene-PTFE) during processing to achieve the desired hydrophobicity for better liquid water transport [8]. The anisotropic nature of the PTFE coating yields a complex bi-modal pore size distribution with mixed wettability. The existence of the bi-modal pore network bifurcates the transport paths of two-phase systems, therefore complicating the transport phenomena.

To date, the fraction of hydrophobic additive (PTFE) is determined through inefficient trial-and-error testing. Acknowledging the existence of minute length scale and presumed anisotropic nature of the thin-film porous DM, existing efforts rely on simply changing the hydrophobic additive content of the DM and observing the change in cell performance. Those findings were somewhat qualitatively coupled with the transport phenomena inside DM. Oedegard et al.[9] demonstrated that adding Teflon (PTFE) to the DM increases the electric resistance, therefore reducing the cell performance. In another study, Antolini et al. [10] reported that increasing the PTFE content of the DM promotes the gas transport, leading to a better cell performance. They concluded that the amount of PTFE should be optimized for better cell performance and effective water removal.

There are also several attempts available in literature [11-13] regarding the determination of the optimal PTFE content. Mathias et al. [4] performed experiments to correlate the amount of PTFE loading as a function of cell performance. They reported that the best performance is achieved for the DM coated with 35% wt. of PTFE.
Furthermore, Bevers et al.[11], Giorgi et al. [12] and Park et al. [13] attempted to determine the optimum PTFE loading as a function of operating conditions for effective two-phase transport. Even though these studies have not reached a common base in terms of defining an optimum amount of PTFE content, one common conclusion is that the considerable increase in fuel cell performance is observed at high PTFE loadings. This finding is directly linked to the physical reasoning of enhanced water removal under high PTFE loadings. However, currently, no truly direct quantitative value regarding the optimum PTFE loading of the porous DM has been defined.

2.3 Fundamentals of Two-phase Flow in Porous Diffusion Media

Existence of two-phase flow in DM significantly complicates the transport phenomena because of the coupled flow of liquid water and reactant gases within the complex pore structure of the DM. Inside the DM, viscous forces and gravitational forces are smaller compared to capillary forces due to the minute length scale of the DM. Therefore, the liquid water transport in DM is governed by capillary (wicking) action [14]. In the following sections, definitions of the governing two-phase flow parameters are briefly explained.
2.3.1 Definitions of Basic Two-phase Flow Parameters

2.3.1.1 Porosity

Porous media (PM) is composed of a solid backbone material and void pores. Porosity ($\varepsilon$) is defined as the ratio of void space to the bulk volume of porous media. To further distinguish the connected and isolated pore sites, another term called effective porosity ($\varepsilon_{\text{eff}}$) is used in soil science. Effective porosity ($\varepsilon_{\text{eff}}$) represents the interconnected pore volume that contributes to fluid flow within the porous media, and excludes the isolated pores. Typically, effective porosity is less than the total porosity of the media due to the pores. Bulk porosity is defined as:

$$\varepsilon = \frac{\text{pore volume}}{\text{total volume}} \quad [2.1]$$

Effective porosity is defined as:

$$\varepsilon_{\text{eff}} = \frac{\text{connected void volume}}{\text{total pore volume}} \quad [2.2]$$

2.3.1.2 Wettability

When two or more fluids occupy a porous medium, one of the fluids is adsorbed on the surface more strongly. The fluid mostly adsorbed on the surface represents the wetting phase, whereas the displaced fluid is called non-wetting phase. Generally, a porous solid will tend to imbibe the wetting phase, while displacing the non-wetting phase [15]. Inside the pore, the wetting phase has a tendency to compress the non-wetting
phase due to its high adsorption on the surface. In a hydrophobic pore of the fuel cell DM, the liquid water will be the non-wetting phase, whereas the gas phase (reactant gas) will be the wetting phase. The behavior of the non-wetting and wetting phases in hydrophilic and hydrophobic pore space is illustrated in Fig. 2-2.

Wettability can also be considered to be the measure of the speed with which fluids spread over solid surfaces. The speed of spreading is directly controlled by the interfacial forces at the interface of solid surface and flowing fluid. The spreading can be increased by lowering the surface tension or lowering the viscosity of the flowing fluids. The wettability on any surfaces is conveniently characterized in terms of contact angle [15]. For two-phase flow in porous media, the wetting angle influences the strength of the capillary pressure considerably, and therefore it is considered to be an important parameter affecting the liquid water transport mechanism in the DM.

2.3.1.3 Saturation

In two-phase systems such as liquid and gas, the volume fraction of total pore volume occupied by a phase is called saturation. Saturation ($s$) is a key parameter for two-phase flow because it represents the available pore space that the gas phase can diffuse. The greater the liquid saturation is the greater the restriction in gas-phase transport. Phase saturation, $s_j$ is expressed as:

$$s_j = \frac{\text{volume taken by } j}{\text{total pore volume}}$$  \[2.3\]
Saturation of all phases adds up to unity, therefore for a gas-liquid system, gas phase saturation is defined as $1-s_j$. For **fully saturated flow**, the saturation volume equals the total void volume, $s_j=1$, whereas for **unsaturated flow** (most common in fuel cells), the pore volume is not fully occupied by liquid water, therefore saturation is less than unity, ($0<s_j<1$). The open pore space available for the gas transport can be represented by the effective saturated porosity:

$$
\varepsilon_{\text{eff}} = \varepsilon \cdot (1 - s_j)
$$

Another important parameter is irreducible liquid saturation or immobile saturation ($s_{irr}$), which represents the amount of trapped water in the isolated pores of the DM. It can be considered as a threshold point, below which the liquid water remains immobile. That is, even when a high flow rate of gas is introduced into the porous media, some fraction of liquid will remain (unless evaporated) primarily due to the discontinuity within the pore network. The irreducible fraction has been confused by some as representing the fraction which cannot be removed from the fuel cell media. In fact, removal from evaporation or convective forces is still possible.

### 2.3.1.4 Contact Angle and Surface Tension

Contact angle is a critical parameter in two-phase flow and defined as the angle between the gas-liquid interface and solid surface. It is measured at the triple point, where all three points intersect. It can be interpreted as the measure of wetting of a surface by a liquid. Contact angles depend on the base material of surface and surface morphology (roughness). For a static system, solid surface interfacial tensions can be calculated from...
the measured contact angles by using a mechanical equilibrium relation derived by Young in 1805 [16]. The liquid droplet contact angle on any solid surface can be defined by the mechanical equilibrium of the droplet under the action of three interfacial tensions [17]. The interfacial tension $\gamma_{ij}$ is defined as the amount of work that must be performed in order to separate a unit area of fluid $j$ from $k$. The term $\gamma_j$ is the surface tension between substance $j$ and its own vapor phase. The work to separate two phases is expressed as:

$$W_{jk} = \gamma_j + \gamma_k - \gamma_{jk}$$  \hspace{1cm} [2.5]$$

Figure 2-3 represents a droplet of liquid ($l$) on top of solid ($s$), equilibrated with gas ($v$). A simple force balance on the droplet contact surfaces in the $x$ direction gives the surface tension components of the solid material.

$$\cos \theta = (\gamma_{sv} - \gamma_{sl})/\gamma_{lv}$$  \hspace{1cm} [2.6]$$

where $\gamma_{lv}$, $\gamma_{sl}$ and $\gamma_{sv}$ represents the liquid-vapor, solid-liquid and solid-vapor surface tensions, respectively. Depending upon the molecular force balance at the contact line, the surface tends to either contract or stretch the liquid droplet like an elastic membrane. A surface can be considered as hydrophilic when contact angle ($\theta$) is smaller than $90^\circ$, whereas a surface is defined as hydrophobic for contact angles greater than $90^\circ$. On a hydrophilic surface, liquid water droplets tend to spread over the surface, whereas on a hydrophobic surface, the droplets tend to be more of a sphere-like shape, covering less surface area, as shown in Fig. 2-4.
2.3.1.5 Permeability and Darcy’s Law

Permeability refers to the tendency of a porous material to allow fluid to move through its pores. Permeability of a porous medium is one of the controlling factors that affect the rate at which fluids travels through the pores of the porous medium. For instance, porous media with higher permeability facilitates the transport of reactants and products. The intrinsic permeability is a property of the porous media only, not the flowing fluid, and is defined as:

\[ k = C \cdot d^2 \]  \hspace{1cm} [2.7]

where \( k \) and \( d \) are intrinsic permeability and average pore diameter. \( C \) represents the dimensionless constant describing the configuration of the flow path. Permeability is either directly measured or empirically estimated using Darcy’s law. Darcy’s law was established by Henry Darcy, and it states that the flow rate through a porous body is equal to the product of permeability of the medium and pressure gradient across the porous body, divided by the viscosity of the flowing fluid [15]. Darcy’s law is defined as:

\[ Q = \frac{-kA}{\mu} \cdot \frac{\Delta P}{L} \]  \hspace{1cm} [2.8]

where \( Q, A \) and \( \mu \) represents the flow rate, cross-sectional area to flow and viscosity of the fluid. \( \Delta P/L \) is the pressure gradient across the porous medium having a thickness of \( L \). \( k \) is the absolute permeability of the porous medium and represented by unit Darcy (1 Darcy \( \sim 10^{-12} \ \text{m}^2 \)). When a measured value of absolute permeability is unavailable, Cozeny-Karman equation given in Eq. 2.9 [18] can be used to estimate the absolute permeability of the porous medium.
Here, $r$, $\varepsilon$ and $\tau$ are the mean radius of the pores, porosity and tortuosity of the medium, respectively.

**Relative Permeability**

In a liquid-gas two-phase flow in porous media, the available pore space is shared by liquid and gas, thus the effective cross sectional area available for each fluid is less than the total available pore space. This effect is taken into account by the relative permeability parameter ($k_r$), which is defined as the ratio of the intrinsic permeability for a phase ($k_a$) to the total intrinsic permeability ($k_{abs}$) of the porous media. Figure 2-5 shows a typical relation of the relative permeability versus liquid saturation for unconsolidated sands.

\[
k_{r-a} = \frac{k_a}{k_{abs}}
\]  

[2.10]
2.3.2 Capillary Pressure and Transport

2.3.2.1 Capillary Pressure

Whenever two or more fluids co-exist in a system, there exists a pressure difference at the interface caused by the imbalance of the molecular forces at the line of contact. The difference between the pressures of any two-phases at the interface is referred as the capillary pressure. The capillary pressure between non-wetting and wetting phase is defined as:

\[ P_c = P_{nw} - P_w = \gamma \cdot \left( \frac{1}{r^1} + \frac{1}{r^2} \right) \]  \[ \text{[2.11]} \]

where \( r^1 \) and \( r^2 \) are the two principle radii of the interface between the solid pore surface and the liquid surface curvature, as shown Fig. 2-6. This equation is also called the Laplace equation, and is used for describing the capillary transport.

The effect of wettability characteristics of the porous media can be explained through the capillary tube model. If the walls of the capillary tube are hydrophilic to the flowing fluid, a net capillary suction force will draw fluid up the walls of the tube until the gravity force balances the surface tension force, as shown Fig. 2-7. However, if the walls of the tube are hydrophobic to the fluid, the meniscus will be concave down, and the air will be the wetting fluid. Most fuel cell models adopt a capillary tube model, in which the porous media is composed of capillary tubes of different radii. Using a representative mean radius (\( r \)), the variable contact angle produced by a hydrophobic
additive can also be included. The final form of the capillary pressure formulation for the capillary tube model can be written as:

$$P_c = P_{nv} - P_w = \frac{2 \cdot \gamma \cdot \cos \theta}{r}$$  \[2.12\]

2.3.2.2 Capillary Transport

To model the flow in fuel cell DM, it is reasonable to assume immiscible flow, meaning that the gas phase and liquid phase are treated as non-mixing (even though some amount of gas phase will dissolve into the liquid phase). This allows us to separate the non-wetting and wetting phases. In fuel cell DM, once the gas phase is fully saturated with water vapor, assuming evaporation and condensation do not take place in the DM, liquid water flow becomes the only mode of the water transport across the DM. As the hydrophobic pores of the DM are filled by the liquid water, the liquid phase pressure increases, eventually reaching to a level to drive the liquid water from higher to lower liquid pressure regions. As a result, the liquid water in the DM is driven via capillary action caused by the liquid saturation gradients in DM. In an operating PEFC, the higher saturation generally occurs in the catalyst layer, and it decreases in the vicinity of the channel, implying the fact that capillary transport takes place from high to low saturation regions in DM [19,20], as illustrated in Fig. 2-8.
2.3.2.3 Pore Entry Pressure

At a microscopic level, transport of liquid droplets from one pore to another pore requires a pressure gradient, which must exceed the pore entry pressure. The pore entry pressure ($P_e$) is defined as the pressure required for non-wetting phase to intrude into that pore. Wetting phase is preferentially adsorbed by the pore surface; therefore does not require any threshold pressure to occupy that pore. The pore entry pressure depends upon the dimension of the pore, hydrophobicity and surface contact angle. As the capillary pressure is increased from $P_{C-1}$ to $P_{C-2}$ ($P_{C-2} > P_e$), either by increasing the wetting phase pressure or decreasing the non-wetting phase, a certain volume of non-wetting phase is transferred from one pore to another pore [15]. Once the path is formed, the energy required to transport the liquid water to a similar sized pore is less than the energy required to overcome the surface energy of that pore, so continuous liquid flow is attained.

Generally, in a hydrophobic fuel cell DM, liquid water (non-wetting phase) transport preferentially takes places in large pores due to the less resistance (lower $P_e$); whereas gas phase (wetting phase) flows through the small pores.

2.3.2.4 Leverett Approach

The most important relationship that must be established for an accurate prediction of the liquid-gas transport in the fuel cell DM is the relationship between the capillary pressure ($P_C$) and the liquid saturation ($s_l$). Capillary pressure depends on a
variety of parameters, including: temperature through surface tension, pore morphology, wettability characteristics, and pore size, but most importantly liquid saturation.

Several empirical and semi-empirical expressions are available which attempt to describe the behavior of capillary pressure in terms of a porous media and fluid properties. Since many porous media share similar characteristic behavior, a generic Leverett approach has been adopted to describe the capillary pressure-saturation relation of the DM as a first step toward achieving an accurate two-phase transport model. Leverett [21] developed a semi-empirical relation correlating capillary pressure and saturation data for clean unconsolidated sands of various permeability and porosity. Leverett defined the capillary pressure in the porous media such as:

\[ P_c = \gamma \cos \theta \left( \frac{\varepsilon}{k} \right)^{1/2} J(s_i) \]  \[2.13\]

where \( k, \varepsilon \) and \( \theta \) are permeability, porosity of the porous media and a representative contact angle, respectively. \( J(s) \) represents the Leverett \( J \)-function incorporating the effects of liquid saturation on capillary pressure.

\[ J(s_i) = \begin{cases} 
1.417(1-s_i) - 2.120(1-s_i)^2 + 1.263(1-s_i)^3 & \theta < 90^\circ \Rightarrow \text{Hydrophilic} \\
1.417s_i - 2.120s_i^2 + 1.263s_i^3 & \theta > 90^\circ \Rightarrow \text{Hydrophobic} 
\end{cases} \]  \[2.14\]

The Leverett approach incorporates the effects of interfacial tension, but uses a simple relation for the average pore radius \( (k/\varepsilon)^{0.5} \), basically ignoring the tortuous nature of porous media [15]. Although this approach serves as a useful starting point, the applicability of a generic Leverett function to the highly anisotropic thin film DM is
unclear and unverified. Specific concerns center around the differences in fuel cell DM and conditions under which the Leverett function was derived.

1. Pore size and contact angle are taken as a statistical average over the entire medium, obscuring local effects which may differ from the whole.

2. Most porous DM material is impregnated with an anisotropic coating of hydrophobic material (PTFE or other), thus yielding a complex bi-modal (hydrophobic and hydrophilic) pore size distribution. However, the traditional Leverett approach is derived from isotropic soil beds having uniform wettability.

3. Leverett approach in its original form does not account for observed hysteresis in fuel cell DM, and its coefficients are empirically derived for a range of common soils.

4. Leverett approach is basically derived for soil beds having a high volume to surface area ratio, whereas in porous media, volume to surface ratio is considerably low.

In addition to those, depending upon the power requirements of the application, the fuel cell DM can be subjected to a wide range of operating temperatures and compressions, which may cause significant changes in the capillary transport characteristics of the DM. However, the traditional Leverett approach in its original form may not be capable of tracking the corresponding changes in the capillary transport characteristics of the fuel cell DM due to the variations in operating environments.
2.3.2.5 Drainage and Imbibition Process

The process for wetting fluid replacing non-wetting fluid in a porous media is called imbibition. The opposite process is called drainage. Figure 2-9 [22] shows a typical relationship $P_c = P_c(s_i)$ during imbibition and drainage for a porous hydrophilic and hydrophobic medium. Similarly, $s_{nw}$ is called residual saturation of the non-wetting fluid and it limits the maximum saturation achievable with imbibition (condensation in the pores can still fill this residual fraction unless these pores are totally orphaned). Point A on Fig. 2-9 [22] shows the bubbling (or breakthrough) pressure $P_b$, which is the minimum pressure needed to initiate displacement of wetting fluid by non-wetting fluid. The hysteresis in porous media is a result of several effects, including the so-called ink-bottle and rain drop effect, as shown in Fig. 2-10 [22]. In the ink-bottle effect, as liquid enters a widening pore, the capillary forces change with the increasing diameter, which can trap a droplet. The rain drop effect is a result of gravity on non-horizontal surfaces, and can result in asymmetric droplet shape and capillary forces.

2.4 Flooding in a PEFC

The liquid water condensed in the cathode catalyst layer accumulates the available pores of the DM, hindering the ability of oxygen to diffuse towards the active electrochemical sites in the catalyst layer. This phenomenon is referred to as ‘flooding’ of the electrode and it significantly limits the fuel cell performance. Operational parameters such as pressure, relative humidity and flow rate directly affect the level of flooding.
Flooding is generally categorized into three types, based on the location of water accumulation. These are: i) channel level flooding, ii) diffusion media flooding, and iii) catalyst layer flooding. The modes of flooding phenomena are illustrated in Fig. 2-11. In the following section, each type of flooding is briefly explained.

2.4.1 Channel Level Flooding

Channel level flooding is commonly seen under high current densities or low air flow rates. The excess liquid water accumulates through the pores of the DM by the capillary action, emerging as a droplet at the interface of DM surface and the flow channel. As the DM becomes saturated with liquid water, the droplets emerged on the surface increase in size, eventually collapsing into water slugs in the flow channel. The water slugs do not allow the reactants to flow smoothly in the channel, causing fuel starvation along the flow channels. This concentration loss by channel blockage forms an additional resistance, thereby reducing the cell voltage significantly [23]. This phenomenon is referred to as “channel flooding”, (Fig. 2-11) and it adversely affects the cell performance.

Water purging is considered to be one solution to avoid channel level flooding, especially in automotive applications. Today, automotive companies have been conducting extensive research in order to adapt fuel cell systems to their next generation vehicles. There are, however, several challenging issues which fuel cell vehicles face today. One of the major problems that must be overcome is residual water in the fuel cell stack, which is a key parameter for design specifications in start up and shut down
procedures. Remaining water in the manifold and the flow field is considered to be the residual water sources in the fuel cell stack. The freezing of this residual water can block the flow channels and prevent reactants from reaching the catalyst layer. In addition, freezing ice can increase the thermal mass of the total system and retard the heat-up process. Thus, an important issue in the shut down process concerning the automotive industry is to minimize residual water inside the flow channels. Therefore, efficient water purge from fuel cell stacks and reduction in steady state water content with proper material selection are the essential issues, which require extensive knowledge of transport phenomena in the fuel cell, especially at the channel level.

2.4.2 Diffusion Media Flooding

Due to the water generation at the catalyst layer, the water concentration gradient between the catalyst layer and flow channel creates a driving force for the generated water to diffuse through the pores of the DM. As the pores are filled with liquid water, it significantly hinders the diffusion of oxygen to the catalyst layer. The limited mass transport of reactants due to the accumulation of liquid water into the available pores of DM is referred to as “diffusion media flooding” and shown in Fig. 2-11.

Condensation in the DM is of utmost important factor contributing the occurrence of DM flooding and governs the degree of DM flooding level. In typical PEFC operations, fully humidified air is supplied from the cathode inlet. As the reactant gas stream becomes over humidified, the flow can not hold more vapor and starts to condense, increasing the saturation level. The reduction in reactant diffusion or the mass
transport resistance in DM is directly related to the saturation level of the DM. Kaviany et al. [24] reported that higher condensation rates result in higher water saturation in the DM. Regardless of other parameters, an increase in liquid saturation creates a significant drop in the vapor flux due to the convective resistance to oxygen diffusion. In another study, Pak et al. [25] reported that as the condensation rate increases, the removal of liquid water becomes difficult, especially in higher PTFE-loaded DMs. This can be attributed to the fact that in a high PTFE loaded DM, the water vapor can be condensed at a lower saturation pressure in a small pore rather than in a large pore (known as capillary condensation). They concluded that for some cases, the dominant driving force for water removal mechanism in DM may not be the capillary force but shear or evaporation of the liquid water.

The DM flooding can be determined experimentally by the measuring the in-situ current distribution within the cell. The current distribution enables to quantify the degree of flooding in the DM, since flooding in a fuel cell is a strong localized function of current and temperature gradients. Mench et al. [23] have conducted distributed current density measurements in order to quantify the localized performance drop of the fuel cell as a function of degree of flooding. The measurements revealed that the fuel cell is exposed to more water near the cathode exit due to the water generation.

Due to the limited experimental data, to date Bruggeman relation from soil science is commonly used in fuel cell models to describe gas phase transport through the pores of the DM as a function of liquid saturation [26].

\[
D_{\text{eff}} = D(\varepsilon - s_l)^{1.5}
\]  
[2.15]
The Bruggeman model assumes an effective diffusivity ($D_{eff}$) calculated based upon the saturation level ($s_l$) and bulk porosity ($\varepsilon$) of the DM. However, since the background of this model is related to soil science, it overestimates the amount of water at flooded conditions and intrinsically assumes an uninterrupted gas-phase path exists, even with 99 % saturated pores [27]. Therefore this approach may not be appropriate to estimate the restricted gas phase diffusion in the DM under flooding conditions.

2.4.3 Catalyst Layer Flooding

The third type of flooding is catalyst layer flooding. It occurs due to the generation of water via electrochemical reaction in the catalyst layer. The generated water condenses and causes a reduction of active reaction area due to the accumulation of water. As the liquid water accumulates over the surface of nano-size platinum (Pt) particles, it leads to formation of liquid micro-layer, which in turn, causes a significant decrease in the diffusion rate of reactant gases to the available catalyst sites. As a result, the reduction in active catalyst area causes an increase in the required reaction over-potential. Lin et al. [28] stated that the flooding in the catalyst layer is more severe than in the DM, therefore excessive catalyst (Pt) loading is not desirable for PEFC operation as it promotes the water generation rate and consequently cathode electrode flooding.
Micro-Porous Layer

One common approach to reduce catalyst flooding is to introduce an additional driving force for maximizing the water removal rate from the catalyst layer. It has been expressed repeatedly in literature \[14,20,24,29\] that introducing an additional micro-porous layer (MPL) between the DM and the catalyst layer enhances the cell performance significantly. Micro-porous layer provides an additional resistance for the diffusion of liquid water to the cathode DM as illustrated in Fig. 2-12, and it directs the liquid water flow towards the anode side. Physically, MPL creates a pressure difference between the anode and the cathode, leading to an increase in the hydraulic permeation of water across the membrane \[32\].

Several experiments \[30,31\] have demonstrated that the DM coated with MPL is observed to have more uniform water distribution in the MEA. Existence of such a fine layer is found to prevent drying out of membrane and reduce the flooding of the catalyst layer. Physically, as the condensed water in the catalyst layer can not penetrate through the DM, it is directed to the anode side. Therefore the liquid saturation level in DM and catalyst layer is prone to be reduced significantly. Pasaogullari and Wang \[32\] developed a two-phase multi-component fuel cell model to analyze the effects of MPL properties such as porosity, pore-size and thickness on the cell performance. The wetting characteristics of the MPL is found to cause a discontinuity in the liquid saturation at the MPL-DM interface, yielding a reduction in the amount of liquid water in the cathode by directing the flow to the anode side. This water back diffusion is observed to be improved by increasing MPL thickness, rendering the MPL more hydrophobicity, decreasing the pore size and bulk porosity of the MPL.
2.5 Pertinent Literature on Two-phase Transport and Water Management

As mentioned previously, maintaining the polymer membrane hydrated and eliminating or reducing the cathode flooding are currently the key issues for obtaining high cell performance. Thus much fuel cell research are devoted to obtaining a more sophisticated understanding of the water transport mechanism and flooding issue. In the following section, an extensive literature survey on water management and two-phase transport is provided.

Modeling Efforts

Because of the complex structure and small length scale involved in fuel cell components, the transport mechanism inside the cell has not yet been fully quantified experimentally. Thus, developing approximate mathematical models becomes imperative to the understanding of the transport phenomena. There have been numerous modeling efforts available in the literature [34-36], which attempt to describe the cell performance as a function of operating conditions and liquid water content of the fuel cell. Until recently, continuum modeling is the most preferred approach to describe the two-phase flow and predict the cell performance [14]. This approach consists of macroscopic mass, momentum and species conservation equations. On the other hand, Darcian flow approach is commonly employed for describing the momentum exchange between the species and phases in the porous DM. All these models, involving two-phase flow and transport, are based on some simplifying assumptions, such as an infinitely thin catalyst layer, isotropic and homogenous DM, isothermal cell, uniform wettability, and the ideal
gas law [14]. Due to the limited available experimental data and the high computational overhead, such simplified assumptions during the development of models became inevitable.

Early pioneers have developed simple models that are based on one dimensional analysis of the single phase flow in fuel cells [37,38], ignoring the effects of the reactant consumption along the channels. Springer et al. [39] developed a one dimensional steady-state single phase model to describe the water transport mechanism in an isothermal fuel cell. Bernardi and Verbrugge [40] developed a similar one dimensional model to analyze the water transport in the membrane and electrodes. Based on these one dimensional models, Fuller and Newman [38] developed a two dimensional transport model to account for the effects of the reactant consumption along the channels and predict the water vapor and reactant species concentrations in the flow channels for different current densities. Nguyen [41] developed a similar model to elucidate the effects of humidification levels of reactant gases on the fuel cell performance. In another study, Meng et al.[42] presented a two dimensional model that accounts for the effects of the reactant species distribution and humidification of the inlet gas streams along the channel length. A limiting current density value corresponding to first appearance of liquid water at the membrane/electrode interface was reported, and the threshold current density was found to be highly dependent on the diffusion and mass transport resistance of the porous DM, inlet flow velocity, operating temperature and channel height.

Even though these models provide useful information regarding the strong relationship between the water content and the cell performance, they are incapable of accounting for the interfacial boundary conditions among the components of the cell,
which is, in fact, of critical importance to accurately couple the fluid flow, the mass transfer and the electro-kinetics.

**Liquid Water Saturation and Transport**

Accurate estimation of the liquid water saturation in the DM during the operation is of paramount importance to determine the capillary pressure and describe the water transport mechanism in the DM and catalyst layer. An extensive physical water transport model is proposed by Kaviany *et al.*[24]. In this physical model, two types of water transport, micro and macro water transport, are considered to occur simultaneously. At the catalyst layer, micro droplets are formed due to the large numbers of condensation sites. The water generation in the catalyst layer leads to over-saturate the gas phase, promoting the condensation rate. The enhanced condensation rate leads to formation of a continuous liquid film that consists of several macro-droplets. The continuous liquid film yields a high water concentration gradient, driving the macro-droplets towards the surface pores of the DM at the catalyst layer interface [24].

Effects of phase change on transport phenomena are also validated by other studies. Bradean *et al.*[43] presented numerical simulations showing the liquid water, oxygen and temperature distribution within the fuel cell. The phase change is found to significantly affect the transport of reactants to the catalyst layer, which basically supports Kaviany’s model. In another two-phase transport model proposed by Wang’s group [35], the threshold current density for onset of liquid formation is determined by defining single and two-phase regimes for the water transport mechanism in PEFC cathode. Their model predictions revealed that molecular diffusion and capillary action
are the main controlling transport mechanism of liquid and water transport. Recently, Natarajan and Nguyen [44] developed a three dimensional two-phase water transport model by discretizing the flow channel into a series of control volumes to determine the oxygen concentration variations along the channel and its effect on the current density. The simulation results indicate that the variations in the current density along the channel seem to arise from the changes in the oxygen consumption rate along the flow channel. Based on the model predictions, the liquid water transport mechanism is found to be the slowest and however the most dominating factor influencing the performance of the cathode.

*Operating Conditions and Optimization*

The optimization of the operating conditions is also of great importance to avoid the flooding problems and achieve higher cell performance. Natarajan and Nguyen [44] performed an experimental study to determine the optimal operation conditions that would lead to enhance the water removal by evaporation. They observed that higher temperature, higher inlet gas flow rate and lower inlet stream humidity result in a higher net current density and internal temperature, promoting the water removal by evaporation. You and Liu [45] reported that the two-phase flow characteristics and the amount of liquid water in the cell are strong function of current density, operating temperature and reactants inlet humidity. In another study, Yuan and Sunden [46] proposed that operating conditions such as low inlet temperature and high inlet humidity of gas species increase the liquid saturation level, reducing the current density. Fuller and
Newman [38] also emphasized that humidification level and flow rate of reactants are the key controlling parameters of PEFC performance and two-phase flow characteristics.

**Temperature Distribution**

Probing the internal temperature distribution in a PEFC is also of critical importance for better understanding the water transport mechanism, as well as for other kinetic and transport phenomena that are known to be functionally dependent on temperature. At a typical PEFC having an operating temperature of 80 °C and 1 atm pressure, every 1 °C change in temperature results in an approximately 5% change in the equilibrium saturation pressure [47,48]. Thus, even small variations in temperature can dramatically affect the optimal inlet humidity values, location of the condensation sites, the membrane hydration, and the cell performance. Even some thermal models based on the energy balance indicate that the temperature change has a significant impact on the water management since the variations in internal temperature is strongly correlated with the operating current density [49-51].

Recently, Cheng et al.[52] suggested an approach to determine the internal temperature distribution of PEFC by employing a non-destructive inverse method. They reported that the inner surface temperature of bipolar plates in contact with MEA can be predicted based on the measured temperature data on the outer surface. Burford et al. [47] directly measured the temperature distribution inside the MEA by embedding an array of micro-thermocouples directly in the Nafion® electrolyte. They reported almost 6 °C temperature differences between the membrane and the flow channel, indicating that
there is a considerable temperature variation within the component of the PEFC, which may significantly affect the liquid saturation distribution.

2.6 Bibliography


Figure 2-1: SEM images of a) carbon paper, b) carbon cloth, and c) cross sectional view of carbon paper with a micro-porous layer.
Figure 2-2: Air and liquid water behavior a) in a hydrophilic pore, and b) in a hydrophobic pore of the DM.
Figure 2-3: Schematic view of droplet sitting on a hydrophilic surface.
Figure 2-4: Liquid droplet surface contact angle on the surface of a hydrophobic and a hydrophilic DM.
Figure 2-5: Typical relative permeability curve of unconsolidated sands as a function of the liquid saturation [22].
Figure 2-6: Equilibrium of a curved interface and interfacial tensions [22].
Figure 2-7: Illustration of capillary action in a column for a) hydrophilic walls, and b) hydrophobic walls.
Figure 2-8: Capillary-induced water transport and saturation profile in DM.
Figure 2-9: Typical wetting/drying curves for a) hydrophilic porous media illustrating hysteresis [22], and b) hydrophobic porous media illustrating hysteresis [22].
Figure 2-10: Illustration of hysteresis effects [22].
Figure 2-11: Schematic view of three modes of flooding phenomena in a PEFC.
Figure 2-12: Schematic of micro-porous layer placed between the DM and catalyst layer.
Chapter 3
LIQUID DROPLET BEHAVIOR AND INSTABILITY IN A POLYMER ELECTROLYTE FUEL CELL FLOW CHANNEL

As the first step of the present study, a combined experimental and analytical study of the liquid droplet behavior and instability in the reactant flow channel was performed to better understand the water transport mechanism in the reactant flow channel. This integrated study is particularly focused on elucidating the effects of operational conditions and PTFE treatment on the contact angle hysteresis (a measure of droplet instability) of a liquid droplet on the DM surface.

3.1 Background

Understanding the channel level water transport is of critical importance for achieving high performance and reducing the parasitic losses in a PEFC. Due to the complex two-phase flow, managing the transport of reactants and products in the flow channels is a challenging issue. Channel level flooding is commonly observed under low air flow rates at high operating current density [1]. At higher flow rates, the cathode side is more prone to accumulation of excess liquid water. Excess liquid water accumulates to the surface of the flow channel, restricting the reactant gas flow and increasing the parasitic pressure loss. Furthermore, the liquid water in the flow channel can also facilitate the transport of ionic impurities, which can accelerate the ionomer degradation. On the anode side, the channel blockage can cause voltage reduction and fuel starvation.
for the catalyst layer [2], leading to the oxidation of carbon support and accelerated
degradation. In order to avoid the partial coverage of the flow channel by liquid water,
the droplet behavior at the interface of DM and the flow channel should be well
understood. The most common way to enhance the liquid water removal from the PEFC
flow channel is to impregnate the DM with the hydrophobic material PTFE. To date, the
fraction of hydrophobic additive used is generally determined through inefficient trial-
and-error testing.

The existing literature [3-5] has followed a phenomenological approach, and has
yet to develop any clear rationale or fundamental knowledge regarding the liquid droplet
transport mechanism in the flow channel. There have been a few qualitative direct
visualization studies in the flow channel of the actual working fuel cell [6-8]. Several
fundamental studies unrelated to fuel cells [9-12] investigated the effects of droplet
contact angle hysteresis (the difference between advancing and receding angle), surface
tension and surface roughness on the droplet instability. Even though these studies are not
motivated by the problems present in an operational fuel cell, the physical phenomenon
of droplet interaction on different surfaces is similar to that occurring in fuel cell flow
channels. Dussan et al. [9], Dimitrakopoulos and Higdon [10], Vafaei and Podowski [11]
and Lam et al. [12] have performed studies (experimental and theoretical) designed to
explain the droplet deformation mechanisms under a wide range of conditions. Recently,
Chen et al. [13] developed a model to predict the onset of droplet removal. The droplet
removal is found to be facilitated by increasing flow channel length and mean gas flow
velocity and decreasing the contact angle hysteresis. However, the effects of channel
geometry, droplet aspect ratio (height to chord length ratio) and the PTFE surface
coverage on the droplet deformation and removal have not been conclusively investigated.

The study presented in this chapter is motivated by the need to discern the critical conditions leading to droplet removal in the reactant flow channels of a PEFC. The following sections provide the detailed explanations of the integrated approach and important conclusions of this specific study.

3.2 Theoretical Analysis of Droplet Deformation in Shear

An analytical model based on a macroscopic force balance has been developed for a droplet in the flow channel in order to predict the advancing and receding contact angle hysteresis and identify the conditions under which the droplet tends towards an unstable state as a function of engineering parameters.

Figure 3-1 shows a captured image of a droplet on a DM in the experimental flow channel, and schematic view of the control volume chosen, where the droplet starts to emerge on surface of the DM. In the macroscopic force balance model, the air flowing over the droplet is assumed to be Newtonian and incompressible, and the flow in the channel is presumed to be uni-directional, steady, fully developed, and laminar. The droplet is assumed to be spherical.

In Fig. 3-1, the control volume is defined as $AA'BB'$ plane, with a depth equal to the diameter of the droplet (into page). The channel height is defined as $2B$, the droplet height is shown as $h$, and the chord length, or contact length, of the droplet on the DM
surface is $c$. The advancing and receding contact angles of the droplet are given as $\theta_A$ and $\theta_R$, respectively. The static force balance in the $x$ direction gives:

$$F_p + F_{\text{Shear}} + F_{\text{Drag}} = 0$$  \[3.1\]

where $F_p$ represents pressure force created by pressure difference in the flow field, $F_{\text{Shear}}$ represents the shear force which the fluid exerts on the top wall due to the no slip condition, and $F_{\text{Drag}}$ is the total drag force exerted on the droplet (equal to the opposite of the surface tension force for a static droplet in equilibrium). The drag force is caused by fluid shear along the droplet surface and it is a function of the flow velocity and pressure gradient. The adhesion force (surface tension force) originates from the molecular interaction of the droplet and the DM surface, and serves to resist the drag force on the droplet through droplet deformation and contact angle hysteresis. If the adhesion force is equal to or greater than the drag force, the droplet will not be removed from the channel and the droplet remains at its nucleation point on the DM surface. This stable condition is represented by Eq. 3.2.

$$|F_{\text{ST}}| \geq |F_{\text{Drag}}| = -(F_{px} + F_{\text{Shear}})$$  \[3.2\]

Note that in the force balance model, the critical condition is defined as the point, where $F_{\text{Drag}}$ is balanced by $F_{\text{ST}}$ (surface tension force). Any increase in $F_{\text{Drag}}$ above this critical point represents a condition under which the droplet becomes unstable, thus the critical condition represents a lower bound for droplet removal and defines the point of instability.
The surface tension force \((F_{ST})\) is a critical parameter in the force balance equation, since it is directly related to the adhesion tension and surface contact angles of droplets emerging on the porous DM. Assuming that the advancing \((\theta_A)\) and the receding \((\theta_R)\) angles change linearly along the circumference of the contact surface (wetted surface), a mathematical expression for contact angle on the DM wetted surface can be derived. For simplicity, the wetted surface (contact surface) of the DM is illustrated in Fig. 3-2. In this force balance model, the shape of the wetted surface (contact surface) is assumed to be circular, thus the diameter of the wetted surface is equal to the chord length of the droplet.

The boundary conditions for the linear contact angle \((\theta)\) distribution are: i) at \(\alpha = 0 \quad \theta = \theta_A\) and ii) at \(\alpha = \pi \quad \theta = \theta_R\), where all angles are in radians and \(\alpha\) represents the azimuthal angle \((\alpha=0\) represents the advancing edge). Thus the contact angle \((\theta)\) is defined as:

\[
\theta = -\frac{\Delta}{\pi} \cdot \alpha + \theta_A \quad [3.3]
\]

where \(\Delta = \theta_R - \theta_A\) represents the contact angle hysteresis. The streamwise surface tension force \((F_{ST})\), is calculated by integrating around the wetted perimeter of the DM surface in the streamwise \((x)\) direction. The differential surface tension force in the streamwise direction is:

\[
dF_{ST} = \left(\frac{\gamma_{lv} \cdot c}{2} \cdot d\alpha\right) \cdot \cos(\pi - \theta) \cdot \cos(\alpha) \quad [3.4]
\]

where \(\gamma_{lv}\) represents the surface tension of the liquid vapor interface of water. Performing the integration, the overall surface tension force in the \(x\) direction yields:
where $\Delta$ represents the difference between the advancing and receding angles ($\Delta = \theta_A - \theta_R$). (Note that at the onset of droplet removal or detachment, $|F_{ST}| = |F_{Drag, i}|$)

Using the simplifying assumption of fully developed laminar flow, pressure drop across the control volume can be calculated in terms of average velocity, droplet chord length, droplet height, and viscosity of the flowing fluid.

The average velocity in the $FF'$ plane ($u'$) can be related to the average velocity of the air in the channel by applying the conservation of mass relation between the $AA'$ and $FF'$ cross sections. Approximating the air as incompressible, $u' = (B/b) \, U$, where $U$ is the average velocity of the air in the channel before the droplet, $u'$ is the average velocity of the air flow above the droplet, $B$ is the half thickness of the channel and $b$ is the half thickness of the distance between the droplet and top wall of the channel. Based on the fully developed laminar flow assumption in a rectangular channel, the pressure drop across the control volume can be written,

$$P_A - P_B = \frac{3 \cdot \mu \cdot u'}{b^2} \cdot 2 \cdot r$$

where $P_A$ and $P_B$ represent the local pressures at the $AA'$ and $BB'$ cross sections respectively. Substituting for $u'$ in terms of $U$, the pressure force acting on the control volume in the $x$ direction then becomes: Eq. 3.8
where \( 2B \cdot 2r \) represents the cross sectional area of the control volume. Substituting for \( b \) in terms of \( B \), \( (b = B-h/2) \); the pressure force acting on the control volume in the \( x \) direction becomes,

\[
F_{x} = \left( P_{A} - P_{B} \right) \cdot \text{Area} = \left( P_{A} - P_{B} \right) \cdot 2 \cdot B \cdot 2 \cdot r \tag{3.8}
\]

where \( 2B \cdot 2r \) represents the cross sectional area of the control volume. Substituting for \( b \) in terms of \( B \), \( (b = B-h/2) \); the pressure force acting on the control volume in the \( x \) direction becomes,

\[
F_{p_x} = \frac{24 \cdot \mu \cdot B^2 \cdot U \cdot h^2}{\left( B - \frac{h}{2} \right)^3 \cdot (1 - \cos(\theta_A))^2} \quad \text{where} \quad r = \frac{h}{1 - \cos(\theta_A)} \tag{3.9}
\]

The remaining term in the macroscopic force balance equation (Eq. 3.1) represents the shear force \( F_{\text{Shear}} \) acting on the control volume. It is assumed that a no-slip boundary condition is applicable at the top wall of the control volume. The liquid droplet covers the bottom interface of the channel wall and the specified control volume; therefore it is assumed that there is no air flow through the bottom wall of the flow channel (Fig. 3-1). The fully developed laminar flow velocity distribution in a rectangular enclosure in the \( FF' \) plane can be represented by [14]:

\[
u(y') = \frac{3 \cdot u'}{2} \cdot \left( 1 - \left( \frac{y'}{b} \right)^2 \right) \tag{3.10}
\]

where \( y' = y + b \) and \( y' = 0 \) represents the centerline of the \( FF' \) plane. The one-dimensional shear stress in a Newtonian fluid is given as \( \tau_{yy} = \mu \frac{dU}{dy} \). The shear stress at the top wall \( (\tau_{xy} \big|_{y=b}) \),

\[
\tau_{xy} \big|_{y=b} = -\mu \frac{\partial u}{\partial y} \bigg|_{y=b} = \frac{3 \cdot \mu \cdot u'}{b} \tag{3.11}
\]
Substituting \( u' \) and \( b \) in terms of \( U \) and \( B \), the shear force in the streamwise (x) direction at the upper wall of the control volume can be shown as:

\[
F_{\text{Shear}_x} = \tau_{xy} y'_{yb} A = \frac{3 \cdot \mu \cdot B \cdot U}{(B - \frac{h}{2})^2} \cdot (2r)^2
\]  

[3.12]

Including the derived expressions for the surface tension force (\( F_{ST_x} \)), pressure force and shear force terms in the \( x \) direction force balance, the final form of Eq. 3.1 becomes:

\[
F_{p_x} + F_{\text{Shear}_x} + F_{\text{Drag}_x} = 0 \quad \text{where} \quad F_{\text{Drag}_x} = -F_{ST_x}
\]

\[
\frac{24 \cdot \mu \cdot B^2 \cdot U \cdot h^2}{\left( B - \frac{h}{2} \right)^3 \cdot (1 - \cos(\theta_a))^2} + \frac{12 \cdot \mu \cdot B \cdot U \cdot h^2}{\left( B - \frac{h}{2} \right)^2 \cdot (1 - \cos(\theta_a))^2}
\]

\[
\gamma_{hc} \cdot \frac{\pi}{2} \left[ \sin(\Delta - \theta_a) - \sin(\theta_a) \right] \left[ \sin(\Delta - \theta_a) - \sin(\theta_a) \right] = 0
\]

[3.13]

The final form of the macroscopic force balance (Eq. 3.13) includes a number of engineering parameters, including the surface contact angle hysteresis (\( \Delta \), the difference between advancing and receding contact angles), channel flow velocity, droplet height and chord length, and channel height.

### 3.3 Experimental Method

In order to observe droplet deformation at the interface of the DM and flow channel, and investigate conditions under which the droplets become unstable (e.g. may be removed by the shear flow), an experimental model cell was fabricated and mounted.
in a test stand that allowed for precise control of system parameters. While the non-operational model flow channel does not include electrochemical reaction, it allows simulation of the activity of a cell, and precise visual study of droplet deformation and stability on DM surface, inside the flow channel.

3.3.1 Method of Approach

The hydrogen PEFC flow channel experimental model consists of a rectangular flow channel (5x4 mm), optically-accessible from the top, with the bottom side consisting of a DM affixed to a feeder plate. A detailed schematic view of the experimental setup is shown in Fig. 3-3. Three different DMs with controlled hydrophobic treatment were utilized in this study (PTFE content of 5%, 10%, and 20% of wt.). A controlled liquid flow rate is achieved with a syringe pump apparatus. A combination of a regulator, throttling valve and mass flow meter are used to control and monitor the air flow rate.

The model cell consists of two aluminum end blocks, an aluminum washer, a Lexan(TM) plate, an aluminum flow channel, prisms, an aluminum settling layer and a hole-pattern feeder plate. The desired flow rate of water simulating the electrochemical water generation is applied through the machined feeder plate by a syringe pump and a capillary tube with a diameter of 0.177 mm. An air flow corresponding to operational fuel cell conditions is externally imposed into the channel through a pressurized gas system and heating system.

Visual images of droplet formation and growth were acquired using a standard video microscopy setup with a telecentric lens and strategically-placed prisms. The
prisms (each 5x5 mm) are aligned on the side walls of the channel in order to enable a simultaneous top and side view of the droplet. The telecentric lens provides an advantage over a conventional lens, in that it mitigates distortion of the shape of small droplets and provides more precise measurements of droplet size and shape than those obtained using a conventional lens. As the liquid droplet formed on the DM surface, images were recorded to allow for measurement of the droplet size and shape.

### 3.3.2 Contact Angle Measurements

Knowledge of surface tension is critical for predicting the conditions under which a droplet may be removed from the channel, since the drag force required for removing a liquid water droplet from the DM surface depends on the interfacial interaction of water molecules and carbon fibers or PTFE on the surface of the DM. However, in the existing literature, indirect approaches are traditionally used to measure the surface tension, due to experimental difficulties [15]. Direct force measurements, contact angles, capillary penetration, sedimentation of particles and gradient theory are some of the indirect approaches commonly used. Among those, contact measurements are considered to be the easiest way to estimate interfacial surface tensions [16].

The contact angle is a measure of the amount of wetting of the DM by a liquid. It is directly related to the interfacial energy of solid, liquid and vapor phases along the three phase boundary. The contact angles depend both on the base material of surface and surface morphology (roughness). Therefore, investigating the contact angles on different surfaces provides information on the energy of the surface of the interest [16]. However,
due to the complexity and small length scale involved in the fuel cell DM, this interface in an enclosed channel is not easily accessible.

Two dynamic contact angles are seen when the liquid droplet is under the influence of air shear flow in the channel. These angles are defined as the dynamic advancing angle and dynamic receding angle ($\theta_A$ and $\theta_R$ in Fig. 3-1). These angles could be interpreted as the measure of the ability of the droplet to resist the drag force. The difference between advancing and receding contact angle (contact angle hysteresis, $\Delta$) is a key parameter in determining the adhesion energy and the instability of the droplet which is deformed by the air flow [11-16].

Several experiments were performed to measure the contact angles on the DM with varying PTFE contents under different air flow rates. The porous media used in this experiment was the 200 to 300 µm thick SIGRACET® Gas Diffusion Layers (SGL CARBON), which are “graphitized” carbon fiber-based nonwovens specifically designed to transport reactant gases into, and excess liquid product water out of the electro catalyst layers of PEFCs. The DM pore size generally ranges from 50 to 100 µm, although individual surface pore diameter was observed to be as high as to 150 µm. The DM has an uncompressed porosity of 0.84. Three DMs with different level of hydrophobic treatment (PTFE content 5%, 10%, and 20% of wt.) placed on the feeder side of the assembly were utilized in these experiments. PTFE was assumed to be sprayed homogenously throughout the surface of the DM, although microscopically, variations occur. Contact angles at the interface of three different DMs and gas flow channel were measured at 60 °C at air flow rates ranging from 0 to 5500 ml min$^{-1}$ in increments of 440 ml min$^{-1}$. Liquid water was injected with a controlled flow rate of 0.023 ml min$^{-1}$ into the
DM through the capillary tube with a diameter of 0.177 mm. This water flow rate is used to simulate a current density 1 A cm\(^{-2}\) at an equivalent cathode stoichiometry of 2 and an active DM surface area of 4 cm\(^{2}\). Unhumidified air at 60 °C was supplied to the inlet of the flow channel with a controlled flow rate. For each PTFE content, 15 images at each operating \(Re\) number (based on channel hydraulic diameter, \(d_c\)) were acquired for analysis of the droplet deformation under shear flow. Each image was carefully processed, and advancing and receding contact angles were measured by using IMAGE TOOL\(^{®}\) software. Although the high magnification camera and telecentric lens were used to minimize the distortion on each image, each angle was measured five times and then averaged in order to minimize the measurement errors. The measurement error associated with the contact angle measurements was determined to be ± 2.8°. A total of 5940 contact angle measurements were made. For each image, the chord length and the height of the droplet were measured and tabulated with contact angle data. The overall test matrix is summarized in Table 3-1.

3.4 Results and Discussions

3.4.1 Contact Angle Interpretation

It was expected that contact angle hysteresis \((\Delta = \theta_a - \theta_b)\), depends on channel air flow rate (Reynolds number based on channel hydraulic diameter, \(d_c\)), droplet size (\(c\) and \(h\)), and surface treatment of the porous DM (PTFE content) and surface roughness. A functional form of the contact angle hysteresis \((\Delta)\) can be written as: Eq. 3.14
Once all the data for three different PTFE cases (5%, 10%, and 20% of wt.) were collected, the contact angle hysteresis ($\Delta$) versus $h/c$ ratio was plotted at different Reynolds numbers, as shown in Fig. 3-4. As seen from the Fig. 3-4, there is scattering in the data, especially at low contact angle hysteresis ($\Delta$). Therefore, a statistical approach was utilized to correlate and understand the behavior of the experimental data. Kwok et al. [15] explained that obtaining meaningful contact angles for the determination of solid surface tensions is a difficult task due to the effects of swelling, chemical composition (inert) and roughness on contact angle measurements, and concluded that statistical tools may help to improve the meaning of measured contact angles to minimize the measurement errors. In Fig. 3-4, the model output (contact angle hysteresis) was computed by solving the final form of the macroscopic force balance equation (Eq. 3.13). Experimental data such as droplet height, droplet chord length, air velocity, viscosity were input into that equation and contact angle hysteresis (predicted delta) for each droplet size were found. Note that the Reynolds number is not constant across all of the points included in Fig. 3-4, yet we know that contact angle hysteresis is a function of Reynolds number. The intent of Fig. 3-4 is primarily to show the relative agreement between the experimental data, linear regression, and model predictions.

Roughness can be interpreted as the measure of the disturbances on the surface due to the disarrangement and misalignment of the carbon fibers on the DM surface. It is expected that roughness directly affects the line tensions and three phase boundary; therefore it may lead to errors in contact angle measurement and interpretations. Kwok et
al. [15] also stated that there is no general criterion to quantify the level at which roughness has a significant effect on contact angle measurements, however in this study, the error in the contact angle measurements induced by roughness can be estimated, based on a typical droplet size \((h=1 \text{ mm and } c=1 \text{ mm})\) and maximum roughness element. As measured from the cross sectional scanning electron microscope (SEM) image of PTFE DM samples, the maximum disturbance on the 20% PTFE DM surface is around 35 µm (Fig. 3-5), and it was estimated that this maximum roughness results in a \(\pm 2^\circ\) error on contact angle measurements.

A multi-dimensional linear regression model was chosen to correlate measured contact angle hysteresis \((\Delta)\) with the relevant non-dimensionelized experimental parameters such as \(Re\), \(c/d_c\) and \(h/d_c\), where \(d_c\) is the hydraulic diameter of the flow channel. The contact angle hysteresis \((\Delta)\) also depends on surface treatment (PTFE content) and, to a minimal extent, surface roughness. However, surface roughness of the DM is not a controlled parameter in these experiments and as discussed, introduced only a small error in contact angle measurement. Therefore, in our regression model, contact angle hysteresis \((\Delta)\) is functionally defined as:

\[
\Delta = A + B \cdot Re + C \cdot (c/d_c) + D \cdot (h/d_c) \tag{3.15}
\]

The chord length \((c)\) and height of the droplet \((h)\) are non-dimensionelized by \(d_c\), and a different multi-dimensional linear regression model was deduced for each PTFE
content. The three multi-dimensional linear regression fits were derived for three different PTFE contents, based on the extensive experimental data taken. These are:

\[
\Delta \text{PTFE}_{65} = -11.2 + 0.0156 \cdot \text{Re} + 139 \cdot (c/d_\text{c}) - 86 \cdot (h/d_\text{c}), \quad R^2 = 74.1\%
\]
\[
\Delta \text{PTFE}_{60} = 6.02 + 0.018 \cdot \text{Re} + 177 \cdot (c/d_\text{c}) - 163 \cdot (h/d_\text{c}), \quad R^2 = 75.1\%
\]
\[
\Delta \text{PTFE}_{52} = -6.52 + 0.0214 \cdot \text{Re} + 145 \cdot (c/d_\text{c}) - 96.4 \cdot (h/d_\text{c}), \quad R^2 = 82.1\%
\]

The normal plot of residuals, the histogram of residuals, chart of residuals and residuals versus fits were used in order to check the validity of the regression model (*i.e.* homogeneity of variance, non-independence of variables, normality) as well as to detect outliers on experimental data. It was noted that the linear regression for contact angle hysteresis (Δ) in the prescribed functional form provided an adequate fit to the experimental data. In addition to these regression model diagnostics, the analytical equation (Eq. 3.13) derived from the macroscopic force balance analysis was solved for contact angle hysteresis (Δ) by using a Newton Raphson method. Specifically, for each experimental condition, known values of droplet height, droplet chord length, air velocity, viscosity, channel height, and advancing contact angle were input into the final form of the force balance equation along with the experimentally derived values of surface tension. For each case, the contact angle hysteresis (Δ) was predicted and compared to the actual measured contact angle hysteresis (Δ) and values of Δ based on the linear regression fits, and a reasonable agreement between these data was observed. Since contact angle hysteresis depends on air flow rate, droplet aspect ratio (height to chord ratio) and surface treatment of the DM (PTFE content or surface tension), these
effects were separately investigated in this study and are reported in the following sections.

### 3.4.2 Effects of Air Flow Rate

As shown in Eq. 3.13, the drag force on the droplet depends linearly on the air flow velocity. As the velocity of the air increases, the drag force increases and the droplet deforms along the flow direction, causing an increase in contact angle hysteresis ($\Delta$). As flow rate increases, the hysteresis increases and the surface energy (adhesion energy) between DM and water gradually becomes insufficient to resist increasing drag force. As a result, at some point, droplets will detach from the DM surface and will form an annular film, or roll over the DM surface in the direction of flow. The point at which the droplet can no longer resist the drag force is termed the point of instability.

Figure 3-6-a shows a sequence of captured images of the same size droplets under different air flow rates. It can be clearly seen that contact angle hysteresis ($\Delta$) increases with flow rate and the droplet tends towards an unstable condition. To investigate the air flow rate effects on contact angle hysteresis ($\Delta$), contact angle hysteresis ($\Delta$) versus air flow rate was plotted by using the linear regression data for 5%, 10% and 20% PTFE DMs for a specified droplet size ($c=1.7$ mm and $h=1.9$ mm). The macroscopic force balance equation (Eq. 3.13) was also solved for contact angle hysteresis ($\Delta$) at the specified droplet size ($c=1.7$ mm and $h=1.9$ mm) for different air flow rates. The output of the model and linear regression fits for 5% and 20% PTFE DM samples are presented in Fig. 3-7. Both the force balance model and the regression show that contact angle
hysteresis (Δ) is a linear function of air velocity. As seen from Fig. 3-7, for each PTFE case, the discrepancy between the model prediction and linear regression is relatively small, which also validates the applicability of applying linear regression fits to the experimental data. As expected, the results shown in Fig. 3-7 indicate that imposing high air flow rates into the flow channel increases the contact angle hysteresis, thereby causing the droplet to move towards an unstable condition. Thus, imposing high flow rates may enhance the liquid water droplet removal from the flow channel; however, one consequence is that parasitic losses in a fuel cell system also increase with air flow rate.

3.4.3 Effects of Droplet Aspect Ratio and Critical Reynolds Number

In this study, it was experimentally observed that the droplet aspect ratio (h/c) has a significant influence on the droplet instability, since any instability is closely related to the balance between the drag force and surface adhesion force, both of which are related to droplet size and shape. Figure 3-6-b shows the captured images of three droplets with different aspect ratios subjected to a constant air flow rate. As seen from Fig. 3-6-b, the droplets with relatively higher aspect ratio (e.g. taller droplets) deform more in response to the same shear flow. A larger deformation means that the droplet experiences a greater difference between advancing and receding contact angles (Δ) to resist increased drag. As the droplet spreads over the DM surface, its chord length increases more than its height, and the surface tension force (proportional to c) becomes more dominant than the drag force acting on the droplet surface (proportional to h²). Therefore, the ratio of droplet height to droplet chord length (aspect ratio) is useful in describing droplet behavior.
Using the analytical model based on a macroscopic force balance, the critical Reynolds numbers for which a droplet with specified chord length will be sheared off the surface were determined over a range of droplet aspect ratios and for two specific chord lengths. Reynolds numbers corresponding to the critical condition (onset of detachment) for 5% and 20% PTFE DMs for a droplet with specified chord length \( (c=1.9 \text{ mm} \text{ and } c=2.3 \text{ mm}) \) versus droplet aspect ratio are shown in Fig. 3-8 and Fig. 3-9, respectively. The experimental data corresponding to the condition in which the droplet chord length is 1.9 ± 0.1 mm for 5% PTFE and 2.3 ± 0.1 mm for 20% PTFE, and for which the droplet remained attached on the DM surface are shown in Figs. 3-8 and 3-9. The 9.81% of the points corresponding to experimental observation of stable conditions lie in the theoretically predicted stable region.

Droplet detachments tests for 5% and 20% PTFE DM samples were also performed. For different droplet aspect ratios, the critical \( Re \) number leading to droplet detachment are also shown in Figs. 3-8 and 3-9. For both 5% and 20% PTFE cases, all the experimental points corresponding to the detachment conditions lie in the theoretically predicted unstable region.

Based on the present model prediction, the Reynolds number required to shear off the droplet is found to increase with decreasing the droplet aspect ratio (height to chord ratio). In other words, any spreading of a droplet (increase in chord length and/or decrease in height) serves to stabilize it and increase the critical \( Re \) number required for detachment, due to the increased surface adhesion force. Spreading of droplets along the DM surface can eventually lead to the formation of a thin film, which is very difficult to remove regardless of the \( Re \) number of the imposed gas flow, and which is undesirable.
for fuel cells. On the other hand, relatively taller droplets (higher aspect ratio) are easier to remove (lower critical $Re$), since larger frontal area gives rise to a relatively larger drag force. The greater drag force causes a larger difference between advancing and receding angle (contact angle hysteresis, $\Delta$) hence the droplet becomes more unstable.

As expected, at a specified droplet aspect ratio, the droplet on the 5% PTFE DM requires a higher critical $Re$ number for detachment than the DM with 20% PTFE content, since higher PTFE content reduces the surface adhesion force. Thus growth of the droplet in the cross stream direction (in $y$ direction) rather than in the streamwise ($x$) direction is desirable. Hence the surface hydrophobicity of the DM should be tailored such that it discourages droplet growth in the streamwise direction, since streamwise spreading leads to a stable condition. Spreading in any direction also increases the probability of coalescing of the multiple droplets due to the increased surface coverage of droplets, which in turn may lead to local channel flooding and a stable annular flow film in the channel, the least desired outcome.

### 3.4.4 Surface Tension Calculations as a Function of PTFE Content

The surface tension components of the DM, air, and liquid droplet system have been estimated based on measured data. For a static system, solid surface interfacial tensions can be calculated from the measured contact angles using the mechanical equilibrium relation published by Young in 1805 [19]. The liquid droplet contact angle on any solid surface can be defined by the mechanical equilibrium of the droplet under the action of three interfacial tensions, including solid surface tensions [15]. Figure 3-2
represents the schematic view of the liquid droplet sitting on a solid surface, where $\gamma_{lv}$, $\gamma_{sl}$ and $\gamma_{sv}$ represent the liquid-vapor, solid-liquid and solid-vapor surface tensions respectively. A simple force balance on the droplet contact surfaces in the x direction gives the surface tension components of the solid material.

Since the macroscopic force balance model requires a value of solid surface tensions, Young’s relation [19] was used in conjunction with the experimental linear regression fits, in order to define the surface tension forces of the tested DMs with 5%, 10%, and 20% PTFE content. Substituting the liquid-vapor surface tension term in terms of solid-liquid, solid-vapor and contact angle into the previously derived form of the macroscopic force balance equation (Eq. 3.13), a final version of the force balance equation becomes:

$$
\frac{24 \cdot \mu^2 \cdot B^2 \cdot \text{Re} \cdot h^2}{(B - \frac{h}{2})^2 \cdot (1 - \cos(\theta_d))^2 \cdot \rho \cdot d_e} + \frac{12 \cdot \mu^2 \cdot B \cdot \text{Re} \cdot h^2}{(B - \frac{h}{2})^2 \cdot (1 - \cos(\theta_d))^2 \cdot \rho \cdot d_e} - 
\frac{\gamma_{sv} - \gamma_{sl}}{\cos \theta_d \cdot c \cdot \pi}{\frac{\sin(\Delta - \theta_d) + \sin(\Delta)}{(\Delta - \pi)}} + \frac{\sin(\Delta - \theta_d) - \sin(\theta_d)}{(\Delta + \pi)} = 0
$$

[3.17]

Substituting the three different linear regressions fits (derived from the experimental data for 5%, 10%, and 20% PTFE content) into Eq. 3.17 with $U$, $c$, $h$ terms from the experimental data for each PTFE content, one can solve the equation for the surface tension terms ($\gamma_{sl} - \gamma_{sv}$) term for each PTFE content. Surface tension terms ($\gamma_{sl} - \gamma_{sv}$) were tabulated for each different PTFE value and shown in Table 3-2.

To date, empirical studies have been inconclusive regarding the best DM structure for two-phase flow management at the channel level, and to the authors’ knowledge, no
empirical correlation relating the surface tension to the PTFE coverage of DM has been reported. Equation 3.18 represents the linear regression fit (Fig. 3-10) showing the solid surface tensions \((\gamma_{sl} - \gamma_{sv})\) of the DM in terms of PTFE content. As anticipated, the surface tension values decrease as the PTFE content increases, assuming all other parameters are held constant. The adhesion force on a droplet decreases as well. Thus, as expected, droplet removal is facilitated under a higher PTFE loading.

\[
\gamma_w \cdot \cos \theta_A = \gamma_{sv} - \gamma_{sl} = 0.0006 \cdot \% \text{PTFE} - 0.0274 \\
R^2 = 0.95 \text{ (N m}^{-1} \text{ @ 60 °C )} \tag{3.18}
\]

The linear equation relating \((\gamma_{sl} - \gamma_{sv})\) and PTFE content (Eq. 3.18) may be used to estimate surface tension values over the range of 5% to 20% PTFE loadings, although an asymptotic approach for high PTFE loadings is expected over the entire range. In order to validate the surface tension values found by the force model, each solid surface tension terms were compared to literature. The surface tension component approach and equation of state approach are known to be the two basic models used to find values \(\gamma_{sl}\) and \(\gamma_{sv}\) separately [16]. Kwok et al. [15] provided a FORTRAN program to calculate the solid-liquid and solid-vapor interfacial tensions \((\gamma_{sl}, \gamma_{sv})\) by solving the equation of state. Using this code, the equation of state was computed and three different values of \(\gamma_{sv}\) and \(\gamma_{sl}\) for each PTFE content were found and listed in Table 3-3;

When these values are compared to Zisman et al. [20], excellent agreement is reached. The average value of all three \(\gamma_{sv}\) is 0.008 N m\(^{-1}\) at 60 °C. Zisman et al. [20]
calculated the solid-vapor interfacial tensions for different materials by using experimental static contact angles with the equation state approach. He found a solid-vapor interfacial tension ($\gamma_{sv}$) value of PTFE of 0.018 N m$^{-1}$ with a static contact angle 108°. When this value is compared to the value predicted by the present macroscopic force balance model, it is seen that the model prediction and Zisman’s prediction are at the same order of magnitude; however the force balance model predicts the value $\gamma_{sv}$ slightly lower than the Zisman et al. [20], due to the dependence of surface tension on temperature. The present model predicts the solid-vapor surface tension of DM at 60 °C, however Zisman et al. [20], listed the solid surface tension values of the materials at 20 °C. The discrepancy between these values arises due to the fact that as the temperature increases, the molecular interaction at the interface increases, hence molecules behave more independently due to the excess stored kinetic energy. As a result of this, adhesion forces decreases.

3.4.5 Impact of PTFE Content

3.4.5.1 Contact Angle Hysteresis

The macroscopic force balance model was solved for contact angle hysteresis for three different PTFE samples of SGL® carbon paper in order to obtain a reasonable estimate of the droplet instability as a function of PTFE content. Contact angle hysteresis ($\Delta$) versus channel air velocity at a specified droplet chord length ($c=1.7$ mm and $h=1.9$ mm) and different PTFE loading DMs is shown in Fig. 3-11. At a specified air velocity,
the maximum contact angle hysteresis occurred in DM with 20% PTFE content and minimum contact angle hysteresis occurred in DM with 5% PTFE content. Physically, the surface adhesion force is reduced by rendering the DM surface more hydrophobic. As a result, at higher PTFE loadings of the DM (decreased adhesion energy of the water molecules onto the treated carbon fiber), the droplet deforms more readily, causing high contact angle hysteresis. Hence, the liquid water droplets located on a high PTFE loading surface tend to be more unstable, and the drag force required to remove the water droplets of a given size decreases.

### 3.4.5.2 Flow Rate Effects

The two primary parameters affecting the droplet instability are PTFE content and air flow rate. However, in order to develop a new design criterion for effective water removal from the flow channel, an optimal balance between the amount of PTFE content of the DM and air flow rate must be considered. Engineering consequences of increasing PTFE content and air flow rate include the material cost, electrical resistance of the DM increase as the amount of PTFE content increases, and increased parasitic losses due to the increase in air flow rate.

To assess the relative significance of PTFE content and air flow rate on the stability of the droplet, the variation in contact angle hysteresis on different PTFE content of the DM was compared at different air flow rates using the macroscopic force balance equation. Using the experimentally-correlated surface tension values for each PTFE content, the force balance equation was solved for the contact angle hysteresis (Δ) and air
velocity at a constant chord length and height ($c=1.7$ mm and $h=1.9$ mm), shown in Fig. 3-11. A linear functional dependence between the contact angle hysteresis ($\Delta$) and air velocity was also observed, although there was some scatter. Note also that the difference in the predicted $\Delta$ between each PTFE value diverges as the velocity of the air increases in the channel; however, at low velocity, the difference in $\Delta$ between three PTFE contents is almost negligible.

The dependence of contact angle hysteresis ($\Delta$) on PTFE content of the DM, over a range of Reynolds numbers has also been investigated using the analytical force balance model, as shown in Fig. 3-12. It is observed that increasing the PTFE content for low Reynolds number does not change the contact angle hysteresis significantly, but for Reynolds numbers greater than 600, increases in PTFE content do significantly impact contact angle hysteresis ($\Delta$). Effectively, the influence of PTFE content on contact angle hysteresis is more dominant in the high air flow rate (Reynolds number) regime. However, under low air flow conditions, water removal from the channel is relatively unaffected by the surface PTFE content, and therefore high PTFE content is not necessary, or desirable since PTFE additive will have the additional effect of increasing thermal and electrical contact resistance. Therefore it can be concluded that using higher PTFE content DMs enhances the water droplet removal from channels significantly, only under higher Reynolds numbers.
3.4.6 Effect of Channel Height

Equation 3.13 was solved for contact angle hysteresis (Δ) in order to predict the effect of channel aspect ratio on droplet hysteresis. The contact angle hysteresis was predicted for a droplet with constant dimensions (c=0.5 mm, h=0.5 mm) over a range of different channel heights (Fig. 3-13). As shown in Fig. 3-13, for a constant droplet size and average flow velocity over all PTFE contents, the contact angle hysteresis (Δ) is reduced as the channel itself becomes taller (increasing height), resulting in a more stable condition for the droplet. Physically, since $\Delta P \sim U^2 A / d_c$, for a constant droplet size and average flow velocity, as the channel gets taller (with no corresponding change in width), the pressure required to drive the flow at that given velocity decreases, reducing the pressure force on the droplet, thus decreasing the acting drag force.

For the varying channel heights shown in Fig. 3-13, contact angle hysteresis (Δ) is affected more strongly by PTFE content at the higher average flow velocity ($U=8.5$ m s$^{-1}$, $Re=760$ to 2030). Specifically, in the force balance model, for average air velocities of $2.13$ m s$^{-1}$ ($Re=190$ to 507) and below, the variation in contact angle hysteresis (Δ) over all PTFE tested is less than 5° and can be considered negligible for this lower range of average flow velocities.

In summary, the present model predicts that, in the absence of wall interactions, and for constant air velocity, droplet size, and PTFE loading, the lowest tolerable channel height within the limits of other constraints provides the most efficient water droplet removal from the flow channel. Within the set of parameters considered in the current study, the model predicts that the best water removal can be achieved in flow channels
having the shortest height, at high average air velocities \((U > 2.13 \text{ m s}^{-1})\), and with 20 % PTFE loading of DM. Liquid water accumulation and residual water content in the flow channels and DM for different flow-field geometries were also investigated by Turhan et al. [21]. Using neutron imaging, they reported that channel water content increased with increasing the channel aspect ratio, in agreement with the present results. They concluded that there can be large differences in the stored water content, which is a function of channel geometry [21].

3.5 Summary

Data on surface droplet deformation and removal from a fuel cell DM (DM) surface was determined by employing simultaneous visualization of both the top and side views of a water droplet under an imposed shear flow. Additionally, an analytical force balance model was derived to show the droplet instability boundary in shear flow. Since numerical values for surface tension of a droplet on DM as a function of PTFE content are not available in the literature, an empirical correlation of surface tension versus PTFE content was developed based on the experimental data. Overall, the theoretical and experimental data agree reasonably well. It was observed that channel flow rate, droplet chord length and height, channel geometry, and surface properties of porous DM such as hydrophobicity directly affect the degree of droplet deformation, and therefore influence droplet removal. As expected, imposing high air flow rates into the flow channel increases the contact angle hysteresis, promoting droplet removal. Other specific conclusions that can be drawn for this study include:
1. The removal of the relatively taller droplets (higher aspect ratio) is easier than that of relatively spread out droplets and films, due to the squared dependence of the drag force acting on the droplet on height and the linear dependence of the surface adhesion force on droplet chord length.

2. Using higher PTFE loadings of the DM promotes increased deformation of the droplet, causing higher contact angle hysteresis, due to the decreased surface interfacial tensions of the water molecules onto the carbon fibers. In addition, the influence of PTFE content on contact angle hysteresis is more important in a high air flow rate regime ($Re \geq 600$). Under a low air flow condition, droplet instability (and removal) is unaffected by the surface PTFE content, and so at low air flow rate operations such as in an anode, high PTFE content is not necessary, or desirable, since increased surface PTFE increases electrical resistance and material cost.

3. Given a constant droplet size and constant channel width, the lowest channel height is found to be the most effective for droplet removal, in the absence of channel-wall interactions.
3.6 Bibliography


Table 3-1: Summary of the test matrix (at 60 °C).

<table>
<thead>
<tr>
<th>Measured Parameter</th>
<th>5% PTFE DM Re=100 to 1200 at increment of 100 (15 images at each Re)</th>
<th>10% PTFE DM Re=100 to 1200 at increment of 100 (15 images at each Re)</th>
<th>20% PTFE DM Re=100 to 1200 at increment of 100 (15 images at each Re)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Advancing angle, $\theta_A$</td>
<td>In each image, measured 5 times</td>
<td>In each image, measured 5 times</td>
<td>In each image, measured 5 times</td>
</tr>
<tr>
<td>Receding angle, $\theta_R$</td>
<td>In each image, measured 5 times</td>
<td>In each image, measured 5 times</td>
<td>In each image, measured 5 times</td>
</tr>
<tr>
<td>Chord length, $c$</td>
<td>In each image, measured 5 times</td>
<td>In each image, measured 5 times</td>
<td>In each image, measured 5 times</td>
</tr>
<tr>
<td>Height, $h$</td>
<td>In each image, measured 5 times</td>
<td>In each image, measured 5 times</td>
<td>In each image, measured 5 times</td>
</tr>
</tbody>
</table>

Table 3-2: The model prediction of surface tension terms ($\gamma_{sl} - \gamma_{sv}$) for different DM.

<table>
<thead>
<tr>
<th>Amount of PTFE Surface Coverage of DM ( % wt)</th>
<th>Interfacial Tension Difference of DM (N m$^{-1}$) (Model Prediction)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5 % PTFE</td>
<td>$\gamma_{sl} - \gamma_{sv} = 0.02516$</td>
</tr>
<tr>
<td>10% PTFE</td>
<td>$\gamma_{sl} - \gamma_{sv} = 0.02004$</td>
</tr>
<tr>
<td>20% PTFE</td>
<td>$\gamma_{sl} - \gamma_{sv} = 0.01562$</td>
</tr>
</tbody>
</table>
Table 3-3: Calculated solid-vapor, $\gamma_{sv}$, and solid-liquid, $\gamma_{sl}$, surface tensions of the tested DMs coated with different PTFE loading

<table>
<thead>
<tr>
<th>Amount of PTFE (% wt.)</th>
<th>Solid-Vapor Tension, $\gamma_{sv}$, (N m$^{-1}$) @ 60 °C</th>
<th>Solid-Liquid Tension, $\gamma_{sl}$, (N m$^{-1}$) @ 60 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>5% PTFE</td>
<td>0.00636</td>
<td>0.03152</td>
</tr>
<tr>
<td>10% PTFE</td>
<td>0.00805</td>
<td>0.02809</td>
</tr>
<tr>
<td>20% PTFE</td>
<td>0.00967</td>
<td>0.02529</td>
</tr>
</tbody>
</table>
Figure 3-1: a) Captured image of the droplet in the presence of an air shear flow, and b) schematic of control volume chosen for analysis.
\[ \gamma_{lv} \cos \theta_l = \gamma_{sv} - \gamma_{sl} \]

Figure 3-2: Schematic view of a) droplet contact surface, and b) droplet sitting on a surface.
Figure 3-3: Schematic view of experimental setup.
Figure 3-4: Comparison of experimental data, linear regression data and macroscopic force model for 3 different PTFE regression fits a) 5% PTFE, b) 10% PTFE, and c) 20% PTFE.
Figure 3-5: SEM picture of the cross sectional view of 20% PTFE DM.
Figure 3-6: Captured images of a) droplets with same height under different air flow rates, and b) droplets with different height under same air flow rate.
Figure 3-7: Contact angle hysteresis (Δ) versus air velocity for a droplet with constant chord length=1.7 mm and height=1.9 mm a) 5% PTFE, and b) 20% PTFE.
Figure 3-8: Reynolds number versus droplet aspect ratio for a droplet with specified chord length of 2.3 mm on 5% PTFE DM.
Figure 3-9: Reynolds number versus droplet aspect ratio for a droplet with specified chord length of 1.9 mm on 20% PTFE DM.
Droplet removal is facilitated, as the DM is rendered more hydrophobic.

Figure 3-10: Solid surface tension difference ($\gamma_{sl} - \gamma_{sv}$) of DM versus % PTFE content.
Figure 3-11: Contact angle hysteresis ($\Delta$) versus air velocity at $h=1.9$mm and $c=1.7$mm for three different PTFE contents (model prediction and experimental data).
Figure 3-12: Contact angle hysteresis ($\Delta$) versus % PTFE surface coverage (model prediction) for a droplet with $c=1.7$ mm and $h=1.9$ mm.
Figure 3-13: Contact angle hysteresis ($\Delta$) versus channel height (mm) for a constant droplet size ($c=0.5$ mm and $h=0.5$ mm) at different average air velocities (model prediction).
Chapter 4

ON THE EFFECTIVENESS OF TRADITIONAL LEVERETT APPROACH TO DESCRIBE WATER TRANSPORT MECHANISM

This chapter reports a detailed comparative analysis of the constitutive relations describing the capillary-induced flow in fuel cell diffusion media (DM), particularly focusing on the applicability of the commonly employed standard Leverett approach to describe the water transport in thin-film fuel cell DM with mixed wettability. The saturation prediction of the Leverett approach in its original form (as applied to the most fuel cell models) was compared with the prediction of the empirical capillary pressure-saturation correlation derived from the experimental data provided by [10]. The reasons underlying the variations in liquid saturation predictions within the DM were linked to the prediction potential of the Leverett approach. With the aid of these analyses, the ineffectiveness of employing Leverett approach in its original form is discussed and the necessity of development of a modified Leverett approach appropriate for thin-film fuel cell media is addressed.

4.1 Background

Because of the minute length scales and presumed anisotropic nature of the thin-film DM, the multi-phase transport behavior inside the DM is not yet fully understood. Within the DM, gravitational and viscous forces are relatively small compared to capillary forces [1-5]. Hence, two-phase transport in the DM is primarily controlled by
capillary action. The pressure difference arising from the interfacial tensions at the liquid-gas interface front is referred to as the capillary pressure. The capillary pressure is a strong function of liquid saturation ($s_i$), which is a key parameter representing the available pore space, through which reactant gases can diffuse.

Fuel cell performance is known to exhibit hysteresis, for a variety of reasons, but often because of liquid water motion. Many studies [5-9] reveal that liquid water transport is a dominating factor influencing the performance of the fuel cell, and is closely related to the liquid saturation distribution in DM. Therefore, accurate prediction of the liquid water distribution in the DM as a function of material properties is of great interest to understand the capillary transport phenomenon in the DM [6-11]. An extensive review of the recent modeling efforts is provided in [12]. Since the vast majority of the background work on defining the capillary pressure-saturation relation has been performed in the soil science and oil extraction fields, a generic Leverett approach from soil science has been commonly employed to represent the water transport or retention behavior of the fuel cell DM as a first step toward achieving an accurate two-phase transport model for fuel cells studies [5-7]. The Leverett approach, indeed, is viewed as an indispensable tool for many modelers and serves as a useful starting point to model the liquid transport in the DM. Although the usefulness of the Leverett approach is clear, the degree of the applicability of the traditional Leverett approach in its original form to the highly anisotropic thin-film DM has not been conclusively established. Since the naturally hydrophilic fuel cell DM material itself is impregnated with an anisotropic coating of hydrophobic material (PTFE or other), it yields a complex bi-modal pore size distribution with mixed wettability, complicating the transport phenomena therein.
Specific concerns center around the characteristic morphological differences in fuel cell DM and conditions under which the Leverett approach equipped with $J$-function was derived, including the fact that it was: empirically derived to simulate a range of common soils with uniform wettability, ignoring the observed hysteresis in porous media and most importantly, developed for isotropic soil beds with a high volume to surface area ratio [13]. As a result of the anisotropic coating of hydrophobic material (PTFE or other), the liquid water can be both the wetting (on untreated DM fiber), and non-wetting phase (on PTFE coated fiber) phase [12], complicating the mathematical description of the transport phenomena. Furthermore, the definition of contact angle representing the wettability characteristics of the anisotropic DM with mixed wettability is typically taken as a statistical average over the entire medium, obscuring local effects which may differ from the whole. Therefore, the applicability of the traditional Leverett approach to thin-film fuel cell DM is questionable, and is the focus of this paper.

Another important parameter governing the capillary transport inside the DM is relative permeability, which is also a strong function of liquid saturation. In PEFC modeling studies, a typical relative permeability expression for non-consolidated sands is adapted to describe the phase transport in DM due to its simplicity, that is:

$$k_{r-nw} = s_{nw}^3$$

[4.1]

where $k_{r-nw}$ and $s_{nw}$ represent the relative permeability of non-wetting phase and non-wetting saturation, respectively. However, the applicability of this correlation to the thin-film DM is also questionable and yet unproven. Direct experimental evidence is still
needed to verify the applicability of these empirical correlations, since the reliability of the computational output is directly related to the quality of the input parameters.

The direct measurement of liquid saturation distribution through the pores of the DM is an experimental challenge and only limited experimental studies are yet available in the open literature [1,2]. Recently, Gostick et al. [10] reported a novel experimental approach for determining the dependence of capillary pressure on wetting phase saturation along a desaturation path (drainage) for various DMs. This technique, the method of standard porosimetry (MSP), is capable of distinguishing the hydrophilic pore distribution from the total pore network, unlike mercury intrusion porosimetry. Using standard porosimetry, Gostick et al. [10] measured the static capillary pressure as a function of saturation during the drainage process for a certain PEFC DM materials under a limited set of conditions.

4.2 Theoretical

4.2.1 Theoretical Analysis of Liquid Transport through DM

An analytical model describing the capillary liquid flow has been developed to predict the liquid saturation distribution inside the DM. This model is constructed to provide a tool to assess the saturation predictions of the constitutive relations while isolating all other effects, including: humidity, 2-D effects, inlet cell conditions and time dependent parameters etc. Figure 4-1 shows a schematic of the chosen control volume in the fuel cell. In the present model, the liquid water flowing inside the DM is assumed to
be Newtonian and incompressible, and the flow in the pores of the DM is presumed to be uni-directional, steady and laminar.

In the steady state, once the gas phase is fully saturated with water vapor, assuming evaporation and condensation do not take place in the DM, liquid water flow becomes the only mode of the water transport across the DM [6]. Water generation in the catalyst layer, water transport across the membrane, and condensation or evaporation within the DM pores cause non-uniformity in the saturation distribution. As hydrophobic DM pores are filled by the liquid water, the liquid phase pressure increases, eventually driving the liquid water from higher to lower liquid pressure regions. As a result, the liquid water in the DM is driven via capillary action produced by the liquid saturation gradients in DM. This phenomenon is illustrated in Fig. 4-2.

In a hydrophobic DM, capillary pressure is defined as the difference between liquid pressure (non-wetting phase) and reactant gas pressure (wetting phase).

\[ P_c = P_l - P_g \]  \hspace{1cm} [4.2]

The liquid flow through the porous DM can be described by Darcy’s law. Darcy’s law relates the flow rate through a porous medium to the pressure gradient across the porous media and the permeability of the porous media. Assuming constant gas phase pressure \((P_g \approx \text{const})\) and no convective gas flow, the governing liquid transport equation in the porous DM can be expressed as:

\[ \vec{v}_l = -\frac{k}{\mu} \nabla P_c \text{ where } \nabla P_c \approx \nabla P_l \]  \hspace{1cm} [4.3]
where \( k \) is absolute permeability of the porous media, \( k_r \) is fluid relative permeability, \( \mu \) is the absolute viscosity of the fluid and \( \tilde{v}_i \) is the velocity of the flowing fluid.

A generic Leverett approach has been commonly employed to describe the capillary pressure-saturation relation of the DM in two-phase PEFC models. Leverett [21] related capillary pressure to saturation in porous media by:

\[
P_c = \gamma \cos \theta \left( \frac{\varepsilon}{k} \right)^{1/2} J(s_l)
\]

where \( k, \varepsilon, \theta, \gamma \) and \( J(s_l) \) represent the gas phase or liquid absolute permeability, porosity of the DM, contact angle between liquid-solid phase, surface tension and the Leverett function in terms of liquid saturation, respectively. The standard Leverett function, \( J(s_l) \), is given as [21]:

\[
J(s_l) = \begin{cases} 
1.417(1-s_l) - 2.120(1-s_l)^2 + 1.263(1-s_l)^3 & \text{if } \theta < 90^\circ \Rightarrow \text{Hydrophilic} \\
1.417s_l - 2.120s_l^2 + 1.263s_l^3 & \text{if } \theta > 90^\circ \Rightarrow \text{Hyrophobic}
\end{cases} \quad [4.5]
\]

The liquid pressure \( (P_l) \) is a function of local liquid saturation; hence the capillary pressure gradient can be expressed as:

\[
\tilde{\nabla} P_l \approx \tilde{\nabla} P_c = \gamma \cos \theta \sqrt{\frac{\varepsilon}{k} \left( \frac{dJ}{ds_l} \right)} \tilde{\nabla} s_l
\]

Inserting Eq. 4.6 into Eq. 4.3, the governing equation yields:

\[
\tilde{v}_l = -\frac{k k_r \gamma \cos \theta}{\mu_l} \sqrt{\frac{\varepsilon}{k} \left( \frac{dJ}{ds_l} \right)} \tilde{\nabla} s_l
\]

Assuming all the water produced by electrochemical reaction in a PEFC is in liquid form, the mass flux of liquid water going into the cathode DM is equal to sum of
the net water transport from the anode side and the amount of water generated in the catalyst layer due to the electro-chemical reaction. The net water flux across the membrane from anode to cathode can be characterized by a net water transport coefficient, $\alpha$ [29]. Combining the net water transport with the water production, the net water flux to the cathode DM yields:

$$\rho_i V = \frac{I}{2F} (2\alpha + 1) MW_{H_2O}$$

[4.8]

where $MW_{H_2O}$ is the molecular weight of the water, $\alpha$ is the net water transport coefficient to the cathode DM, $I$ is the current density and $F$ is the Faradic constant (96,485 C-mole eq$^{-1}$). Assuming one-dimensional flow, substituting Eq. 4.8 into Eq. 4.7, the final form of the governing equation becomes:

$$\frac{I(2\alpha + 1) MW_{H_2O} \mu_i}{2F \gamma \rho_i \cos \theta \sqrt{k}} = -k_r \frac{dJ}{ds_i} \frac{ds_i}{dx}$$

[4.9]

This relationship describes the steady-state liquid water transport across the fuel cell DM. As seen from Eq. 4.9, the operational conditions and DM material properties are coupled with the fluid properties and the mass transport rate are explicitly linked to the liquid saturation.

**Micro-Porous Layer Interface**

Generally, the cathode side of PEFC consists of a coarse DM and a finer micro-porous layer (MPL), both of which are generally classified as hydrophobic, based on surface contact angle. However, the DM is actually a mixed wettability network, since the base material of carbon-fiber is hydrophilic. Micro-porous layers are introduced
between the DM and catalyst layer (CL) to provide better membrane electrical contact and improve the water management. The liquid water transport of the MPL is governed by capillary action. In equilibrium, the capillary pressure across the interface between the DM and MPL is continuous. The different material properties of these two layers cause a discontinuity in the liquid saturation across the interface [7], as illustrated in Fig. 4-3. The magnitude of the discontinuity or the jump in the saturation at the interface strongly depends on the material properties of these two layers, specifically the hydrophobicity and pore radius. Imposing the capillary pressure balance at the interface yields:

\[
P_c^{DM}\big|_{DM-MPL\ Interface} = P_c^{MPL}\big|_{DM-MPL\ Interface}
\]

\[
\cos \theta_{MPL} \left( \frac{e_{MPL}}{k_{MPL}} \right)^{1/2} J(s_{l-int, MPL}) = \cos \theta_{DM} \left( \frac{e_{DM}}{k_{DM}} \right)^{1/2} J(s_{l-int, DM})
\]  

[4.10]

With a known liquid saturation at the DM interface, the equilibrium MPL liquid saturation at the interface can be calculated from Eq. 4.10. Since the structural characteristics of MPL and physics of the flow through the MPL are similar to the DM, the governing equation (Eq. 4.9) can also be applied to the MPL in order to map the saturation distribution profile inside the MPL.
4.2.2 Constitutive Equations

4.2.2.1 Relative Permeability

When two or more fluids are present in the porous media, an additional parameter, known as relative permeability, is used to represent the ability of the porous media to conduct various fluids simultaneously. Relative permeability is defined as the ratio of the effective permeability of one fluid to the absolute permeability of the porous media [13,14]. Direct experimental measurement of relative permeability for different types of soils has been performed. Mathematical approximations based on previous experiments are generally preferred for estimating the relative permeability because of the difficulty in conducting direct experiments.

Various researchers have proposed correlations based on mathematically-derived relationships or experimental data to predict the relative permeability [15]. Most of the existing relative permeability correlations are based on the following types of physical models: capillary model, statistical model, empirical model and network model [15]. Empirically-derived models based on direct experimental observation provide the most reasonable approximations due to their simplicity and reliance on direct measurements compared to other types of models [15]. Even though all of the above-mentioned models have been used to predict the relative permeability [16], they may not be appropriate for use in a fuel cell DM. Typically, the general shape of the relative permeability curves is estimated by the following equations [15]:

\[ k_{r_{\text{nw}}} = A(s_{nw})^n \quad \text{and} \quad k_{r_{-w}} = B(1 - s_{nw})^m \]  \[4.11\]
where $A$, $B$, $n$ and $m$ are constants depending upon the structure of the porous media.

In the present study, four well-established empirical correlations describing the water-air two-phase system (Wyllie model, Corey model, Brooks-Corey model and the Van-Genuchten model) are used to predict a representative non-wetting phase (liquid) relative permeability for differently engineered DMs, based on the experimental capillary pressure data provided by [10]. The relative permeability calculation in each model is based on the effective saturation ($s_e$), which requires the irreducible water saturation ($s_{irr}$) as an input. The irreducible saturation or immobile saturation, ($s_{irr}$), is the amount of trapped water in the pores of the DM. It can be considered as a threshold point below which liquid remains immobile.

\[
s_e = \frac{s - s_{irr}}{1 - s_{irr}} \quad [4.12]
\]

**Wyllie Model**

Wyllie [14,15] suggested simple liquid-gas relative permeability equations for well and non-consolidated sands, based on the capillarity concept developed by Purcell [17] and Burden [18]. The Wyllie approach is widely applied in fuel cell modeling studies due to its simplistic application [12].

\[
\begin{align*}
k_{r-nw} &= (s_{e-nw})^3 \\
k_{r-w} &= (1 - s_{e-nw})^3
\end{align*} \quad [4.13]
\]

where $s_e$, $nw$ and $w$ represents the effective saturation, non-wetting phase and wetting phase, respectively.
Corey Model

Purcell developed an analytical expression to compute the relative permeability from experimental capillary pressure data [16]. Burdine [18] introduced the tortuosity factor concept into the original capillary pressure model developed by Purcell [17] and extended this equation to calculate the multiphase relative permeability. Corey combined these two approaches into a single form, based on the assumption that capillary curves over a certain range of saturations can be approximated using the linear expression, \( 1/P_c^2 = C \cdot s_{e-w} \), where \( C \) is a constant, and obtained the following relative permeability equations for non-wetting and wetting phases [15]:

\[
k_{r-nw} = \left[1 - (s_{e-nw})^2\right] \cdot \left[1 - s_{e-w} \right]^2
\]

\[
k_{r-w} = (s_{e-w})^4
\]

Brooks-Corey Model

Brooks and Corey modified the original Corey capillary pressure-saturation relationship to predict the relative permeability for any pore size distribution [15].

\[
k_{r-nw} = (1 - s_{e-nw})^2 \cdot \left[1 - (s_{e-nw})^{\frac{2+\lambda}{\lambda}} \right]
\]

\[
k_{r-w} = (s_{e-w})^{\frac{2+\lambda}{\lambda}}
\]

where \( \lambda \) is the pore size distribution index of the porous media, which is a specific characteristic of the pore size distribution, and it is typically determined by fitting the water retention data to the Brooks-Corey correlation.
**Van Genuchten Model**

One of the most recent relative permeability correlations was proposed by Van Genuchten [19,20]. Van Genuchten derived an empirical correlation that accounts for variable pore size and connectivity concepts of the porous media. This model unites the entire range of saturation in a single curve, even though not all of the saturation regions (e.g., dry end, wet end) are governed by the same physics [19,20]. According to the Van Genuchten model, the relative permeability of the non-wetting and wetting phases can be calculated as follows:

\[
\begin{align*}
    k_{r_{-nw}} &= (1 - s_{e-w})^{1/3} \cdot [1 - (s_{e-w})^{1/m}]^{2m} \\
    k_{r-w} &= (s_{e-w})^{0.5} \cdot [1 - (1 - (s_{e-w})^{1/m})^m]^2
\end{align*}
\]  

[4.16]

where \(m\) is a fitting parameter and can be extrapolated from capillary pressure-saturation data. The models utilized in the present study are summarized in Table 4-1. In all these models, the capillary pressure and the relative permeability are coupled; thus each model requires the knowledge of capillary pressure as a function of water saturation. However, the standard porosimetry technique is incapable of distinguishing the isolated pores [10], thus the capillary pressure data presented in [10] is associated with the total saturation. Therefore, a lower limit value of \(s_{yr}, 0.05\), is used in the present study, assuming all the pores are almost connected, to minimize the isolated pore size effect and estimate the bulk multi-phase connectivity of a typical fuel cell DM.
4.2.2.2 Capillary Pressure-Saturation Empirical Fit

The capillary pressure-saturation curves obtained by Gostick et al. [10] were used as benchmark data to obtain a polynomial fit explicitly relating the $P_c$ versus $s_l$ for the tested fuel cell DMs under a limited set of conditions. Four different types of diffusion media including: SGL 10BA, SGL 10BB, Toray 090 and E-TEK Cloth A, were selected, and the material properties of these DMs including the total and hydrophilic porosities are tabulated in Table 4-2 (adapted from [10]).

Figure 4-4-a depicts the measurements of capillary pressure-saturation (provided by [10]) for the DM chosen in this study. As seen in Fig. 4-4-a, the measured capillary pressure for all DM samples follows the same qualitative trend, even approaching similar capillary pressures especially at low saturations ($s_{nw}<0.6$). The difference in capillary pressure can be attributed to the differences in the specific morphological and characteristics and PTFE loading of the chosen DMs. As also stated in [10], a sudden increase in capillary pressure is observed after the threshold saturation value of 0.8. The sudden change in the measured data at high saturation values ($s_{nw}>0.8$) causes a significant amount of scattering, which in turn, complicates the representation by an accurate curve-fit. Typically, a fuel cell operates in a saturation range of 0 to 0.6, therefore the capillary pressure measurements within the saturation range of 0 to 0.8 were considered to be appropriate benchmark data. A single equation representing the actual $P_c$–$s_l$ relation of the tested DMs (Eq. 4.17) was deduced based on the best fit of the data ($0<s_{nw}<0.8$) and shown in Fig. 4-4-b. Even though the empirical curve-fit starts to deviate from the actual data at high saturations ($s_{nw}>0.8$) due to the sudden increase in the
measured capillary pressure, the curve-fit reasonably predicts the measured data within the saturation range of 0 to 0.8 covering the range, in which a polymer electrolyte fuel cell typically operates.

\[ P_c = -4854.1 \cdot s_i^2 + 12958 \cdot s_i \text{ (in Pascals) } \quad R^2 = 0.80 \quad 0 < s_{nw} < 0.8 \quad [4.17] \]

It is worthwhile emphasizing that Eq. 4.17 was utilized solely to evaluate the saturation predictions of the traditional Leverett approach equipped with \( J \)-function for the DM samples tested by [10]. Equation 4.17, therefore, should not be considered as a generalized relationship appropriate for all type for fuel cell DM, although such a relationship is definitely required.

The distinctive feature of the presented empirical fit is that it implicitly accounts for the variations in the relevant transport properties of the tested DMs including porosity, surface tension and contact angle, since it relies on the actual experimental capillary pressure data of [10]. Therefore such a representative curve-fit based on experimental measurement of the tested DM samples eliminates the requirement of porosity, surface tension and \( J \)-function as an input. In addition, the contact angle parameter, which is a required input in Leverett approach, is implicitly embedded into the empirical curve-fit, thereby accounting for variations in internal contact angle caused by the anisotropic nature of the hydrophobic coating. This feature enables us to eliminate the need for the selection of a single (and unrealistic) surface contact angle.
4.3 Mapping the Liquid Saturation Distribution

4.3.1 Modified Constitutive Relations

*Characteristic Relative Permeability*

A new characteristic relative permeability correlation appropriate for uncompressed room temperature thin-film fuel cell DM was obtained by compiling the experimental capillary pressure data presented in [10] to the empirical models described in Section 2.2. The relative permeability correlation obtained from these models was fit onto a single curve in the form of $k_r = A (s_r) m$ to represent the overall relative permeability behavior of the tested DMs. Equation 4.18 shows the predicted relative permeability relation for DMs tested by [10] at room temperature and under no compression.

$$k_r = (s_r)^{2.16} \quad R^2 = 0.978 \quad [4.18]$$

This relationship should be used with caution, as it is a bulk fit for the four different DMs tested by [10], under no compression at room temperature. Nonetheless, it is an improvement of the existing models applied without linkage to the measured experimental data. Figure 4-5-a depicts the predicted relative permeability curve as a function of liquid saturation. The predicted relative permeability curve for the non-wetting phase shows a modest increase at low saturations, because at low saturations only a small portion of the pores are occupied by the liquid water, whereas a large portion of the pores are still available for the gas-phase transport. Hence, there is no significant impact of saturation on the reactant flow. However, at high saturations, the
predicted relative permeability exhibits a considerable increase with small increases in saturation, because as the available pores are nearly all filled by the liquid water and gas-phase transport is highly restricted.

Figure 4-5-b shows the percentage deviation of the typically used Wyllie model ($s^3$ model) from the predicted curve-fit at different saturation values. When the present prediction is compared with the commonly used Wyllie model ($k_{r,nw} = (s_{nw})^3$) over the entire spectrum of water saturation ($0<s_{nw}<1$), a significant difference between the predicted relative permeability values is observed, especially at low water saturation values ($s_{nw}<0.4$). The discrepancy between the predictions diminishes at relatively higher saturation values ($s_{nw}>0.6$). Physically speaking, the coefficients in Wyllie model were generated for non-consolidated sands. Thus the applicability of the Wyllie model by itself may not accurately describe the relative permeability of the fuel cell DM. Currently, the presented approach (Eq. 4.18) takes into account a broader range of theoretical analysis of relative permeability in porous media with the intent of providing an improved relative permeability relation and it incorporates direct experimental data obtained in [10] for various common DMs. However, the direct measurement of relative permeability for thin fuel cell DM as a function of temperature, compression and PTFE content is still needed to verify the applicability of present prediction.
4.3.2 Implementation of Different Constitutive Relations

Different constitutive relations were implemented within the theoretical model described in Section 2.1 to predict the local liquid saturation profiles. The local saturation profiles were predicted for two different cases (Case 1 and Case 2 as described below), governed by different relations. Furthermore, operational conditions and relevant structural properties of thin-film porous DM, including net water transport coefficient, current density, thickness and hydrophobicity, were examined for these two cases in order to capture the significance of the differences in liquid saturation profiles.

In Case 1, the standard Leverett function and Wyllie relative permeability relation \( k_{r-nw} = s_{nw}^3 \) were used in Eq. 4.9, whereas in Case 2, along with the modified relative permeability \( k_{r-nw} = s_{nw}^{2.16} \), an empirical curve-fit (Eq. 4.17) representing the measured \( P_C -s_l \) relation of the DMs tested by [10] was directly integrated into the theoretical model. The relations used in each case and the final form of the governing equations for these two cases are shown in Table 4-3.

Analytical solution of the equations in Table 4-3 enables determination of the local saturation, \( s_l \), at any location, \( x \), of the DM. The final form of the governing liquid transport equations overall include a number of engineering parameters, including the porosity of the DM, permeability, current density, contact angle, surface tension (function of temperature), net water transport coefficient and liquid saturation.
4.3.3 Validation of the Empirical Curve-fit

To evaluate the accuracy of the empirically derived curve-fit (Eq. 4.17), an additional assessment was performed. The saturation prediction of Eq. 4.17 was compared with the saturation profiles predicted by the measured capillary pressure-saturation curves of the tested DM samples [10]. The capillary pressure-saturation curve of each DM was separately implemented into the analytical framework and the corresponding saturation profiles were calculated at 1 A cm⁻², assuming a typical DM thickness of 300 µm. Figure 4-6 presents the predicted saturation profiles of Case 2 by implementing the measured capillary pressure-saturation curves of SGL 10BA, SGL 10BB, TORAY 090, ETEK-A and the curve-fit given in Eq. 4.17. The saturation profiles over the entire thickness appear to follow the similar qualitative trend, even predicting very close saturation values. More importantly, the curve-fit given in Eq. 4.17 is observed to reasonably well-predict the saturation values for all DM samples, with an uncertainty of ± 6.8%, strongly supporting the effectiveness and applicability of this approach for comparing the experimental data with the prediction of Leverett approach.

In addition, the small deviation between the saturation predictions indicates that even though the change in PTFE content may affect the transport parameters, within the context of the experimental data provided for the tested DM materials, the predicted saturation values appear to be relatively insensitive to the change in PTFE within the specified range of DM samples (from 0% to 5 wt. % PTFE).
4.4 Results and Discussions

4.4.1 Effects of DM Properties

The theoretical model was solved to predict the liquid saturation profiles for different thicknesses and various hydrophobicity levels. The predicted saturation profiles corresponding to different DM thicknesses were compared. However, the effect of hydrophobicity on the predicted local saturations was only performed for Case 1, since Case 2 is a curve fit for four different DMs tailored with similar PTFE content (ranging from 0 to 5% of wt.) and the contact angle parameter is implicitly embedded into this empirical fit, thus not required as an input. The liquid saturation was set to zero at the DM-flow channel interface as a boundary condition, representing a drainage condition. The condition of zero liquid surface coverage in the flow channel by liquid water is reasonably valid for carbon cloth and conditionally expected for carbon paper DM under large air stoichiometry [6].

DM Hydrophobicity

As expected, the hydrophobicity of the DM has a strong impact on the liquid saturation distribution predicted by Leverett approach. The liquid saturation profiles for different contact angle values were determined for Case 1 and shown in Fig. 4-7-a. At any specified location, the maximum liquid saturation is predicted for contact angle 95°, whereas the minimum local saturation occurred for contact angle 150°. In addition, for a constant fractional distance from the catalyst layer, the theoretical model was solved for Case 1 to predict the local saturation values as a function of contact angle values (shown
in Fig. 4-7-b). As the contact angle increases from 95° to 110°, a relatively severe decrease in local saturation values is observed. Above 90°, the liquid water transport is enhanced noticeably by an increase in hydrophobicity, but with diminishing dependence. Physically, the surface adhesion force in carbon fibers is reduced by rendering the DM surface more hydrophobic, causing higher surface contact angle. As a result, at higher PTFE loadings of the DM, the liquid water molecules on high PTFE loading fibers tend to be more unstable, enabling enhanced liquid transport through the pores of the DM.

**DM Thickness**

Figure 4-8 presents the predicted saturation profiles of Case 1 and 2 for two different DM thicknesses (200 µm and 300 µm). All cases (Case 1 and 2) demonstrate the same qualitative trend, but predict lower saturation values for thinner DM at any specified location. Physically, for a thinner DM, the liquid water concentration gradient becomes larger, causing a higher driving force, which in turns facilitates the liquid transport. Any decrease in DM thickness shortens the path length of the liquid water, thus reducing the liquid transport resistance. Therefore a smaller liquid saturation difference becomes sufficient to drive the liquid water from higher saturation region to lower saturation region for a thin DM.

In terms of saturation predictions of these two Cases (Case 1 and 2), it can be observed from Fig. 4-8 that while the cases follow the same qualitative trend, the predicted saturation values differ significantly as a function of constitutive relation. While the capillary-induced transport is defined by Leverett approach in Case 1, the discrepancy in saturation predictions between Case 1 and 2 is noticeable at each location.
In Case 1, the standard Leverett function \((J(s_l))\) is used, however, in Case 2, a polynomial fit purely derived from experimental data of ref. [10] has been employed. The difference in predicted saturation values between each case is relatively more pronounced, even reaching a peak value of 0.13 at the MPL interface, as shown in Fig. 4-8.

This vast difference in predicted saturation values indicates that the standard Leverett function fails to accurately describe the capillary transport behavior of the fuel cell DM. This noticeable difference can be attributed to the fact that the actual \(P_C - s_l\) relation is directly input into the liquid transport model in Case 2. The fuel cell DM has a mixed wettability network, while the Leverett approach integrates a constant porosity and a representative surface contact angle (uniform wettability), which is not the case in fuel cell DM. The discrepancy in the model outputs brings into question of the appropriateness of assuming constant values for porosity and contact angle. An improved approach would not only include the rigorous interaction of effective porosity and liquid saturation, but would also include the effects of compressibility, temperature and the mixed wettability (non-uniform contact angle).

Significant structural complexity in the DM behavior leads to difficulty in defining a meaningful internal contact angle parameter. The wettability on any surface can be characterized in terms of contact angle, which is closely related to the molecular interaction of matters at the contact interface [11,22]. To date, empirical studies have been inconclusive regarding the representative average internal contact angle at the microscopic level. Due to experimental limitations at the pore-level, external contact angle measurements are commonly employed to estimate the internal contact angle, and it is doubtful that an average contact angle approach is appropriate since the connected
hydrophilic/hydrophobic pores of the DM act in parallel. Moreover, external contact angle measurements fail to include the effects of the different levels of surface energy associated with the carbon fibers. Therefore, measured external contact angles may not reflect a statistical average of contact angles associated within the highly heterogeneous DM pores [23].

In addition, the standard Leverett function utilized in Case 1 accounts for the porous DM in terms of a single dry porosity value. However, the accumulation of liquid water into the available pores and associated change in effective porosity can lead to a substantial influence on transport properties of the DM [23-25]. Once the available pore space is occupied by the liquid water, the liquid flow path resistance increases. Therefore selecting a representative value of DM porosity may fail to account for the liquid transport phenomena occurring in fuel cells.

4.4.2 Operating Conditions

Optimization of the operating conditions is also of great importance for the avoidance of flooding problems in the DM. The level of liquid saturation in the cathode DM is strongly related to the operating current density and net water diffusion flux across the membrane [26-29]. The net water transfer coefficient, \( \alpha \), is strongly coupled with the current density, since the rate of water transport across the membrane via diffusion and electro-osmotic drag is proportional to the cell operating current density. This parameter can be influenced by the selection of DM and MPL properties. In the present model, current density and net water transfer coefficient are treated as independent parameters to
distinguish the significance of each effect separately. The theoretical model (Eq. 4.9) was solved for different current densities and net water transfer coefficients, while holding the other parameters constant. The predicted liquid saturation profiles were analyzed and compared. The boundary condition is again defined such that the liquid saturation is zero at the DM-flow channel interface.

**Net Water Transfer Coefficient**

Figure 4-9-a shows the effect of net water transfer coefficient, $\alpha$, on the liquid saturation profile for Case 1. As expected, the present model predicts higher liquid saturation in the cathode DM for the higher net water transfer coefficient ($\alpha=0.1$ versus $\alpha=1$). As the net water transfer rate increases, the cathode side becomes more prone to the accumulation of excess liquid water, which in turns, increases the local liquid saturation values in the cathode DM.

**Operating Current Density**

Figure 4-9-b shows the liquid saturation distribution for Case 1 under different operating current densities (0.2, 1 and 2 A cm$^{-2}$). At any specified location, the predicted saturation value is higher for the highest current density (2 A cm$^{-2}$), whereas the lowest liquid saturation is predicted for the lowest current density (0.2 A cm$^{-2}$), as expected [5]. The same behavior is also observed in the MPL.

The saturation profiles predicted by the model for Case 1 and 2 are compared for a current density of 0.2 A cm$^{-2}$ and $\alpha$ value of 0.5 in Fig. 4-10. As previously discussed, the origin of the considerable difference in predicted saturation values arises from
employing the standard Leverett function in Case 1, which assumes a constant porosity and contact angle. However, Case 2 is represented by an experimental $P_C-s_f$ curve, which implicitly accounts for the variation of DM structural properties such as internal contact angle and effective porosity. This remarkable deviation in the predicted local saturation values between Case 1 and 2 further demonstrates the inapplicability of using the standard Leverett approach.

### 4.4.3 Case Sensitivity Analysis

A sensitivity analysis was performed to ascertain how each specified case prediction depends upon the DM thickness, the net water transfer coefficient and the current density, and to assess the range over which the model predictions become sensitive to changes in these parameters.

As a first step, the functional dependence of the liquid saturation as a function of a chosen input parameter was determined at a specified location (e.g. a fractional distance from the catalyst layer of 0.8). Then the derivative of this function with respect to the chosen input parameter was computed to evaluate the sensitivity of the model prediction corresponding to any change in that input parameter. A greater slope implies a greater sensitivity, as shown in Eq. 4.19. The derivatives with respect to the specified inputs are also compared between Case 1 and Case 2.
The first investigated input parameter is the DM thickness. Figure 4-11-a depicts the predicted saturation profiles for two different DM thicknesses. As the DM thickness increases from 200 µm to 300 µm, the predicted saturation values at each location increases for all cases. It is observed that the average percentage increase in predicted saturation values as the thickness is increased from 200 to 300 µm is found to be 10.3% for Case 1 and 10.5% for Case 2, approximately equal. The sensitivity of the case predictions corresponding to any change in DM thickness was also investigated at a fractional distance from catalyst layer of 0.8. Figure 4-11-b shows the rate of change of the predicted saturation values corresponding to the DM thicknesses from 100 to 500 µm. As seen from the graph, the magnitudes of the slopes are on the order of $10^{-4}$, meaning that DM thickness seems to have minor effect on case predictions.

A case sensitivity analysis of the net water transfer coefficient was also performed. Two different values of net water transfer coefficient ($\alpha = 0.1$ and $1.0$) were implemented and the predicted saturation profiles are shown for Case 1 and 2 in Fig. 4-12-a. The increase in net water transfer coefficient from 0.1 to 1 appears to cause a slight increase in the predicted saturation values. However, the amount of increase is different for Case 1 and 2. In order to identify the relative significance of changing the net water transfer coefficient on case predictions, the sensitivity analysis was performed at a specified location (a fractional distance from the catalyst layer of 0.8). Figure 4-12-b depicts that the sensitivity of the each case is reduced as the net water transfer coefficient
increases from 0.1 to 0.5 and then starts to increase as the net water transfer coefficient increases from 0.5 to 1.0. As seen from Fig. 4-12-b, Case 2 exhibits relatively smaller slope change, ranging from 0.013 to 0.085, whereas Case 1 has higher slope values (varies from 0.03 to 0.2) over the entire net water transfer coefficient, meaning that model predictions for Case 1 is relatively more sensitive, (by an average factor of 2.2) than that of Case 2.

The final investigated input parameter is current density. Two different operating current densities ($I = 0.2$ and $1.0 \text{ A cm}^{-2}$) were implemented in two cases and the behavior of the model predictions were analyzed. Figure 4-13-a shows the predicted liquid saturation distribution for Case 1 and 2 under different current densities. As expected, the increase in current density gives rise to the predicted saturation values at each location due to the enhanced water generation. However, when the amount of average increase in predicted saturations is compared, Case 1 exhibits relatively smaller percentage increase (59 %) compared to Case 2 (65 %), in response to the change in current density. Figure 4-13-b depicts the rate of change of the predicted saturation values as a function of current density at a specified location (a fractional distance from catalyst layer of 0.8). As seen from Fig. 4-13-b, Case 1 is observed to be more sensitive compared to Case 2 with an average factor of 2.08, corresponding to any changes in current density over the range of $I = 0$ to $2 \text{ A cm}^{-2}$. The sensitivity is more pronounced for these two cases when the current density varies from 0 to 0.5 $\text{ A cm}^{-2}$ and from 1.5 to 2 $\text{ A cm}^{-2}$. Conversely, the predicted sensitivity for all cases becomes relatively small when the current density is in the range of $0.5 < I < 1.5 \text{ A cm}^{-2}$.
The magnitude of the slope with respect to any specified input parameter can be used to compare the relative significance of each input parameters on the model prediction. Among the input parameters of concern (thickness, current density and net water transfer coefficient), the current density seems to be the most crucial input parameter for both Case 1 and Case 2, when the magnitude of the rate of change is compared between the each input parameters. Based on these analyses, it can be concluded that the model prediction for all cases is relatively more sensitive to any change in current density rather than the changes in the DM thickness and net water transfer coefficient.

4.5 Summary

The effectiveness of the traditional Leverett approach (equipped with $J$-function) to describe the capillary-induced flow in thin-film fuel cell DM was investigated. An empirical polynomial fit ($P_{c-s_i}$) describing the capillary pressure-saturation relation of the DMs listed in Table 4-2 was derived based on the experimental capillary pressure-saturation curves provided by [10]. In addition, a new representative relative permeability correlation ($k_{r-nw} = s_{nw}^{2.16}$) compiling a broader range of theoretical basis for the tested fuel cell media by [10] was obtained. These correlations, along with the Leverett approach equipped with $J$-function, were integrated into an analytical framework to predict liquid saturation profiles for differently engineered DMs under various operating conditions. The variations in liquid saturation predictions associated with employing different
correlations were assessed and the effectiveness of the traditionally used Leverett function was determined to be poor.

The Leverett approach consistently over-predicts the DM saturation values compared to the ones obtained with the empirical fit of the experimental data. The significant variation in the predicted saturation profiles suggests that using the traditional Leverett approach is indeed inadequate to describe the capillary transport characteristic of a fuel cell DM, indicating the need to develop a modified approach appropriate for thin-film fuel cell media with mixed wettability. Finally, a sensitivity analysis was performed to ascertain how each specified correlations prediction depends upon the different input parameters. The model predictions are found to be relatively more sensitive to any change in current density rather than the changes in the DM thickness and net water transfer coefficient over the range of values tested.

Note that the presented correlations were generated based on the data [10] for a set of DMs tailored with PTFE ranging from 0 to 5% of wt. at room temperature under no compression. However, hydrophobicity of the DM, along with the operational environments such as temperature and compression needs to be investigated in a broader range to further isolate the effects of these parameters on the capillary transport characteristics of a fuel cell DM.
4.6 Bibliography


Table 4-1: Summary of relative permeability models utilized in this study.

<table>
<thead>
<tr>
<th>Models</th>
<th>Relative Permeability (non-wetting phase)</th>
<th>Relative Permeability (wetting phase)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wyllie Model</td>
<td>( k_{r-nw} = (s_{e-nw})^3 )</td>
<td>( k_{r-w} = (1 - s_{e-nw})^3 )</td>
</tr>
<tr>
<td>Corey Model</td>
<td>( k_{r-nw} = [1 - (s_{e-nw})^2] \cdot [1 - s_{e-w}]^2 )</td>
<td>( k_{r-w} = (s_{e-w})^4 )</td>
</tr>
<tr>
<td>Brooks-Corey Model</td>
<td>( k_{r-nw} = (1 - s_{e-nw})^2 \cdot [1 - (s_{e-w})^{2+\lambda \over \lambda}] )</td>
<td>( k_{r-w} = (s_{e-w})^{2+3\lambda \over \lambda} )</td>
</tr>
<tr>
<td>Van Genuchten Model</td>
<td>( k_{r-nw} = (1 - s_{e-w})^{1/3} \cdot [1 - (s_{e-w})^{1+\gamma \over m}]^{2m} )</td>
<td>( k_{r-w} = (s_{e-w})^{3 \cdot 5} \cdot [1 - (s_{e-w})^{1+\gamma \over m}]^{2} )</td>
</tr>
</tbody>
</table>

* \( s_e \) represents the effective saturation

Table 4-2: Material properties of the tested DMs adapted from [10].

<table>
<thead>
<tr>
<th>Material</th>
<th>Type</th>
<th>Thickness (µm)</th>
<th>PTFE (wt. %)</th>
<th>Hydrophilic Porosity</th>
<th>Total Porosity</th>
</tr>
</thead>
<tbody>
<tr>
<td>SGL 10BA</td>
<td>Paper</td>
<td>380</td>
<td>5</td>
<td>0.63</td>
<td>0.91</td>
</tr>
<tr>
<td>SGL 10BB</td>
<td>Paper w/MPL</td>
<td>420</td>
<td>5</td>
<td>0.45</td>
<td>0.87</td>
</tr>
<tr>
<td>Toray 090</td>
<td>Paper</td>
<td>190</td>
<td>0</td>
<td>0.63</td>
<td>0.79</td>
</tr>
<tr>
<td>E-Tek Cloth</td>
<td>Cloth</td>
<td>350</td>
<td>0</td>
<td>0.74</td>
<td>0.72</td>
</tr>
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Table 4-3: The constitutive relations used and the final form of the governing equations for Case 1 and Case 2.

<table>
<thead>
<tr>
<th>CONSTITUTIVE RELATIONS</th>
<th>Capillary Pressure-Saturation Relationship</th>
<th>Relative Permeability</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Case 1</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Standard Leverett Function</strong></td>
<td>$P_c = \gamma \cdot \cos \theta \cdot \left(\frac{e}{k}\right)^{0.5} \cdot J(s_i)$</td>
<td>Wyllie Model</td>
</tr>
<tr>
<td></td>
<td>$J(s_i) = 1.417s_i - 2.120s_i^2 + 1.263s_i^3$</td>
<td>$k_{r-nw} = s_{nw}^3$</td>
</tr>
<tr>
<td><strong>Case 2</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Empirical Fit</strong></td>
<td>$P_c = -4854.1s_i^2 + 12958s_i$</td>
<td>Present Model</td>
</tr>
<tr>
<td></td>
<td>$(0 &lt; s_{nw} &lt; 0.8) \ R^2 = 0.80 \text{ (in Pascals)}$</td>
<td>$k_{r-nw} = s_{nw}^{2.16}$</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>FINAL GOVERNING EQUATIONS (Eq. 4.9)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Case 1</strong></td>
<td>$-\frac{I \cdot (2\alpha + 1) \cdot MW^{H-O} \cdot V_L(x)}{2 \cdot F \cdot \gamma \cdot \cos \theta \cdot \sqrt{k \cdot e}} = 0.354s_i^4 - 0.848s_i^5 + 0.630s_i^6$</td>
</tr>
<tr>
<td><strong>Case 2</strong></td>
<td>$-\frac{I \cdot (2\alpha + 1) \cdot MW^{H,0} \cdot V_L(x)}{2 \cdot F \cdot k} = 4100.6 \cdot s_i^{3.16} - 2333.7 \cdot s_i^{4.16}$</td>
</tr>
</tbody>
</table>
Figure 4-1: Schematic view of control volume.
Figure 4-2: Direction of capillary-induced liquid flow in a fuel cell DM.
Figure 4-3: Boundary conditions and saturation jump at the interface of DM and MPL.
The DMs follow the same qualitative trend, approaching the similar capillary pressures especially when $s_{nw} < 0.8$.

The curve-fit predicts well $P_c = -4854.1 s_{nw}^2 + 12958 s_{nw}$, $R^2 = 0.80$ for $0 < s_{nw} < 0.8$.

Figure 4-4: a) Measured capillary pressure-saturation data for tested DM samples (adapted from Gostick et al. [10]), and b) Comparison of the curve-fit and experimental data provided by [10].
Figure 4-5: a) Predicted liquid relative permeability curve, and b) Percentage deviation of the Wyllie model from the predicted curve-fit.
Figure 4-6: Predicted saturation profiles for Case 2 (using empirical curve-fit) implementing the individual measured capillary pressure curves for all DM samples and the curve-fit presented in Eq. 4-17.
Figure 4-7: a) Predicted saturation profiles of Case 1 (using standard Leverett approach) for different contact angle values, and b) Saturation predictions of Case 1 (using standard Leverett approach) at various locations for different contact angle values.
Figure 4-8: Predicted saturation profiles for Case 1 (using standard Leverett approach) and Case 2 (using empirical curve-fit) for different DM thicknesses.
An increase in $\alpha$ increases the local saturation values at any location.

Figure 4-9: Predicted liquid saturation profiles for Case 1 (using standard Leverett approach); a) for different net water transfer coefficients, and b) under different current densities.
Figure 4-10: Predicted saturation profiles for Case 1 (using standard Leverett approach) and Case 2 (using empirical curve-fit) for 200 µm DM and α value of 0.5; a) at current density 1.0 A cm$^{-2}$, and b) at current density 0.2 A cm$^{-2}$. 
Figure 4-11: a) Predicted saturation profiles for Case 1 (using standard Leverett approach) and Case 2 (using empirical curve-fit) for different DM thicknesses, and b) Rate of change of saturation predictions for the two cases with varying DM thickness.
Figure 4-12: a) Predicted saturation profiles using Case 1 (using standard Leverett approach) and Case 2 (using empirical curve-fit) for different net water transfer coefficients, and b) Rate of change of saturation predictions for all cases with varying net water transfer coefficients.
Figure 4-13: a) Predicted saturation profiles using Case 1 (using standard Leverett approach) and Case 2 (using empirical curve-fit) under different current density, and b) Rate of change of saturation predictions for all cases under various current densities.
Chapter 5

CAPILLARY TRANSPORT CHARACTERIZATION OF A FUEL CELL DIFFUSION MEDIA: HYDROPHOBICITY EFFECT

Based on the results presented in Chapter 4, the second part of the present Ph.D. study is motivated by the need to develop an appropriate transport function describing the capillary pressure-saturation relationship of the fuel cell diffusion media (DM). Direct measurement of capillary pressure-saturation for different types of DMs (cloth and paper) tailored with polytetraflouroethylene (PTFE) content ranging from 0 to 20% of wt. is performed. A modified Leverett function, which precisely defines the capillary pressure of the tested DMs as a function of liquid saturation and hydrophobic additive content, is deduced. Furthermore, a detailed comparative analysis of the modified Leverett function and the traditional Leverett function is also performed.

5.1 Background

The proper engineering of fuel cell materials may lead to an optimized water balance, increasing power and durability. However, the prediction of material design and micro-fluidic management are currently hindered by the lack of understanding of the proper transport relationships governing the multi-phase flow in the porous fuel cell DM and catalyst layer. There is also a paucity of experimental data and analysis in the existing literature necessary for guiding the engineering of fuel cell DM materials [1-5].
Many studies [6-8] reveal that liquid water transport is a dominating factor influencing the performance of the fuel cell, and is closely related to the capillary transport characteristics of thin-film fuel cell DM. Therefore, the morphological characteristics of a bi-layered DM, along with the localized anisotropic nature of transport parameters should be well-known in order to establish a physical theory of capillary transport within these materials.

Unfortunately, the science of multi-phase transport through the thin-film DM tailored with mixed wettability is not well-developed, and much of the present level of understanding is based on application of porous media theory from civil and petroleum engineering studies of fluid flow through packed soil beds with uniform wettability. The direct application of such uniform wettability theory has been determined to be inappropriate to adequately describe the capillary pressure-saturation relationship in typical fuel cell DM [1], potentially due to the fact that fuel cell porous media, including the catalyst layer and DM, are actually a heterogeneous mixture of various components. This heterogeneous composition represents a class of materials with mixed wettability, and has not been previously treated by soil science. New relationships governing the multi-phase transport are needed for application to these thin-film materials to enable well-defined micro-fluidic management and provide necessary guidance for material engineering of PEFCs. Additionally, the effects of fuel cell compression, Teflon® content of the DM and the operating temperature have not yet been adequately assessed and should be considered to fully elucidate the capillary transport mechanism in these thin-film porous media.
Acknowledging the existence of minute length scale and presumed anisotropic nature of the thin-film porous DM, many studies [9-14] have focused on bulk material optimization of the DM, neglecting the complex interaction of the material properties and transport phenomena. Several studies [15,16] investigated the morphological properties of the porous DM. The porosity and total pore distribution of several DMs measured using the mercury intrusion technique were reported [15,16], even though the mercury intrusion technique is incapable of distinguishing the hydrophobic and hydrophilic pore distribution of DM and requires high pressures (more than hundred atm), which can lead to a substantial deformation of the DM structure. Due to these inherent limitations of the mercury intrusion technique, these studies were limited to qualitatively explaining PEFC performance on the basis of observed DM morphological features.

Recently, Gostick et al. [17] reported a novel experimental approach for determining the dependence of capillary pressure on wetting phase saturation along a desaturation path (drainage) for various DMs. The dual pore distribution (hydrophobic and hydrophilic) of several DMs was obtained [17]. However, no benchmark relationships relating the tailored material and geometric properties of the DM with the multi-phase flow parameters were explicitly developed. Recognizing the experimental limitations associated with the complex nature of DM. The development of approximate mathematical models is imperative to the understanding and prediction of multi-phase transport phenomenon in the DM. An extensive review of the recent modeling efforts is provided in [7] and the current challenges are addressed in [18]. However, the accuracy of the existing models is inherently limited due to the scarcity of novel experimental data representing the accurate capillary transport physics in porous DM.
5.2 Method of Approach

5.2.1 Diffusion Media Samples

The thin-film fuel cell DMs utilized in the present study are constructed from a sheet of electrically conductive macro-porous substrate with varying degree of mixed wettability, such as a non-woven carbon paper or a woven carbon cloth, both of which are coated with a micro-porous layer on one side [7].

In order to elucidate the structural variation between carbon paper and cloth, both SGL 24 series (SIGRACET® gas diffusion layers) carbon paper and E-TEK Elat 1200W carbon cloth were investigated. The DM samples tested are commonly used in various fuel cell applications and were designed for a wide range of operating conditions. In terms of morphological structure, both carbon paper and cloth have heterogeneous structure with pore size ranging from a few microns to tens of microns. The porosities range from 70 to 90%, whereas the thickness varies from 200 µm to 300 µm. These naturally hydrophilic DMs are typically tailored during processing by addition of hydrophobic material polytetrafluoroethylene (PTFE), known as Teflon® to improve the liquid water transport. An additional thin micro-porous layer (MPL) of carbon black mixed with PTFE is also introduced on one side of the DM substrate to provide better electrical contact with catalyst layer and reduce water saturation in the macro-porous substrate [20].

The material properties of the DM samples, as supplied by the manufacturers, are provided in Table 5-1. In the present study, SGL 24BC (5% PTFE content of wt.), SGL 24CC (10% PTFE content of wt.) and SGL 24DC (20% PTFE content of wt.) from SGL
24 carbon paper series, and E-TEK Elat 1200W carbon cloth (non-uniform PTFE content >20 % of wt.) were included in the experimental matrix in order to cover the hydrophobic treatment range and woven or non-woven characteristic of the DMs typically used in fuel cell applications. Figure 5-1 shows scanning electron microscopy (SEM) images of the structure of the selected carbon cloth and carbon papers.

5.2.2 Experimental Approach

Capillary pressure-saturation measurements were performed using the method of standard porosimetry (MSP) technique developed by POROTECH Inc. This technique is based on the capillary equilibrium principle, providing a means of non-destructive measurement of the capillary pressure-saturation curves in porous materials [19]. A descriptive schematic of the technique is illustrated in Fig. 5-2. The DM samples were placed in capillary contact between two standard samples having a known capillary pressure-saturation curve, one of which was placed at the open surface of the stack (where the liquid evaporates) and the other at the closed surface. The standard sample was chosen such that its pore size is in the range of the typical fuel cell DM [19]. Different liquids were utilized as working fluids to evaluate the mixed wettability characteristics of DMs. Highly wetting liquid octane was used as a working liquid to determine the overall pore distribution, whereas de-ionized water allowed for the determination of the hydrophilic pore network because it is naturally imbibed only by the hydrophilic pores.
Periodically, a small portion of the liquid was slowly evaporated by a flow of dry inert gas while the standard sample and tested DM were kept in capillary contact to allow the establishment of a new capillary equilibrium. At each equilibrium, the mass of each sample was measured to obtain the wetting phase saturations, enabling the determination of the corresponding capillary pressure of the standard sample from its known characteristics [19]. In capillary equilibrium, this pressure is equal to the capillary pressure of the fuel cell DM sample. This process was continuously repeated until most of the liquid had evaporated from the test samples [17].

5.3 Results and Discussions

5.3.1 Morphological Characteristics

The existence of a bi-modal pore size and wettability distribution bifurcate the transport paths of wetting and non-wetting phase, complicating the transport phenomena. Therefore it is necessary to first determine the full spectrum of dual-pore distribution of the bi-layered DM.

The dual pore distribution (hydrophilic and total) of the DM samples is shown in Fig. 5-3. Three distinctive pore size ranges are observed for all DM samples. To distinguish the pore characteristics of the micro-porous layer and macro-porous substrate, the pores are classified according into three classes, namely: macro-pores (pore diameter from 1 to 10 µm), meso-pores (pore diameter from 0.1 to 1 µm) and micro-pores (pore diameter from 0.1 to 0.01 µm). Note that the classification of pore size is based on the
current observation of pore-distribution of the tested DM samples, and hence, it is different from the general criteria defined in soil science. The micro-porous layer generally consists of relatively smaller pores ranging from 100 nm to 500 nm, which can directly be identified from the presented pore distributions in Fig. 5-3. The average pore size of the DM samples ranges from 3.8 to 5.3 µm, indicating that the macro-pores dominate the entire structure, which in turn, yields an average open pore volume of 0.1 cm³ for all samples, as shown in Table 5-2. On the other hand, the total surface area per volume is found to vary from 13 to 30 m² cm⁻³, and a significant difference is observed between the paper and cloth. The maximum surface area is observed in SGL 24CC (30 m² cm⁻³), whereas the minimum one (13.2 m² cm⁻³) is found for E-TEK Elat 1200W cloth. The existence of a high pore volume (i.e. high porosity) may indicate the possibility of higher transport of reactants to the catalyst layer, and thereby a higher limiting current density. However, high porosity is generally accompanied by excess water accumulation due to the low local capillary pressure. This, in turn, can retard the reactant transport, causing significant decreases in cell voltage.

In terms of hydrophilic pore characteristics, the range of pore-size is broadly distributed between 1 and 10 µm, meaning that the micro-porous layer, which consists of micro-pores ranging from 0.1 to 0.01 µm, apparently contains considerably few hydrophilic pores and therefore can be treated as a completely hydrophobic substrate. This can be linked to the structural properties of the MPL. In fact, the micro-porous layer has a compact (small pores) and rigid structure compared to the ordinary DM, and it acts as a barrier to reduce local saturation and permit reactant gas diffusion to the catalyst
layer. This compactness, rigidity and high PTFE content of MPL provide a higher hydrophobic porosity.

The measured total porosity and hydrophilic porosity for all DM samples are tabulated in Table 5-2. As seen in Table 5-2, the hydrophilic porosity is sensitive to the amount of PTFE loading and, as expected, shows a decreasing trend as response to an increase in the PTFE loading. The minimum connected hydrophilic porosity (0.16) is measured for E-TEK Elat 1200W carbon cloth, in which the PTFE content is greater than 20% of wt. (the manufacturer does not publicly specify), whereas the maximum hydrophilic porosity (0.27) is observed for SGL 24BC with 5% PTFE content of wt.

5.3.2 Interconnected Hydrophilic Pores and Water Retention Capacity

The difference in DM morphologies leads to different mobile phase distributions. At a microscopic level, a pore surface will tend to imbibe the wetting phase, while displacing the non-wetting phase [21]. Inside the pore, the wetting phase has a tendency to compress the non-wetting phase, due to the high absorption of the wetting phase on the surface. In a hydrophilic DM pore, liquid water is the wetting phase (preferentially absorbed by the pore surface), whereas the air (the non-wetting phase) is compressed by the surrounding water. Due to the compression by interfacial tensions, the gas (non-wetting) phase is displaced from the pore. While the non-wetting phase is transported in that manner, the displacement of the wetting phase requires a connected hydrophilic conduit or pathway since an isolated hydrophilic pore spaces can serves as the potential
spots for the wetting phase to reside permanently and can be only occupied via condensation of the saturated water vapor because of the restricted access to such pores.

In fuel cell applications, the liquid water content stored in the DM during operation is of critical importance for freeze/thaw, start-up, degradation, stability and purging, because a higher residual water storage in a DM retards thermal transients, can result in additional damage during freeze/thaw, and can act as a conduit for ionic impurities which degrade the electrode and electrolyte [6]. One approach to determining the potential water storage capacity of a DM would be to isolate the connected hydrophilic pore network from the total network. Based on this approach, a detailed knowledge of the connected hydrophilic pore configuration appears to provide a reasonable estimate of the water retention capacity, \( s_{wrc} \) of the fuel cell DM. The water retention capacity is a characteristic property of a fuel cell porous media and represents the available connected hydrophilic pore space of a fuel cell DM that can be spontaneously imbibe and be occupied by water. To date, direct determination of the volume of connected pore space has not been conclusively established and to the authors’ knowledge, no truly direct values of the water retention capacity of a fuel cell DM as a function of DM material properties have been published.

One distinctive feature of the experimental approach (MSP) used in the present study is that the interconnected hydrophilic pore volume and corresponding capillary pressure-liquid saturation of the hydrophilic pore network can be explicitly determined via spontaneous capillary imbibition tests. The spontaneous capillary imbibition is a natural process and requires existence of interconnected hydrophilic pores. These measurements provide an appropriate estimation for the water retention capacity of the
different DMs as a function of material properties, based on the accessible interconnected hydrophilic pore volume.

Capillary pressure as a function of water saturation for the connected hydrophilic pore network (excluding the isolated pores) was precisely measured for DM samples and shown in Fig. 5-4. Figure 5-4-a depicts the capillary pressure versus liquid saturation for SGL 24BC and SGL 24DC for the connected hydrophilic pore network. The capillary pressure curve follows the same trend for both cases, however, there are slight quantitative differences. The SGL 24BC treated with 5% PTFE content imbibes a maximum of 0.35 saturation ($s_{wrc}>0.35$); whereas SGL 24DC tailored with 20% PTFE can only imbibe a maximum of 0.28 saturation ($s_{wrc}>0.28$). Physically, this can be attributed to the fact that rendering the DM more hydrophobic decreases the total connected hydrophilic pathways, thus reducing the potential water retention capacity. In addition, the measured hydrophilic porosity of the SGL 24BC ($\epsilon_{h-philic}=0.27$) is greater than that of the SGL 24 DC sample ($\epsilon_{h-philic}=0.21$), which supports this physical reasoning. The estimated water retention capacities for tested DM samples are shown in Table 5-3.

A comparison of capillary pressure-saturation curves for SGL 24DC (20% PTFE of wt.) carbon paper and E-TEK Elat 1200W (>20% PTFE of wt.) carbon-cloth is shown in Fig. 5-4-b. Despite the structural difference between a non-woven paper and woven cloth, the capillary transport characteristics via interconnected hydrophilic pores seem to follow a similar qualitative trend. However, a greater imbibition (maximum saturation of 0.28, $s_{wrc}>0.28$) was observed in SGL 24DC tailored with 20 % PTFE content of wt.; whereas the more hydrophobic E-TEK Elat 1200W carbon cloth can only imbibe up to a
maximum saturation of 0.22 \( (s_{\text{wrc}} > 0.22) \), in reasonable agreement with the trend shown in Fig. 5-4-a.

Note that these experiments were performed at room temperature and under no compression; hence the presented values are appropriate for the tested DM samples at this condition. However, compression and temperature can lead to significant morphological changes in pore characteristics of the DM, and are expected to strongly affect the capillary transport characteristics. Effects of these parameters are addressed in detail in succeeding chapters.

### 5.3.3 Capillary Transport Characteristics of Total Pore Network

The capillary pressure between wetting and non-wetting phase is caused by the imbalance of the molecular forces at the line of contact and, for a cylindrical pore, can be represented by the Young-Laplace equation [23]:

\[
P_c = P_{\text{nw}} - P_w = \frac{2 \cdot \gamma \cdot \cos \theta}{r}
\]

where \( \gamma, \theta \) and \( r \) represent surface tension, contact angle, and pore radius, respectively. In order to measure the air-water capillary pressure-saturation curves of the total pore network under drainage, additional experiments were performed. Highly wetting liquid octane was utilized as a working liquid to obtain the overall pore network capillary pressure curves as a function of liquid saturation. The liquid saturation in the DM samples was measured at each capillary equilibrium condition and the corresponding equilibrium capillary pressure was recorded, based on the known capillary characteristics.
of the standard sample [19]. Octane capillary pressure-saturation data provide the necessary database for obtaining the capillary pressure-saturation curves of an air-water system [17]. The equivalent capillary pressure of a multi-phase mixture in a specified pore can be calculated based on the Young–Laplace principle (Eq. 5.1), by converting the known capillary pressure of any known two-phases occupying a pore having the same size to the equivalent water–air capillary pressure.

\[
R = \left( \frac{\gamma \cdot \cos \theta}{P_c} \right)_{\text{Oct}} = \left( \frac{\gamma \cdot \cos \theta}{P_c} \right)_{\text{w}}
\]  

[5.2]

The air-water capillary pressure of the total pore network as a function of non-wetting phase saturation for SGL 24 series is shown in Fig. 5-5. The individual curves follow similar trends; however, due to the different PTFE contents, the measured capillary pressure values differ slightly over the full liquid saturation spectrum. Three distinctive saturation regions are observed in the capillary pressure-saturation curves. At low saturations, especially \( s_{nv} < 0.4 \), the difference in measured capillary pressures between each DM is more pronounced. However, the discrepancy gradually diminishes as the saturation moves towards to the moderate saturation region \( (0.4 < s_{nv} < 0.7) \). In the high saturation region \( (s_{nv} > 0.7) \), the discrepancy between the three DMs increases noticeably again. The overall trend can be attributed to the differences in hydrophobic/hydrophilic pore volume of the DMs due to the different PTFE loadings. The DM tailored with higher PTFE content exhibits a larger capillary pressure, especially for \( s_{nv} < 0.4 \). The highest capillary pressure is observed in SGL 24DC with 20% PTFE, whereas the lowest value at a given saturation is observed in SGL 24BC with 5% PTFE.
Figure 5-6 shows the capillary pressure versus PTFE content of the DM at different saturation values ($s_{nw} \leq 0.4$). At each saturation, a larger hydrophobic pore fraction corresponds to an increased measured capillary pressure. At high saturation ($s_{nw}=0.4$), the increase in capillary pressure corresponding to any increase of the PTFE loading is relatively more severe (an increase of 0.21 bars from 5 to 20% PTFE) than those of at lower saturations, $s_{nw}=0.1$ (an increase of 0.075 bars from 5 to 20% PTFE). Physically, the surface adhesion force in carbon fibers is reduced by rendering the DM surface more hydrophobic, distorting the molecular force balance at the interface. As a result, the liquid water located on high PTFE loading fibers moves towards an unstable state, leading to a higher capillary pressure, which is consistent with the physical reasoning often cited [30] for enhanced liquid transport under high PTFE loadings.

5.3.3.1 Comparison of Carbon Cloth and Paper DM

To elucidate the structural difference of paper and cloth diffusion media substrates, capillary pressure-saturation curves of SGL 24DC and E-TEK Elat 1200W carbon cloth are compared and shown in Fig. 5-7. Generally, carbon cloth and paper have different characteristics of spatial uniformity and degree of anisotropy. Carbon cloth has a spatially heterogeneous woven structure, resulting in three degrees of macroscopic anisotropy. In contrast, carbon paper is relatively more homogenous due to its random lacing, yielding two degrees of anisotropy [7]. Despite the existence of significant structural variations between these two types of DM, the overall capillary pressure curves basically follow the same qualitative trend, even overlapping at moderate saturations and
then deviating from each other at high saturation values, $s_{nw}=0.55$ (Fig. 5-7). In terms of hydrophobicity, even though the exact PTFE content of E-TEK Elat 1200W carbon cloth is not publicly disclosed, both SGL 24DC and Elat 1200W cloth have similar PTFE contents (20% PTFE for SGL 24DC and >20% PTFE for E-TEK cloth), thereby yielding almost the same capillary pressure values over the most of the saturation domain. Surprisingly, this observation indicates that the PTFE content, especially at moderate saturations ($s_{nw}<0.5$), is a more dominating factor affecting the capillary pressure curves, rather than the types of DM base material.

### 5.3.3.2 Effect of Micro-porous Layer

When the capillary pressure curve for each DM is analyzed, a dramatic increase in capillary pressure is noticeable at high threshold saturations ($s_{nw}>0.7$). This sudden vast increase in capillary pressure is a result of the micro-porous layer. Gostick et al. [17] reported that the existence of micro-porous layer can be extracted independently from the capillary pressure curves and pore size distribution. The pore size distribution of the tested DM samples yielded evidence of the existence of bi-layered DM, which is addressed in the previous section. The identification scheme of the micro-porous layer from these observations is shown in Fig. 5-8. The significant increase in capillary pressure at high saturation ($s_{nw}>0.7$) can be linked to the compact structural characteristics of a micro-porous layer. Typically, micro-porous layer has a packed (small pores) and rigid structure, thus requiring higher capillary pressure to overcome the
surface energy of the diminutive and highly hydrophobic pores of the MPL for spontaneous imbibition.

5.3.4 Modified Leverett Approach

5.3.4.1 Standard Leverett J-Function, $J(s_{nw})$

The standard tool currently used in macroscopic modeling studies for predicting the fluid distribution profiles in porous media is the direct implementation of an empirical constitutive correlation describing the capillary pressure as a function of liquid saturation. Several empirical and semi-empirical expressions are available, which attempt to describe the behavior of capillary pressure in terms of a porous media and fluid properties. Leverett (1941) [24] suggested a semi-empirical approach using dimensional analysis to estimate the capillary pressure as a function of liquid saturation in the porous media with uniform wettability. The traditional Leverett approach [24] has been widely adopted by the fuel cell modeling community. Leverett defined a reduced capillary pressure function for the porous media, based on the experimental data for a range of common soils with uniform wettability:

$$P_c = \gamma \cos \theta \cdot \left( \frac{\varepsilon}{k} \right)^{1/2} J(s_{nw})$$  \[5.3\]

where $k$ and $\varepsilon$ are permeability and porosity of the porous media. $J(s_{nw})$ represents the Leverett function for scaling drainage capillary pressure curves and it is given as [24]:
The standard Leverett $J$-function is capable of incorporating the effects of interfacial tension, but uses a simple relation for the average pore radius $(k/\varepsilon)^{0.5}$, essentially neglecting the tortuous nature of porous media [25]. Even though the $J$-function satisfactorily correlates data from unconsolidated sands and sandstones having uniform formation, it is limited in its ability to describe the capillary characteristics when the porous media of the interest exhibit a great deal of heterogeneity or mixed wettability, such as that occurring in fuel cell porous DM [25].

\[ J(s_{nw}) = \begin{cases} 
1.417 \cdot (1 - s_{nw}) - 2.120 \cdot (1 - s_{nw})^2 + 1.263 \cdot (1 - s_{nw})^3 & \text{if } \theta < 90^\circ \\
1.417 \cdot s_{nw} - 2.120 \cdot s_{nw}^2 + 1.263 \cdot s_{nw}^3 & \text{if } \theta > 90^\circ 
\end{cases} \]  \tag{5.4}

5.3.4.2 Modified Leverett Function, $K(s_{nw})$

The capillary pressure-saturation curves for all currently tested samples were used as benchmark data to compile an expanded database. This database was then utilized to deduce an appropriate empirical non-dimensional correlation describing the capillary pressure as a function of PTFE content and liquid saturation. A multi-dimensional linear regression model was employed to precisely correlate the capillary pressure with the relevant non-dimensionalized experimental parameters. A total of 3200 experimental data points were processed and integrated into the computational database to determine the best polynomial fit. The nature of the capillary pressure-saturation curves exhibits a continuous “S” shape yielding four inflection points. In order to improve the precision of the empirical correlation and eliminate the potential uncertainty associated with the
complex shape of the capillary pressure-saturation curves, the overall saturation domain was divided into three regions and three continuous empirical fits were deduced based on the experimental data corresponding to these regions (0<s<0.50; 0.50≤s≤0.65; 0.65<s<1.00). The final form of the modified function, \( K(s_{nw}) \), for SGL 24 carbon paper series at room temperature under no compression is found as:

\[
P_C = \gamma \left( \frac{\gamma}{k} \right)^{1/2} K(s_{nw})
\]

\[
K(s_{nw}) = \begin{cases} 
\text{%wt} \cdot (0.0469 - 0.00152 \cdot \text{%wt} - 0.0406 \cdot s_{nw}^2 + 0.143 \cdot s_{nw}^3) + 0.0561 \cdot \ln s_{nw} & 0. < s_{nw} < 0.50 \\
\text{%wt} \cdot (1.534 - 0.0293 \cdot \text{%wt} - 12.68 \cdot s_{nw}^2 + 18.824 \cdot s_{nw}^3) + 3.416 \cdot \ln s_{nw} & 0.50 \leq s_{nw} \leq 0.65 \\
\text{%wt} \cdot (1.7 - 0.0324 \cdot \text{%wt} - 14.1 \cdot s_{nw}^2 + 20.9 \cdot s_{nw}^3) + 3.79 \cdot \ln s_{nw} & 0.65 < s_{nw} < 1.00 
\end{cases}
\]

[5.5]

where \text{%wt} and \( s_{nw} \) represent PTFE weight percentage in the DM and non-wetting saturation, respectively. As shown in Eq. 5.5, the modified Leverett function is split into three parts, corresponding to the low saturation region (0<s<0.5), the moderate saturation region (0.5≤s≤0.65), and the higher saturation region (0.65<s<1.00). The empirical correlation (Eq. 5.5) captures the sudden increase caused by the micro-porous layer in the measured capillary pressure. The normal plot of residuals, the histogram of residuals, chart of residuals and residuals versus fits were performed in order to check the validity of the presented empirical correlation (\text{i.e.} homogeneity of variance, non-independence of variables, normality) as well as to detect outliers in experimental data.
The approximation in the prescribed functional form provided a close fit to the experimental data.

The key feature of the presented empirical fit in Eq. 5.5 is that the connection between the liquid saturation and the \textit{mixed wettability} characteristics of the DM is linked to the capillary pressure. Adjusting the PTFE variable ($\%\text{ wt}$), which is acting in parallel with other parameters, enables successful determination of the capillary pressure as a function of hydrophobic additive loading of the DM.

Due to the pore level experimental limitations, external contact angle measurements are commonly employed to estimate a statistical average of contact angles associated within the highly heterogeneous DM pores [26], although the appropriateness of this approach has been questioned [26]. Such external contact angle measurements on DM surface may provide quantitative estimations of the average internal contact angle; but these measurements fail to include the effects of the different levels of surface energy associated with the carbon fibers and ignore the mixed wettability characteristics of DM. One distinctive feature of the present empirical correlation (Eq. 5.5) is that no contact angle parameter is required as an input, since the PTFE parameter ($\%\text{ wt}$) accounts for the anisotropic nature of the hydrophobic coating of the DM. However, surface tension, a significant parameter relating the interaction of the flowing fluid and carbon fibers, is included in the modified Leverett approach as an input parameter (Eq. 5.5). Porosity and permeability, the governing transport parameters of the DM, are also retained in the modified approach (Eq. 5.5) as it is in the original Leverett formulation (Eq. 5.4).
5.3.5 Validation and Comparison

Figures 5-9 and 5-10 compare the capillary pressure predicted both the modified Leverett function, $K(s_{nw})$, and the standard Leverett function, $J(s_{nw})$, with respect to the actual experimental capillary pressure data for SGL 24BC and SGL 24DC DMs. As clearly seen from these Figs., the modified Leverett function predicts the measured capillary pressures well, especially for $s_{nw}<0.5$, whereas the standard Leverett function exhibits an enormous deviation from the experimental data over the entire saturation domain, especially at high saturations (more than 100% off). At moderate saturations such as $0.5<s_{nw}<0.6$, the empirical fit deviates slightly from the experimental data to capture the inflection point of the capillary pressure curve trend. However, in the high saturation region ($s_{nw}>0.6$), the deviation is reduced and the modified Leverett function, $K(s_{nw})$, precisely predicts the capillary pressure. The vast difference between approximation of the standard Leverett function, $J(s_{nw})$, and experimental data strongly indicates that the standard Leverett function is ineffective for describing the capillary transport characteristics within the fuel cell DM, as also previously [1].

The physical reason underlying the significant deviation between the standard $J$-function and experimental data may stem from the fact that even though, in a minute length scale, the DM has a similar geometrical structure with the common type of soils, the magnitude of characteristic flow properties, including the grain size, pore radius and relative permeability is relatively smaller in fuel cell DM. Furthermore, the DM is highly heterogeneous and anisotropic with a low volume to surface area ratio, unlike the soils used in the original derivations (Eq. 5.3 and Eq. 5.4). The uniqueness of the modified
Leverett function, $K(s_{nw})$, presented in this study is that it accounts for the non-uniform wettability characteristics associated with the nature of the fuel cell DM and it relies on the actual experimental capillary pressure data for a range of fuel cell DM. Therefore it provides an accurate prediction of capillary pressure in terms of liquid saturation and PTFE content *under no compression and at room temperature*. As seen from Fig. 5-11, the modified Leverett function, $K(s_{nw})$, can accurately capture the effects of PTFE content on capillary pressure over the entire saturation spectrum by resolving the change in interfacial surface energy associated within the pores for the paper-based DM.

Recognizing the fact that the present polynomial fit (Eq. 5.5) was derived purely based on the experimental data for SGL 24 carbon paper series coated with MPL, the applicability of the empirical fit (Eq. 5.5) to a carbon cloth DM with MPL needs to be addressed. To assess the prediction accuracy of the modified Leveret function ($K(s_{nw})$), the predicted capillary pressure by Eq. 5.5 of E-TEK Elat 1200W carbon cloth was compared with the experimental data. The material properties of E-TEK Elat 1200W carbon cloth were directly integrated into the capillary pressure correlation given in Eq. 5.5 and the capillary pressure versus saturation is plotted and shown in Fig. 5-12. Although the exact PTFE loading of E-TEK cloth is not publicly disclosed, a reasonable value of 20% PTFE is assumed depending upon the known PTFE range of E-TEK cloth (>20% PTFE of wt.). As seen from the Fig. 5-12, the modified Leverett function successfully approximates the capillary pressure up to saturation 0.5. After that point, as the saturation increases gradually, the predictions tend to exhibit a deviation from the experimental data, however, with diminishing significance. This could be result of non-uniform PTFE distribution in the cloth material. On the other hand, the vast deviation
associated with the standard Leverett function, \( J(s_{nw}) \), is more pronounced and much greater over the entire region, again demonstrating the inapplicability of the standard Leverett function to predict the capillary characteristics of any type of fuel cell DM.

5.4 Summary

For the first time, a modified Leverett function appropriate for SGL 24 carbon paper series fuel cell diffusion media was developed to describe capillary pressure-saturation relationship under no compression at room temperature. Experimental measurements of capillary pressure-liquid saturation for DMs (cloth and paper) tailored with PTFE content ranging from 0 to 20% of wt. were performed and then utilized as benchmark data. Based on this database, a unique empirical fit, relating the capillary pressure as a function of non-wetting saturation and PTFE content of the DM, was derived.

A key advantage of the presented empirical relation over the standard Leverett function is that it can successfully incorporate the rigorous interaction of liquid saturation and DM material properties, thus it is capable of accounting for the structural heterogeneity associated with the nature of the fuel cell DM. Furthermore, it can implicitly resolve the change in internal contact angle caused by the anisotropic nature of the hydrophobic coating, eliminating any ambiguity regarding the selection of an appropriate representative contact angle. A detailed comparative analysis of the modified Leverett function and the standard Leverett function was performed. The modified Leverett function accurately predicts the measured capillary pressures in almost the entire
saturation range \((0<s_{nw}<1)\), whereas the standard Leverett function exhibits a large deviation (more than 100%) from the experimental data, especially at high saturation \((s_{nw}>0.5)\). In addition, the empirical fit given in Eq. 5.5 reasonably well-predicts the measured capillary pressure of ETEK Elat 1200W carbon-cloth DM compared to standard Leverett approach, supporting the effectiveness of the modified approach.

In addition, the morphological characteristics of bi-layered DMs were investigated to elucidate the effects of the mixed wettability and identify the bimodal pore size distribution. The micro-porous layer is found to contain considerably fewer hydrophilic pores and is almost exclusively hydrophobic in nature, whereas macro DM contains mixed wettability. Spontaneous imbibition experiments were used to estimate the water retention capacity \((s_{wrc})\) of a typical fuel cell DM, which decreases with an increase in PTFE content of the DM.

The presented correlation and experimental data were generated at room temperature and under no compression. However, due to the various operational conditions, DMs can be subjected to different temperatures and different compressions, causing a significant change in the capillary transport characteristics. The effects of compression and temperature deserve deeper examination to further isolate the impact of these effects on transport characteristics, and are the subject of succeeding chapters.
5.5 Bibliography


Table 5-1: Material properties of the tested DM samples.

<table>
<thead>
<tr>
<th>Material</th>
<th>Type</th>
<th>Thickness (µm)</th>
<th>PTFE (% of wt.)</th>
<th>Porosity</th>
<th>Permeability (cm³/cm² · s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SGL 24BC</td>
<td>Paper w/MPL</td>
<td>235</td>
<td>5</td>
<td>0.76</td>
<td>0.45</td>
</tr>
<tr>
<td>SGL 24CC</td>
<td>Paper w/MPL</td>
<td>235</td>
<td>10</td>
<td>0.76</td>
<td>0.45</td>
</tr>
<tr>
<td>SGL 24DC</td>
<td>Paper w/MPL</td>
<td>235</td>
<td>20</td>
<td>0.76</td>
<td>0.45</td>
</tr>
<tr>
<td>E-TEK ELAT 1200W</td>
<td>Cloth w/MPL</td>
<td>275</td>
<td>&gt;20</td>
<td>N/A</td>
<td>&gt;8.00</td>
</tr>
</tbody>
</table>

All values are adapted from manufacturer technical specification sheets.

Table 5-2: Material properties of the tested DMs determined by MSP technique

<table>
<thead>
<tr>
<th>Material</th>
<th>Total Porosity</th>
<th>Hydrophilic Porosity</th>
<th>Full Pore Volume (cm³)</th>
<th>Total Pore Surface Area (m²/cm³)</th>
<th>Hydrophilic Pore Volume (cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SGL 24BC (5% PTFE)</td>
<td>0.75,0.76*</td>
<td>0.27</td>
<td>0.11</td>
<td>23.4</td>
<td>0.0408</td>
</tr>
<tr>
<td>SGL 24CC (10% PTFE)</td>
<td>0.76,0.76*</td>
<td>0.21</td>
<td>0.11</td>
<td>30.0</td>
<td>0.0259</td>
</tr>
<tr>
<td>SGL 24DC (20% PTFE)</td>
<td>0.74,0.76*</td>
<td>0.21</td>
<td>0.10</td>
<td>28.5</td>
<td>0.0287</td>
</tr>
<tr>
<td>ELAT 1200W (&gt;20% PTFE)</td>
<td>0.72</td>
<td>0.16</td>
<td>0.12</td>
<td>13.2</td>
<td>0.0281</td>
</tr>
</tbody>
</table>
Table 5-3: Water retention capacities of the tested DM samples.

<table>
<thead>
<tr>
<th>Material</th>
<th>PTFE content of wt.</th>
<th>Estimated Water Retention Capacity</th>
</tr>
</thead>
<tbody>
<tr>
<td>SGL 24BC</td>
<td>5 %</td>
<td>$s_{wrc} &gt; 0.35$</td>
</tr>
<tr>
<td>SGL 24CC</td>
<td>10 %</td>
<td>$s_{wrc} &gt; 0.30$</td>
</tr>
<tr>
<td>SGL 24DC</td>
<td>20 %</td>
<td>$s_{wrc} &gt; 0.28$</td>
</tr>
<tr>
<td>ELAT 1200W</td>
<td>&gt;20 %</td>
<td>$s_{wrc} &gt; 0.22$</td>
</tr>
</tbody>
</table>
Figure 5-1: SEM images of a) carbon paper, b) carbon cloth, and c) cross sectional view of carbon paper with a micro-porous layer.
Figure 5-2: Schematic view of the MSP technique.
Figure 5-3: Dual pore distribution of a) SGL 24DC carbon paper, and b) E-TEK Elat 1200W carbon cloth
Figure 5-4: Measured hydrophilic pore network capillary pressure versus wetting phase (water) saturation of a) SGL 24BC and SGL 24DC, and b) SGL 24DC and E-TEK Elat 1200W.
For a given saturation, the capillary pressure increases with an increase in PTFE content.

Figure 5-5: Measured total pore network (hydrophobic and hydrophilic) non-wetting phase saturation versus water/air capillary pressure of SGL 24 carbon paper series.
Figure 5-6: Measured capillary pressure versus PTFE content of wt. at specified saturations for SGL 24 series DM samples.
Figure 5-7: Measured total pore network non-wetting phase saturation versus water/air capillary pressure of SGL 24DC carbon paper and E-TEK Elat 1200W cloth.
Figure 5-8: Identification of micro-porous layer from the measured capillary pressure-saturation curves and dual pore distribution.
Figure 5-9: Comparison of modified Leverett function, standard Leverett function and experimental data for SGL 24BC (5% PTFE) over a saturation range of a) $0 < s_{nw} < 0.5$ and b) $0 < s_{nw} < 1$. 
Figure 5-10: Comparison of modified Leverett function, standard Leverett function and experimental data for SGL 24DC (20% PTFE) over a saturation range of a) 0<\(s_{nw}\)<0.5 and b) 0<\(s_{nw}\)<1.
Figure 5-11: Predicted capillary pressure by modified Leverett function given in Eq. 5.5 versus non-wetting saturation for SGL 24 carbon paper series.
Figure 5-12: Comparison of modified Leverett function, standard Leverett function and experimental data for E-TEK Elat 1200W cloth.
Chapter 6

EFFECTS OF COMPRESSION ON THE CAPILLARY TRANSPORT CHARACTERISTICS OF A FUEL CELL DIFFUSION MEDIA

This chapter is devoted to delineating the effects of compression on the capillary transport characteristics of a fuel cell diffusion media (DM). Direct measurement of capillary transport parameters of various fuel cell DMs is performed over a range of compression pressure. Based on the experimental measurements, a modified Leverett approach appropriate for the tested DM samples is deduced. The alternative approach presented in this chapter can precisely determine the capillary pressure as a function of hydrophobic additive content, liquid saturation, compression pressure and uncompressed porosity of the DM.

6.1 Background

Quantification of the multi-phase transport characteristics of the thin-film diffusion media (DM) has come to the forefront as a key step in establishing the most favorable micro-fluidic strategy that can balance the flooding effects (limiting the oxygen transport to the catalyst layer) and the membrane drying phenomena (loss of proton conductivity) in an operational cell [1-3].

The bi-modal pore distribution and the mixed wettability characteristics of the DM greatly influence the multi-phase flow within the pores of the DM [1]. Accurate multi-phase transport characterization of such thin-film media requires an appropriate capillary
pressure-liquid saturation relationship that is fundamentally dependent on material properties and operating conditions, including but not necessarily limited to: PTFE content, pore size, compression and temperature. However, a complete understanding of the multi-phase flow in these unique media has not been well-established, and the basic tools used to correlate the governing transport parameters are borrowed from soil science \[1,2\]. These transport models are incapable of accounting for the *mixed wettability characteristics* of the fuel cell DM. These traditional tools have so far yielded only qualitative guidance for the design of the next generation fuel cell systems. Therefore a higher level of precision is now required.

Proper stack assembly requires careful integration of components with an optimum assembly pressure to prevent leakage and assure proper contact surface from the lands to the DM \[5\]. Typically, low compression in fuel cell stack assembly causes an increase in gas leakage and electrical contact resistance, leading to poor performance, while over-compression of the DM leads to an irreversible deformation in DM structure \[7,8\]. Thus, optimization of the assembly pressure is of great importance \[4-6\]. Furthermore, depending upon the size of the components in the stack, the DM may experience various compression loadings, generating strong local stresses that can alter the morphological structure and the multi-phase transport characteristics of the DM. It has been established that for a given thin-film fuel cell DM, any compression is followed by a decrease in porosity and an increase in tortuosity \[9-11\]. The change in surface area and pore size is reasonably expected to change the behavior of multiphase flow, yielding discrete transport patterns between the channel and land locations. Therefore, it is
necessary to quantify the degree of change in capillary transport characteristics of a DM under different compression loadings.

Much literature is devoted to examining the effects of the stack assembly pressure on cell performance [5,6,11-13], but the changes in the capillary transport characteristics of a DM have not been explicitly addressed. The change in spatial variation of the pressure was modeled under varying compression pressures [7,8,12] and the corresponding reduction in local porosity was qualitatively coupled with the local current density distribution by Lee et al. [13]. The fluctuation in current density profile due to varying compressions is believed to be indicator of the existence of the mass transport resistance [6]. Recently, Bazylak et al. [4] analyzed SEM images of the compressed DMs and reported that the fiber breakage due to the compression leads to a decrease in flow resistance. The decrease in flow resistance is qualitatively attributed to the possible loss of hydrophobicity. However, it is possible that the highly heterogeneous nature of the DM may not be fully accounted for. The existing studies provide insightful background, but to the authors’ knowledge, no truly direct study elucidating the effect of cell assembly pressure on the capillary transport characteristics of a fuel cell DM has been reported.

6.2 Method of Approach

SGL 24 series (SIGRACET® diffusion media) and SGL 10BB non-woven carbon papers were investigated in the present study. The material properties of tested DM samples are provided in Table 6-1 for convenience. The selected DM samples are coated with a micro-porous layer (MPL), which is composed of carbon black powder and
hydrophobic agent called polytetrafluoroethylene (PTFE). The major aim of introducing the MPL on the cathode is to provide better electrical contact with the adjacent component and alleviate the flooding effects. These selected DM samples are treated with PTFE (hydrophobic agent) from 0 to 20% of total wt., which is in a typical hydrophobic treatment range preferred in conventional fuel cell applications.

A new technique, method of standard porosimetry (MSP), developed by POROTECH Inc. was employed to measure the desired transport parameters in thin-film DMs. The MSP provides a means of nondestructive testing for investigation of any type of porous materials, including soft, frail materials and powders [14]. A more detailed discussion of MSP versus MMP is provided in [14]. The current MSP experiments were performed at fixed levels of compression, i.e., 0, 0.6 and 1.4 MPa, providing data on both the structural changes and the corresponding transport properties of the DM samples. Additional compressive strain-stress experiments were also performed using a highly sensitive compression gauge to provide data on the elasticity behavior of the tested DM samples.
6.3 Results and Discussions

6.3.1 Effect of Compression on Morphological Characteristics of a DM

Any fluid displacement across a porous medium is usually more closely associated with the intricate pore morphology rather than the fluid properties [14]. The specific pore structure and the mixed wettability characteristics of the DM are strongly coupled with the compression strain, since any change in the electrode structure (including DM) can cause a substantial change in multi-phase transport characteristics. In that sense, the investigation of the changes in morphological structure of the thin-film DM is of critical importance to establish the accurate multi-phase transport characteristics of the DM placed in the fuel cell assembly.

Pore Characteristics

The DM samples were subjected to compression loadings of 0, 0.6 and 1.4 MPa to isolate the effects of compression on pore network characteristics. Total (hydrophilic and hydrophobic) pore distributions for SGL 24BC and SGL 24DC under different compressions (0 and 1.4 MPa) are shown in Fig. 6-1. For a given DM, the pore network follows a similar qualitative pattern under the influence of compression; however the corresponding pore size distribution shifts to smaller values with increasing compression. The average pore radius of the total pore network is found to be higher under no compression (4.8 µm for SGL 24BC and 3.9 µm for SGL 24DC), whereas the highest compression (1.4 MPa) yields the smallest average pore radius (3.5 µm for SGL 24BC
and 3.1 µm for SGL 24DC). The average pore radius of DM samples corresponding to all different compressions tested is shown in Table 6-2.

The pore characteristics of the individual components (macro- and micro substrates) were investigated by means of the pore-distribution data of the tested DM samples, as described in [1], to identify the relative significance of the morphological changes in different components of the DM. As seen from Fig. 6-1, the pore space of macro-porous substrate (pore radius>1 µm) seems to be more affected by the compression, thereby exhibiting a greater reduction in pore volume than that of the micro-porous layer (pore radius from 0.01 to 0.1 µm). This can be linked to the fact that the compact composition of the MPL provides an initially lower surface area and pore volume, yielding a more rigid structure. This feature, in turn, improves the elasticity of the MPL results in less strain under compression than the macro-porous substrate. As a result, any force exerted on the DM samples is mostly absorbed by the macro-substrate.

**Surface Area**

The specific surface area of a DM is also a particularly important macro-scale parameter. Any change in interfacial surface area available for mass transport can affect the micro-scale distribution of fluids inside the DM. The total (hydrophilic and hydrophobic) specific surface area under the compression of 0, 0.6 and 1.4 MPa for SGL 24BC and SGL 24DC was measured and is shown in Fig. 6-2. For both DM samples, applying compression reduces pore volume (radius from 0.001 to 0.1 µm) and increases the interfacial surface area, distorting the available transport pathways and increasing the tortuosity. The decrease in effective porosity is accompanied by a reduction in
permeability, which in turn, restricts the liquid flow and causing a higher mass (liquid and gas phase) transport resistance.

Effect of DM Thickness

The present results also suggest that the thickness of the bi-layer DM influences the compression characteristics and its effects on pore structure. One distinctive observation is that SGL 10BB (420 µm) exhibits a considerable increase in total pore surface area as regards to the increase of compression. Figure 6-3 shows the total (hydrophilic and hydrophobic) surface area of SGL 10BB under the compression of 0.6 to 1.4 MPa. The increase in total surface area of SGL 10BB, especially in the meso- and micro-porous components (pore radius<0.1µm), is more pronounced at 1.4 MPa compression than that of SGL 24 series (SGL 24BC, 24CC and 24DC). Recalling that SGL 10BB DM has a thickness of 420 µm (almost twice that of the SGL 24 series), the increase in bulk thickness of the DM appears to amplify the effect of compression on reduction in pore volume and causes an increase in interfacial surface area. The thinner DMs (SGL 24 series) appear to be more resistive to deformation and better sustain their pore characteristics under higher compression loadings due to the relatively more compact and rigid structure than that of a thicker DM. Thus, the compressive strain characteristics of the DM and its effect on the capillary transport process should be included in attempts to accurately model the two-phase flow in the DM.
6.3.2 Water Retention Behavior and Hydrophilic Pore Network

The different DM morphologies exhibit a range of surface area to pore volume ratios, yielding different wetting phase configurations and immobile liquid saturations. The water retention characteristic of a DM is an important parameter affecting the water storage behavior of the fuel cell DM. Neutron imaging studies by Mench and co-workers [21,22] have revealed that two different fuel cell configurations can have nearly identical performance, but with large differences in the stored water content. At the stack level, the target of the new designs is to reduce the stored water content in order to promote durability, mitigate freeze/thaw damages and reduce the parasitic purge requirements. Due to these factors, it is desirable to find the best DM configuration that will promote low water retention. For that reason, the water retention behavior in different pore configurations needs to be more thoroughly addressed before an optimized structure can be proposed or complex models are complete.

Spontaneous capillary imbibition experiments were performed to determine the fraction of accessible connected hydrophilic pathways in the mixed wettability DM. The detailed description of experimental approach is outlined in references [1, 14]. The MSP technique provides a means for isolating the connected hydrophilic pore network from the total pore network by utilizing various liquids with different wettability [14]. The corresponding capillary pressure-liquid saturation of the connected hydrophilic pore network was obtained at various levels of compression. The measurement of the connected hydrophilic pore volume enables reasonable estimates of the water retention
capacity of the DM ($s_{wrc}$), which is, in fact, a measure of available pore space that can spontaneously imbibe and tends to store water in the DM.

Figure 6-4 represents the measured capillary pressure-wetting phase saturation relationships of the connected hydrophilic pore network (excluding the isolated pores) for SGL 24BC and SGL 24DC carbon paper under 0 and 1.4 MPa compression. Capillary pressure shown in Fig. 6-4 represents the spontaneous imbibition pressure. As seen in Fig. 6-4, the capillary pressure approaches zero as the DM imbibes the maximum water, meaning that once the threshold saturation is reached, no connected hydrophilic pore space is available for the DM to further imbibe. From Fig. 6-4, the amount of water to fill the available connected hydrophilic sites is observed to decrease with compression. The amount of water imbibed in SGL 24BC (5% PTFE of wt.) is reduced from 0.35 ($s_{wrc}$>0.35) to 0.31 ($s_{wrc}$>0.31) as the compression is increased to 1.4 MPa. However, even though SGL 24DC (20% PTFE of wt.) exhibits a similar decrease in response to increase in compression ($s_{wrc}$>0.28 for no compression, $s_{wrc}$>0.24 for 1.4 MPa compression), the compression yields different quantitative water retention capacities. It is hypothesized that higher PTFE loading of the DM reduces the available hydrophilic pathways for the compressed and uncompressed DM [1].

The results shown in Figs. 6-4-a and 6-4-b also suggest that the tested DM samples appear to preserve their relative wettability characteristics under high compressions, as SGL 24BC treated with 5% PTFE imbibes to a maximum saturation of 0.35 ($s_{wrc}$>0.35); whereas SGL 24DC tailored with 20% PTFE can only imbibe up to a maximum of 0.28 saturation ($s_{wrc}$>0.28). This finding contradicts the observations of Bazylak et al. [4]. They hypothesized that the compression is manifested as irreversible
damage to DM structure, causing PTFE coating breakage on the fiber surface and locally producing more hydrophilic sites.

Effects of bulk thickness on the water retention characteristics of the DM were also investigated. Figure 6-5-a shows the water retention behavior of SGL 10BB (5% PTFE of wt., with a thickness of 420 µm) under 0.6 and 1.4 MPa compression. The noticeable decrease in the imbibed water of the hydrophilic sites compared to SGL 24 series (235 µm) is clearly seen from Figs. 6-4 and 6-5-a. At 0.6 MPa compression, the macro- and micro-porous substrate of SGL 10BB carbon paper can imbibe the water up to a maximum saturation of 0.56 ($s_{wrc}>0.56$), meaning that the available pore space is almost equally shared by the hydrophilic and hydrophobic pores. However, as the compression pressure is increased to 1.4 MPa, the connected hydrophilic pore volume reduces significantly, allowing maximum spontaneous imbibition of only 0.14 ($s_{wrc}>0.14$).

The significant change in water retention capacity can be attributed to a larger reduction in connected hydrophilic pore space with increasing compression in this thicker DM sample (420 µm). The higher deformation of the thicker sample (SGL 10BB) results in decreasing available hydrophilic pore sites and limiting the imbibition of water. The substantial decrease in hydrophilic pore density due to the compression can also be observed from hydrophilic pore distribution shown in Fig. 6-5-b. The measured hydrophilic porosity and the corresponding maximum imbibed water saturation are given in Tables 6-2 and 6-3 respectively.
In summary, compression and increased PTFE content promote a reduction in the connected hydrophilic pore volume and the water retention capacity of the DM (self-imbibed water content). From a fuel cell perspective, the reduction of stored water would provide better control of dynamic transport through thin-film DM, leading to improvement in both the steady and dynamic fuel cell performance, decreased start-up time from frozen conditions, better purge capability, and enhanced durability [17]. The current results are consistent with those in the soil science literature, emphasizing the strong dependence of water retention ability on the spatial heterogeneity of the porous medium, the variation of physical material properties and deformation of media itself [15,16].

6.3.3 Total Pore Network Capillary Pressure-Saturation Curves

The drainage curves of air-water capillary system of the total pore network under the compression of 0, 0.6 and 1.4 MPa were obtained to delineate the effect of compression on the capillary-induced flow within the fuel cell DM. Figure 6-6 shows the total (hydrophilic and hydrophobic) network non-wetting saturation versus air-water capillary pressure of SGL 24BC and SGL 24DC (both coated with MPL) subjected to compression of 0, 0.6 and 1.4 MPa. The individual curves follow similar qualitative trends, yielding slightly different quantitative values. The capillary pressure increases with an increase in non-wetting phase saturation at each compression condition, as expected for a PTFE-coated DM. The compression, shown to cause a decrease in the pore size (Fig. 6-5-b) generally promotes a higher capillary pressure to overcome the increased
surface energy of the distorted pores (Fig. 6-6), though there is little quantitative
difference between the 0.6 MPa and 1.4 MPa curves. The increase in capillary pressure
due to the reduced pore size can also be explained through the Young-Laplace theorem,
which correlates the capillary pressure for a cylindrical pore in terms of pore radius,
surface tension and contact angle [3]. The Young-Laplace equation is given as:

\[
P_c = P_{nv} - P_w = \frac{2 \cdot \gamma \cdot \cos \theta}{r}
\]  

[6.1]

where \( \gamma \), \( \theta \) and \( r \) represent surface tension, contact angle and pore radius, respectively. Compression exerted on the DM causes to change the morphological structure,
decreasing the pore radius. The decrease in average pore radius leads to an increase in capillary pressure, as can be also seen in Eq. 6.1.

Figure 6-6 also illustrates that the increase in capillary pressure with compression is more pronounced between an uncompressed and 0.6 MPa compression condition. However, a further increase from 0.6 to 1.4 MPa seems to have less effect on the measured capillary pressure, which holds true for all tested DMs. For SGL 24DC carbon paper DM, the measured capillary pressure increases with an average of 30.5 % from 0 to 0.6 MPa, whereas there is almost no variation in the measured capillary pressures after 0.6 MPa. Additional compressive strain-stress experiments were performed to create a link between the strain characteristics of the DM and the corresponding change in capillary pressure. The compressive strain versus the applied pressure for SGL 24 carbon paper series and SGL 10BB is shown in Fig. 6-7. The compressive strain is found to be sensitive to changes in pressure, reaching to a value of 0.20 at 3 MPa for SGL 24 series. The slight decrease in the slope of the strain-stress curve (Fig. 6-7) with increasing
compression can be attributed to slight increase in stiffness of the DM with compression. As the DM is compressed, the available pore space reduces, affecting the capillary pressure within the pores. Recalling that the compressive strain governs the degree of the reduction in pore size, the substantial increase in capillary pressure within the range of compression from 0 to 0.6 MPa can be linked to the increase of strain rate (shown in Fig. 6-7), which leads to a higher reduction in pore size.

### 6.3.4 Modified Leverett Approach

Almost every multi-phase transport model requires the specific capillary pressure-saturation relationship of fluid and porous medium to correlate the capillary pressure as a function of saturation, wettability and other material properties. A traditional semi-empirical approach applicable for homogenous water-wet sand with uniform wettability was proposed by Leverett [18] (Eq. 6.2) and is commonly employed in fuel cell models to estimate the capillary pressure as a function of liquid saturation [19].

\[
P_c = \gamma \cos \theta \cdot \left(\frac{\varepsilon}{k}\right)^{1/2} J(s_{mw})
\]

\[
J(s_{mw}) = \begin{cases} 
1.417 \cdot (1 - s_{mw})^2 - 2.120 \cdot (1 - s_{mw})^3 + 1.263 \cdot (1 - s_{mw}) & \text{if } \theta < 90^\circ \\
1.417 \cdot s_{mw}^2 - 2.120 \cdot s_{mw} + 1.263 \cdot s_{mw}^3 & \text{if } \theta > 90^\circ 
\end{cases} \quad [6.2]
\]

The studies presented in Chapter 4 and 5 suggest that a generic Leverett approach is insufficient for describing the capillary transport characteristics of a mixed wettability fuel cell DM. A more complete approach would incorporate a wide range of macroscopic variables, such as the rate of change of wetting phase saturation, the pore size, the wetted
fraction of the solid surface, the specific solid interfacial area of the fuel cell DM and operational conditions such as compression and temperature. The effect of PTFE content and mixed wettability characteristics of the DM was thoroughly investigated and addressed in the first part of this paper series [1]. This article focuses on developing a modified approach including the specific effects of compression. The effect of temperature and an overall unified approach are the subjects of the Chapter 7.

Herein, a new form of capillary pressure-saturation equation (a modified Leverett approach) appropriate for the tested fuel cell DMs was developed to accurately determine the capillary pressure as a function of liquid saturation, PTFE content, uncompressed porosity and compression pressure of the DM. This modified approach is capable of incorporating the necessary adjustments corresponding to the changes in the transport parameters and the wettability characteristics of the DM. Note that the effect of temperature is not included in this modified approach here, but is addressed in Chapter 7.

The procedure of our integrated approach is structured as follows.

The capillary pressure measurements (described in previous sections) of SGL 24 carbon paper series were compiled in an expanded database. The specific compressive strain-stress relationships for the tested DM samples were obtained and the corresponding reduction in pore size under compression was used with the measured parameters and given material properties. The effective porosity was precisely determined based on the corresponding pore volume change and then was linked to the degree of deformation (compressive strain). Subsequently, the non-dimensional effective pore size parameter, \((k/\varepsilon)^{0.5}\), used in the traditional Leverett approach was calibrated to account for the changes in effective porosity due to the compression. Consequently, a general equation
correlating the effective porosity ($\varepsilon_c$) as a function of compressive strain ($s_{TR}$) and uncompressed porosity ($\varepsilon_o$) was derived, based on measured data:

$$\varepsilon_c = \left[ \frac{0.9}{1 + s_{TR}} + 0.1 \right] \cdot \varepsilon_o$$  \[6.3\]

Based on compressive strain-stress experiments, the compressive strain of the tested DM samples as a function of compression pressure is found as:

For SGL 24 series carbon papers,

$$s_{TR} = -0.0083 \cdot C^2 + 0.0911 \cdot C$$  \[6.4\]

For SGL 10BB carbon paper,

$$s_{TR} = -0.0046 \cdot C^2 + 0.0843 \cdot C$$  \[6.5\]

where $C$ represents the compression pressure (MPa). Note that the compressive strain-stress relation is a characteristic property of the DM and varies for different DM materials. The effective porosity versus applied compression stress (MPa) for SGL 24 series DM is also shown in Fig. 6-7. As the compression increases, the effective porosity reduces for both DM types. The effective porosity of SGL 24 series and SGL 10BB is found to be 0.66 and 0.73 at a compression of 2 MPa and it reaches a lower value of 0.62 and 0.67 at 4 MPa, respectively.

Instead of the standard Leverett function ($J(s_{nw})$), a modified Leverett function $K(s_{nw})$, presented in Chapter 5, was implemented into the present approach. The modified
water retention function correlates the capillary pressure as a function of liquid saturation and PTFE content of the DM. At the final step, the benchmark data were categorized according to the different compressions and PTFE loadings of the DM and then integrated into a multi-dimensional linear regression model to deduce a representative semi-empirical correlation describing the capillary pressure as a function of the relevant non-dimensionelized experimental parameters. The general form of the capillary equation is found as:

$$P_c = \gamma \cdot 2^{0.4c} \left( \frac{\varepsilon_a}{k} \cdot K(s_{nw}) \right)^{1/2}$$  \[6.6\]

Inserting the effective porosity and substituting the characteristic strain rate for SGL 24 series in terms of compression pressure, the final form of the modified capillary pressure function for SGL 24 series yields:

$$P_c = \gamma \cdot 2^{0.4c} \left[ \left( \frac{0.9}{1 + (-0.0083 \cdot C^2 + 0.0911 \cdot C)} + 0.1 \right) \cdot \frac{\varepsilon_a}{k} \right]^{1/2} \cdot K(s_{nw})$$

\[6.7\]

$$K(s_{nw}) = \begin{cases} \frac{\text{(%wt.)} \cdot [0.0469 - 0.00152 \cdot \text{(%wt.)} - 0.0406 \cdot s_{nw}^2 + 0.143 \cdot s_{nw}^3] + 0.0561 \cdot \ln s_{nw}}{0.0} \leq s_{nw} \leq 0.50 \\ \frac{\text{(%wt.)} \cdot [1.534 - 0.0293 \cdot \text{(%wt.)} - 12.68 \cdot s_{nw}^2 + 18.824 \cdot s_{nw}^3] + 3.416 \cdot \ln s_{nw}}{0.50 < s_{nw} \leq 0.65} \\ \frac{\text{(%wt.)} \cdot [1.7 - 0.0324 \cdot \text{(%wt.)} - 14.1 \cdot s_{nw}^2 + 20.9 \cdot s_{nw}^3] + 3.79 \cdot \ln s_{nw}}{0.65 < s_{nw} < 1.00} \end{cases}$$
Similarly, substituting the compression stress-strain relationship (given in Eq. 6.5) of SGL 10BB DM, the final form of the modified capillary pressure function for SGL 10BB carbon paper becomes: Eq. 6.8

\[
P_c = \gamma \cdot 2^{0.4C} \cdot \left[ \left( \frac{0.9}{1 + (-0.0046 \cdot C^2 + 0.0843 \cdot C)} + 0.1 \right) \cdot \frac{E_{\infty}}{k} \right]^{1/2} \cdot K(s_{nw})
\]

\[
K(s_{nw}) = \begin{cases} 
\left( \% wt. \right) \cdot \left[ 0.0469 - 0.00152 \cdot \left( \% wt. \right) - 0.0406 \cdot s_{nw}^2 + 0.143 \cdot s_{nw}^3 \right] + 0.0561 \cdot \ln s_{nw} & 0.0 < s_{nw} \leq 0.50 \\
\left( \% wt. \right) \cdot \left[ 0.0469 - 0.00152 \cdot \left( \% wt. \right) - 0.0406 \cdot s_{nw}^2 + 0.143 \cdot s_{nw}^3 \right] + 0.0561 \cdot \ln s_{nw} & 0.50 < s_{nw} \leq 0.65 \\
\left( \% wt. \right) \cdot \left[ 1.7 - 0.0324 \cdot \left( \% wt. \right) - 14.1 \cdot s_{nw}^2 + 20.9 \cdot s_{nw}^3 \right] + 3.79 \cdot \ln s_{nw} & 0.65 < s_{nw} < 1.00 
\end{cases}
\]  

[6.8]

where \( \% \text{ wt} \), \( k \) and \( s_{nw} \) are PTFE weight percentage, absolute permeability of the DM and non-wetting liquid saturation, respectively. \( K(s_{nw}) \) represents the modified Leverett function appropriate for thin-film fuel cell DMs. It is worthwhile to emphasize that Eqs. 6-7 and 6-8 are appropriate for SGL 24 series DM and SGL 10BB carbon papers at room temperature, respectively. Equation 6-7 or 6-8 can be modified to account for compression in any type of DM by implementing the characteristic compression-strain relation of the DM into the general form of the equation presented in Eq. 6-6.

**Validation and Comparison**

Figures 6-8 and 6-9 depict the comparison of capillary pressures predictions by the modified correlation and the standard Leverett approach with respect to the measured capillary pressure at 1.4 MPa compression for SGL 24BC and SGL24DC carbon papers.
As seen from Figs. 6-8 and 6-9, the presented modified approach generally predicts the capillary pressure well with small deviations observed in the saturation range of 0.50 to 0.70. This deviation likely stems from the complex shape of the capillary pressure-saturation curves. However, at high saturations ($s_{nw}>0.70$), the modified approach captures the change in capillary pressure and successfully predicts the measured capillary pressure within an uncertainty of $\pm12\%$ of the measured value. Overall, in the entire saturation domain ($0<s_{nw}<1$), the modified approach in the prescribed functional form predicts the capillary pressure with an uncertainty of $\pm15\%$ of the measured capillary pressure. In contrast, the standard Leverett approach deviates enormously, nearly up to two orders of magnitude from the experimental data over the entire saturation domain, especially at high saturations ($s_{nw}>0.5$), as clearly seen in Figs. 6-8 and 6-9. The standard Leverett approach equipped with the Leverett $J$-function appears incapable of tracking the changes in capillary pressure caused by the applied compression and mixed wettability characteristics of the fuel cell DM.

A further comparison between the predicted capillary pressure (by Eq. 6.8) and measured capillary pressure of SGL 10BB (5% PTFE) carbon paper was also performed to validate the presented modified Leverett approach. Additional stress-strain experiments were performed for SGL 10BB carbon substrate and the corresponding compressive strain-pressure relationship is given in Eq. 6.5. Using the appropriate functional form of modified Leverett approach (Eq. 6.8), the capillary pressure over a full spectrum of non-wetting saturation was predicted under 1.4 MPa compression. Figure 6-10 shows the experimental data and capillary pressures predicted using the modified approach (Eq. 6.8) and standard Leverett approach under 1.4 MPa compression at room
temperature. As shown in Fig. 6-10, the modified Leverett approach successfully approximates the capillary pressure up to saturation 0.52 (to within ±5.6 %). As the saturation further increases, the predictions tend to exhibit a deviation from the experimental data, especially \( s_{nw} < 0.75 \), however the predictions recovers the deviation to some extent at high saturations \((s_{nw}>0.8)\). The curve-fit derived in the present work rely mostly heavily on the SGL 24 series DM data, thus for more accurate prediction of SGL 10BB, additional experiments would be required.

Finally, the capillary pressure of a DM with 5% PTFE was predicted over a wide range of compressions by the modified Leverett approach given in Eq. 6.6 using the SGL 24 series strain-stress relationship, in order to validate and compare the effects of compression with the experimental observations. Figure 6-11 depicts the predicted capillary pressures versus non-wetting saturation under the compression of 0, 1, 2 and 3 MPa. For a specified saturation, the capillary pressure appears to increase with an increase in applied compression pressure, in good agreement with the experimental observations.

The key features of the presented modified Leverett approach (given in Eq. 6.6) are summarized as follows:

a) The modified approach accurately predicts the measured capillary pressure with an uncertainty of ±15% of the measured values, showing considerable improvement over the traditional Leverett approach, which underpredicts the capillary pressure in high saturation region \((s_{nw}>0.5)\) by nearly two orders of magnitude.
b) The new form of the equation accounts for the reduction in effective pore size by adjusting the effective porosity through the specific strain-stress relations of the DM.

c) The phase distributions over a wide range of hydrophobic content can be accurately captured by the well-defined modified Leverett function [1].

d) The modified approach does not require any representative contact angle as an input, overcoming a major limitation of the original Leverett approach. The variations in internal contact angle are implicitly embedded into the PTFE parameter (% wt.) of the modified Leverett function, therefore eliminating the need for the selection of a single (and unrealistic) surface contact angle.

6.3.5 Effects of PTFE Content and Compression: Coupled Effect

The engineering consequences of increasing PTFE content and compression should be systematically addressed in order to achieve the most favorable capillary transport characteristics and minimize the additional losses introduced by these parameters. In order to assess the relative significance of PTFE and compression on the capillary transport, the capillary pressure versus the compression pressure for SGL 24BC (5% PTFE) and SGL 24DC (20% PTFE) was predicted at constant water saturation values by the modified Leverett approach (Eq. 6.7) and the results are shown in Fig. 6-12. SGL 24 DC (20% PTFE content of wt.) carbon paper appears to exhibit a larger increase in capillary pressure (from 40 to 90 kPa at s=0.4) at a compression of 3 MPa. However,
the capillary pressure seems to be increased to a lesser extent with compression for SGL 24BC (5% PTFE content of wt.). In other words, the effect of compression on the capillary pressure is amplified by rendering the DM more hydrophobic. Physically, increasing the compression reduces the effective pore size, restricting the flow in a more confined space.

6.3.6 Further Discussion: Physical Modeling

Inhomogeneous Compression and Capillary Transport Mechanism

Existing water management studies are mostly motivated by a need to relate the macroscopic interaction between the flooding phenomena and the cell performance. Often, as a simplification, the thin-film fuel cell DM is assumed to contain continuous capillaries with the same wettability, and transport phenomena therein is described by bulk transport parameters, ignoring the discrete zones with mixed wettability characteristics. Even in the pertinent literature, there are contradictory hypotheses that portray the transport mechanism in different fashions. Some [15,19] suggest that the capillary transport inside the DM causes the liquid water distribution to occur in a branching geometry, yielding the formation of a tree-like structure, while an opposing idea [20] stresses the fingering and channeling effect, which governs the water transport mechanism.

To construct a complete physical model, it is necessary to first determine the spatial variation in local transport properties. The discontinuity of the surface contact area at the DM-flow channel interface creates inhomogeneous compression distributions,
yielding substantial changes in local physical properties of the DM [7,8]. The portion of the DM in contact with the landings are subjected to higher compression, whereas the portion under the flow channel experiences less compression and tends to intrude into flow channels, thus resulting in increased reactant flow-field pressure drop [3]. The axial variation of the compression in the cell assembly yields discrete regions which can be represented by different characteristic pore radii. Therefore, the capillary transport in porous fuel cell media cannot be appropriately characterized through the concept of a representative pore size, since each region in DM exhibits distinct capillary behaviors. Instead, an improved approach to analyze the transport would be to construct a finite number of discrete zones that represent the measured morphology (i.e., pore size and wettability) and corresponding capillarity characteristics. A conceptual schematic of a limited number of discrete zones (including high capillary and low capillary zone) mapped in the thin-film media is illustrated in Fig. 6-13.

The available pathways for mass transport under the landings, named as “high capillary pressure zones”, are compressed; therefore the corresponding regions experience a larger decrease in effective pore size compared to the less compressed zones (under the flow channel regions). The reduction in characteristic pore radius is accompanied by an increase in the pore entry pressure ($P_e$), which is strong function of pore size and wettability. This effect may inhibit the liquid water flow from the catalyst interface, although transport of vapor and subsequent condensation will occur. The water condensed at the catalyst-DM interface will build up a dynamic pressure that induces the hydrodynamic flow in the preferred direction of the less resistance pathways (low capillary zone). This hydrodynamic liquid flow may promote the branch-like spreading,
leading to the formation of non-uniform saturation distribution in the less compressed zone of the DM. The capillary dispersion in the low capillary zone is followed by the condensation of vapor streams that escaped from the active electro-chemical sites. Subsequently, the small capillaries may congregate into continuous pathways stretching to flow channel surface. As a result, a tree-like structure may occur in the low capillary zone, as illustrated in Fig. 6-13. Once the continuous conduits are formed, the energy required to transport the liquid water in these capillary pathways will be less than the surface energy to initiate the flow, so the continuous liquid flow in the less compressed zone (low capillary pressure zone) will be attained.

While condensed liquid water may be transported from catalyst layer as described above, the vapor phase diffusion is expected to be relatively less affected by the compression due to the low viscosity of the gas molecules. Based on the above hypothesis, the landings-DM interface may be potential spots for the condensation of saturated vapor streams due to its high thermal mass, low temperature and transport blockage. Once the saturation reaches a critical value, the accumulated liquid water may be sucked into the hydrophilic flow channels in lateral directions, as illustrated in Fig. 6-13. For the same liquid saturation, the compressed zone of the DM (underneath the landings) has a higher capillary pressure, therefore leading to the flow from under-landing location to the flow channel. Mench and co-workers [17,21,22] emphasized that there can be large differences in the accumulated water content under the landing area, which is a function of channel geometry. For instance, for a small landing case, the saturation under the landings can be achieved very fast and water will likely to move through channels immediately. However, with large landings, there may be more area for
the water to accumulate, which in turn, the accumulated water under the landings can easily get connected, thus leading to the formation of a micro-layer, as shown in Fig. 6-13. This micro-layer may block the diffusion of reactant significantly and cause severe flooding.

6.4 Summary

The effect of compression on the capillary transport characteristics of thin-film fuel cell DM was thoroughly examined for a series of DM samples. Capillary pressure-saturation measurements at different compressions were performed for DMs tailored with a range of mixed wettability (5% to 20% PTFE of wt.). The corresponding morphological changes were probed and the water retention characteristics of tested DMs were addressed. Based on these benchmark data, the traditional Leverett approach was revised and a modified approach incorporating the mixed wettability and compression effect has been derived. A modified Leverett function [1], which precisely captures the changes in phase saturation at different levels of hydrophobic coating, was implemented into the presented approach. The reduction in pore size from compression is taken into account and the measured capillary pressure is predicted with an uncertainty of ±15% of the measured values, while the traditional Leverett approach exhibits enormous deviation from the measured capillary pressure data (nearly up to two orders of magnitude), especially at high saturations, $s_{nw}>0.5$.

The results show that the compression of the DM leads to an increase in capillary pressure within the compression range from 0 to 0.6 MPa. Rendering the DM more
hydrophobic amplifies the compression effect, resulting in a larger capillary pressure for the same saturation and compression. The connected hydrophilic porosity is observed to decrease with an increase in compression, leading to a reduction in water retention capacity. From a physical perspective, inhomogeneous compression in fuel cell assembly creates distinct zones that have different capillary characteristics. It is hypothesized that the relatively larger pore volume in less compressed zone promotes the hydrodynamic liquid flow, leading to the formation of the tree-like structure in less compressed zone (under-landings). On the other hand, the liquid transport in high compressed zone (high capillary zone) is expected to be mostly governed by the condensation of saturated gas streams underneath the landings.

Note that the temperature is also a key factor affecting the transport mechanism, and is thoroughly investigated in the succeeding chapter.
6.5 Bibliography


Table 6-1: Material properties of tested DM samples.

<table>
<thead>
<tr>
<th>Material</th>
<th>Type</th>
<th>Thickness (µm)</th>
<th>PTFE (% of wt.)</th>
<th>Uncompressed Porosity</th>
<th>Permeability (cm³/cm² s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SGL 24BC</td>
<td>Paper w/MPL</td>
<td>235</td>
<td>5</td>
<td>0.76</td>
<td>0.45</td>
</tr>
<tr>
<td>SGL 24DC</td>
<td>Paper w/MPL</td>
<td>235</td>
<td>20</td>
<td>0.76</td>
<td>0.45</td>
</tr>
<tr>
<td>SGL 10BB</td>
<td>Paper w/MPL</td>
<td>420</td>
<td>5</td>
<td>0.84</td>
<td>3.00</td>
</tr>
</tbody>
</table>

Table 6-2: Material properties of the tested DMs determined by MSP technique.

<table>
<thead>
<tr>
<th>Material</th>
<th>Total Porosity/Hydrophilic Porosity</th>
<th>Total Surface Area (m²/cm³)/Average Pore Radius (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0 MPa</td>
<td>0.6 MPa</td>
</tr>
<tr>
<td>SGL 24BC (5% PTFE)</td>
<td>0.75/0.27</td>
<td>0.72/0.23</td>
</tr>
<tr>
<td>SGL 24DC (20% PTFE)</td>
<td>0.74/0.21</td>
<td>0.72/0.18</td>
</tr>
<tr>
<td>SGL 10BB (5% PTFE)</td>
<td>0.84/0.41</td>
<td>0.78/0.40</td>
</tr>
</tbody>
</table>
Table 6-3: Water retention capacities of the tested DM samples under compression.

<table>
<thead>
<tr>
<th>Material</th>
<th>PTFE content (of wt.), Thickness</th>
<th>Estimated Water Retention Capacity</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>0 MPa</td>
</tr>
<tr>
<td>SGL 24BC</td>
<td>5%, 235 µm</td>
<td>$s_{wrc} &gt; 0.35$</td>
</tr>
<tr>
<td>SGL 24DC</td>
<td>20%, 235 µm</td>
<td>$s_{wrc} &gt; 0.28$</td>
</tr>
<tr>
<td>SGL 10BB</td>
<td>5%, 420 µm</td>
<td>$s_{wrc} &gt; 0.58$</td>
</tr>
</tbody>
</table>
Figure 6-1: Dual (hydrophobic and hydrophilic) pore distribution under 0 and 1.4 MPa compression of a) SGL 24BC, and b) SGL 24DC carbon paper.
Figure 6-2: Total (hydrophobic and hydrophilic) surface area under 0, 0.6 and 1.4 MPa compression of a) SGL 24BC, and b) SGL 24DC carbon paper.
Compression causes considerable increase in the total surface area of SGL 10BB compared to SGL 24 series.

Figure 6-3: Total (hydrophobic and hydrophilic) surface area of SGL 10BB carbon paper (with a thickness of 420 µm) under 0.6 and 1.4 MPa.
Figure 6-4: Capillary pressure versus wetting phase saturation of the connected hydrophilic pore network under 0 and 1.4 MPa compression of a) SGL 24BC, and b) SGL 24DC carbon paper.
Figure 6-5: a) Capillary pressure-saturation for connected hydrophilic pore network of SGL 10BB under 0.6 and 1.4 MPa compression, b) Hydrophilic pore distribution of SGL 10BB under 0.6 and 1.4 MPa compression.
Figure 6-6: Water/air capillary pressure versus non-wetting phase saturation of total pore network (hydrophobic and hydrophilic) under 0, 0.6 and 1.4 MPa compression of a) SGL 24BC, and b) SGL 24DC carbon paper.
Figure 6-7: Compressive strain and effective porosity versus applied compression pressure curves for a) SGL 24 carbon paper series (SGL 24BC, CC and DC), and b) SGL 10BB carbon paper.
Figure 6-8: Comparison of modified Leverett approach (given in Eq. 6.7), standard Leverett approach (Eq. 6.2) and experimental data for SGL 24BC under 1.4 MPa compression over a saturation range of a) \(0<s_{nw}<0.5\), and b) \(0<s_{nw}<1\).
Figure 6-9: Comparison of modified Leverett approach (given in Eq. 6.7), standard Leverett approach (Eq. 6.2) and experimental data for SGL 24DC (20% PTFE) under 1.4 MPa compression.
Figure 6-10: Comparison of modified Leverett approach (given in Eq. 6.8), standard Leverett approach (Eq. 6.2) and experimental data for SGL 10BB (5% PTFE) under 1.4 MPa compression.
Figure 6-11: Predicted capillary pressure (by the modified approach given in Eq. 6.7) versus non-wetting saturation for a DM with 5% PTFE.
The increase in capillary pressure due to the compression is more pronounced at DMs with high PTFE loading.

Figure 6-12: The capillary pressure predicted by modified approach (Eq. 6.7) versus compression pressure of SGL 24 BC and SGL 24DC at specified saturations.
Figure 6-13: Schematic of the hypothesized inhomogeneous compression and the water transport mechanism in the high and low capillary zones.
Chapter 7

EFFECTS OF TEMPERATURE ON CAPILLARY TRANSPORT AND UNIFIED LEVERETT APPROACH

This chapter discusses the effects of temperature on the multi-phase transport characteristics of the thin-film fuel cell diffusion media (DM). Direct measurements of capillary pressure of various commercial DMs coated with a wide range of PTFE loadings (from 0% to 20% PTFE of wt.) were performed at different operating temperatures (20, 50 and 80 °C). The benchmark data gathered from these experiments were compiled into the existing database generated from the first and second phase of this study. The expanded database was then utilized to deduce a unified form of an empirical relation appropriate for the tested fuel cell DMs that correlates the capillary pressure of the DM as a function of the studied transport parameters and operating conditions.

7.1 Background

Proper tailoring of the multi-phase transport in porous fuel cell DM with mixed wettability is essential for achieving the optimal micro-fluidic management strategy and providing operational stability, durability and rapid start-up from a frozen condition in polymer electrolyte fuel cells (PEFCs) [1-4]. In the open literature, the water transport phenomena are generally coupled with the fuel cell performance [5-7], however the specific transport characteristics of these thin-film media over a wide range of operating conditions have not been described in adequate detail. Even most efforts to model the
multi-phase flow in porous fuel cell media are based on bulk empirical correlations alone, and often as simplification, the transport properties of the fuel cell porous media are improperly assumed to be uniform [6-8], which may lead to misinterpretation of capillary transport characteristics and liquid water distribution within the cell. For that reason, the capillary transport characteristics of the DM tailored with different PTFE loadings at various operational environments should be precisely quantified to achieve an accurate two-phase transport model in fuel cell modeling studies.

One important effect that still must be better understood is that of temperature. As repeatedly expressed in the literature [9-12], thermal management is closely coupled with the delicate water balance, which is essential to high performance and longevity of PEFCs. In terms of transport, the fuel cell DM is often exposed to a non-isothermal environment, causing significant changes in heat and mass transport process [10,11]. Such a variation in temperature influences the governing transport properties, including: the permeability, the capillary pressure-saturation relation, fluid viscosity and the surface energy of the medium, thereby directly affecting the capillary transport characteristics in fuel cell or other porous media [13-17]. Moreover, existing efforts in soil science [18-26] have revealed that the variation in equilibrium temperature is the dominating factor determining the equilibrium capillary pressure. Thus, understanding of the effects of operating temperature on the capillary transport characteristics of a fuel cell DM along with the knowledge of the effects of wettability characteristics and the compression, is of paramount importance for achieving an effective water balance and thermal management strategy in PEFCs.
7.2 Method of Approach

SGL 24 series (SIGRACET® gas diffusion layers) carbon paper DMs with varying degree of mixed wettability and SGL 10 series (SGL 10BB) carbon paper were utilized in the experiments. The same types of commercial DMs have been selected in this study to eliminate any possible uncertainties associated with the fabrication processes of these materials. These naturally hydrophilic DMs are typically tailored by addition of hydrophobic material polytetraflouroethylene (PTFE), known as Teflon®, and the base macro-porous substrate is coated with a micro-porous layer (MPL) for improved water transport. The material properties of tested DM samples supplied by manufacturer are provided in Table 7-1. The degree of wettability of these selected DM samples varies from 0 to 20% PTFE of total wt., which is in a typical range utilized in fuel cell applications.

The method of standard porosimetry (MSP) technique developed by POROTECH Inc. was employed to measure the desired transport parameters such as capillary pressure, saturation, hydrophobic and hydrophilic porosity distribution [27]. The present experiments were performed at different temperatures, i.e., 20, 50 and 80 °C. The DM samples were placed in contact between two standard specimens with known capillary transport characteristics for a time sufficient to achieve capillary and thermal equilibrium. At each equilibrium, the corresponding capillary pressure and saturation values were measured. Different liquids (de-ionized water and octane) were utilized as working fluids to evaluate the mixed wettability characteristics of DMs samples over a set of different temperatures.
7.3 Results and Discussions

7.3.1 Effects of Temperature on Mixed Wettability Characteristics of a DM

The bi-modal pore distribution (hydrophilic and hydrophobic) and the wettability characteristics of interfacial surface area are strongly correlated with the temperature. The activity of the PTFE agent bonded on the solid carbon fibers determines the degree of wettability, which strongly depends on the fiber temperature [20,21]. Therefore, probing the wettability characteristics of the thin-film DM at different temperatures is of utmost importance.

The hydrophilic/hydrophobic pore distribution (dual pore network) was measured by means of MSP technique at 20, 50 and 80 °C. Figure 7-1 shows the hydrophilic pore distribution of SGL 24BC (5% PTFE) and SGL 24DC (20% PTFE) at different temperatures. The measured total (hydrophilic/hydrophobic) and hydrophilic porosity of the tested DM samples at different temperatures are also provided in Table 7-2. For a given DM, the hydrophilic pore distribution appears to follow a similar qualitative trend at each temperature. As shown in Fig. 7-1 and Table 7-2, the tested DM samples exhibit an increase in hydrophilic porosity in response to the increase in temperature.

To investigate the degree of change in hydrophilic pore distribution, a further comparison was performed for the tested DM samples. Figure 7-2 shows the hydrophilic pore distribution for SGL 24 series carbon papers at 20 °C and 80 °C. At room temperature, a significant deviation between the hydrophilic pore distributions of the DM samples is observed. This can be attributed to the different levels of hydrophobic agent loadings of the tested DM samples. However, as the temperature is further increased to
80 °C, the hydrophilic pore distributions of the tested DM samples appear to overlap, following a similar quantitative trend regardless of PTFE loading. This observation reveals that increasing temperature contributes to a suppression of the PTFE effect through the reduction of the surface tension, leading to an increase in wettability (hydrophilic) characteristics of the pore network.

The apparent increase in hydrophilic pore volume with increasing temperature can be linked to the change in surface interaction of the fluid and solid pore matrix of the DM. Physically, the interfacial tension [1], which is a strong function of temperature, induces wettability and capillarity, causing the fluid phases to be attracted or repelled by the solid matrix surface of the pores. Adhesion energy is defined as the molecular attraction exerted between two unlike materials in contact [1]. The hydrophobic agent PTFE bonded to the fiber matrix promotes the imbalance of the molecular forces at the interface and determines the magnitude of the instability, which is, in fact, a measure of the surface tension [1]. The surface tension and adhesion energy between the solid fiber and water are strongly linked to the activity of the PTFE particles coated on the carbon fiber [15,18,20]. Any increase in temperature is followed by the reduction of the molecular imbalance (PTFE activity) at the interface that gives rises to the adhesion energy between the water molecules and fiber surface. The increase in adhesion energy (attractive forces) reduces the surface tension, thereby promoting the wetting of the fiber surface by water. As a result, water tends to spread over the fiber surface to achieve the most stable condition (equilibrium state), which in turn, leads to an increase in the wetted pore space (hydrophilic pore space) of the DM pore network.
In terms of water management, the increase in temperature reduces the resistance of the DM to the formation of a continuous film or connected conduits of water inside the pores, yielding a redistribution of water and reactant gas in the pores of DM. The decrease in hydrophobicity promotes the accumulation of water into more pores, thereby restricting the reactant gas transport into the catalyst layer, undesirable for efficient fuel cell operation. Upon cooling the fuel cell at shut-down, however, this residual water may be ejected into the flow channels, blocking the available transport paths for reactant gases during start-up. On the other hand, some studies [15,17,18] suggest that even though any possible temperature change within the porous media can alter the wettability characteristics of the porous media, the change in operating temperature may result in uneven temperature distribution within the DM. The temperature variation within the pores of the DM can induce a favorable internal pressure gradient, promoting the displacement of the gas phase.

One other distinctive observation that can be drawn from Fig. 7-2, is that the change in hydrophilic pore distribution with increasing temperature is more pronounced in the macro-pores (radius range from 1 to 100 µm). Current results reveal that the relatively larger pores (macro-pores, pore radius>1 µm) are subjected to higher change of wettability characteristics with temperature than that of the minute pores in micro-porous layer (pore radius from 0.01 to 0.1 µm). The smaller effect of temperature on the micro-pores may be attributed to the rigid and compact structure of the micro-porous layer (MPL). As explained above, the increase in temperature causes a decrease in interfacial tensions, promoting the wetting of the fiber surface by water. In these experiments, water and octane were used as working fluids to determine the hydrophilic and the total
(hydrophilic and hydrophobic) pore network of the DM, respectively. However, during these experiments, the compactness and rigidity of MPL may have restricted the imbibition of water through the available minutes pores of MPL, therefore impeding the observation of the apparent effects of temperature on the pore characteristics of the MPL. As a result, the loss of hydrophobicity is measured to be relatively smaller compared to the ordinary macro DM substrate due to the restricted access of the water to the available pores of the MPL.

In actual fuel cell operation, the scenario is not much different. The compact nature of the MPL provides an additional resistance, restricting the diffusion of generated water from catalyst layer through the macro-porous substrate. In addition, our previous study [2] along with the Gostick et al. [9] revealed that the micro-porous layer is found to contain considerably fewer hydrophilic pores and is almost exclusively hydrophobic in nature, further hampering the imbibition of liquid into its minute pores. Therefore, even though the temperature has a considerable impact on the surface tension, the higher liquid water resistance of the MPL limits the accessible surface area, suppressing the effect of temperature on the interaction of the water molecules and carbon fiber within the pores of the MPL.

**Dual Pore Network Surface Area**

The mixed wettability of a porous fuel cell DM is directly linked to the respective proportions of hydrophilic and hydrophobic surface area, which has a large degree of influence on the liquid water transport mechanism in the DM [15,16]. The nature of the
pore surface governs the wetting behavior of the fluids, therefore controlling the transport process within the pores of the DM.

The specific hydrophilic surface area of each DM sample was measured at different temperatures (20, 50 and 80 °C) and is shown in Table 7-2. At room temperature, among SGL 24 series, SGL 24BC (5% PTFE) is found to have the higher hydrophilic specific surface area (54.1 m²/g), whereas SGL 24DC (20% PTFE) has the smallest hydrophilic surface area (45.7 m²/g), demonstrating that rendering the DM with more hydrophobic agent leads to more hydrophobic surface area. However, as the temperature is further increased to 80 °C, the hydrophilic surface area is found to increase for all DM samples, as shown in Table 7-2. This can be attributed to the possible loss of hydrophobicity with increasing temperature, confirming our previous discussion in [2]. Furthermore, the tabulated results also indicate that the significance of the degree of PTFE loading seems to be diminished with increasing temperature, confirming the results shown in Fig. 7-2. The measured hydrophilic surface area of SGL 24BC (5% PTFE) and SGL 24DC (20% PTFE) at 80 °C is found to be 58 m²/g and 55 m²/g, respectively, yielding a similar hydrophilic surface area regardless of the amount of PTFE loading.

7.3.2 Interconnected Hydrophilic Pore Network and Capillary Pressure Curves

Water Retention Characteristics of the DM

The mass transport rate through the pores of the DM is closely related to the available connected hydrophilic pore space governing the water retention characteristics of a fuel cell DM. Basically, the water retention is a measure of available connected pore
space of the fuel cell DM that can store water. From a fuel cell perspective, the stored water or residual water in the DM presents technical challenges especially in terms of adapting automotive-based fuel cell systems to the next generation vehicles. Many efforts are now focused on minimizing the residual water inside a stack to eliminate the possible degradation during start-up in frozen conditions and to reduce the parasitic purge energy for activating the rapid start-up [5]. As such, the water retention characteristic of the DM is a key parameter for proper DM material selection.

To evaluate the degree of change in the capillary transport characteristics of the connected hydrophilic pore network, spontaneous capillary imbibition tests were performed at different temperatures (20, 50 and 80 °C). The connected hydrophilic pore volume and the capillary pressure-water saturation of the hydrophilic pore network were measured at specified temperatures for all DM samples. Figure 7-3 shows the measured capillary pressure versus water saturation of the SGL 24CC (10% PTFE) carbon paper. Increasing the temperature appears to have an impact on the water retention or self-wetting characteristics of the DM. For a given wetting phase saturation, the capillary pressure tends to increase with temperature, as seen in Fig. 7-3.

The present results reveal that the capillary pressure in a hydrophilic pore increases with temperature, facilitating the transport of phases from the connected hydrophilic pore space. The reason for such a change in capillary pressure can be explained through the concept of the immiscible fluid transport at the microscopic pore level. In any pore, the wetting phase is preferentially “adsorbed” (adherence of molecules to the surface of solids) by the solid fiber matrix, while non-wetting phase is surrounded by the wetting phase, as illustrated in Fig. 7-4. Spontaneous liquid water imbibition is a
natural process and requires the existence of interconnected hydrophilic pores. Therefore *only the connected hydrophilic pore space* of the tested DMs is of interest in the analysis of these imbibition experiments. In a *hydrophilic pore*, the liquid water (wetting phase) is highly adsorbed by the hydrophilic pore surface, while air (non-wetting phase) is substantially compressed by the surrounding water. The degree of compression is directly controlled by the interfacial forces at the interface of the immiscible fluids. The imbalance of the interfacial forces gives rise to the capillary pressure, which is defined as the pressure difference of any two-phases at the line of contact.

An increase in temperature facilitates the adsorption of water by the fibers, increasing the volume of imbibed water in the hydrophilic pore due to the increased adhesion energy. The increase in amount of water (wetting phase) causes an increase in the exerted pressure on the non-wetting phase. This, in turn, distorts the imbalance at the interface of wetting and non-wetting phase, increasing the capillary pressure. Eventually, once the threshold pressure is reached, the non-wetting phase (gas) is displaced from the *hydrophilic pore*.

*Capillary Pressure- Saturation Curves of Total Pore Network*

The micro-scale parameters measured at room temperature may not be readily applicable to modeling of the actual drainage process of the DM in typical fuel cell environments, where operating temperature is significantly different than the room temperature. To the best of our knowledge, no systematic studies related to the temperature dependence of the drainage process for a fuel cell DM have been published.
In order to assess the significance of the temperature on the drainage of air-water capillary pressure-saturation curves, highly wetting liquid octane was utilized as a working liquid to obtain the total (hydrophilic and hydrophobic) pore network capillary pressures as a function of non-wetting phase saturation. The experiments were performed at 20 °C and 50 °C. (The higher evaporation rate of octane at 80 °C was prohibitive). Using the octane-air capillary pressure-saturation data, the equivalent water–air capillary pressure was calculated by means of Young–Laplace equation given in Eq. 7.1.

\[ P_c = P_{mw} - P_w = \frac{2 \cdot \gamma \cdot \cos \theta}{r} \]  

[7.1]

Figure 7-5 depicts the non-wetting phase saturation versus the capillary pressure of the total (hydrophilic and hydrophobic) pore network for the DM samples; SGL 24BC, SGL 24CC and SGL 24DC. For a given non-wetting phase saturation, the capillary pressure decreases as the temperature increases from 20 °C to 50 °C for SGL 24BC and SGL 24CC carbon papers. SGL 24DC carbon paper (coated with 20% PTFE) seems to behave in the same manner up to a saturation of 0.4. However, at high saturation region \( s_{nw} > 0.4 \), the temperature effect on the capillary pressure curves for SGL 24DC can not be clearly distinguished, since the capillary pressure measurements at both 20°C and 50°C yield similar quantitative values. This observation suggests that for a DM coated with higher PTFE loadings, the effect of temperature on the capillary pressure seems to be more pronounced at low saturations \( s_{nw} < 0.4 \) and low temperatures (~20°C), potentially because of the higher dominance of wettability characteristics on the capillarity of the pores.
Physically, the temperature sensitivity of the capillary transport in fuel cell DM can not be explained through the concept of the surface tension alone. The pertinent studies in soil science [15,16,28] reveal that the interfacial tension and wettability characteristics are strongly coupled. Any increase in temperature influences the molecular interaction between the flowing fluids and solid pore matrix, which is followed by a subsequent increase in adhesion energy. Consequently, the increase in adhesive forces alters the intrinsic contact angle of the (flowing) fluid with the solid surface (The contact angle is considered as a measure of the surface wettability [1]). The pertinent literature in soil science approaches this issue in different fashions. In some studies [15], the possible changes in the capillary transport with temperature are attributed to the adsorption and desorption of the polar components between the liquid phase and solid pore structure. Other research claims that the corresponding change in viscosity of the flowing fluids, the increase of impurity concentrations and the alteration of sand compaction are the potential factors affecting the capillary transport mechanism [15].

Even though a number of possible hypotheses are available to explain the temperature effect for soil beds, the Young-Laplace capillary theory, as shown in Eq. 7.1, offers an indispensable means for providing a physical platform for the interpretation of these results in terms of fuel cell DM. In accordance with Eq. 7.1, the surface tension and contact angle parameters mainly govern the corresponding macroscopic change in capillary pressure as a response of altering the temperature, assuming there is no change in pore size due to the temperature difference. Consider a water droplet (non-wetting phase) sitting on a PTFE coated carbon fiber and surrounded by air (wetting phase), as shown in Fig. 7-6. The intermolecular forces acting at the interface of the droplet and
pore surface creates a state of tension in the surface of the droplet, known as surface tension [15,28]. The surface tension is prone to be suppressed with increasing temperature due to the enhanced stored kinetic energy within the molecules. As the temperature increases, the adhesive (attractive) forces between the water and fiber molecules increase at the interface. In other words, the energy required for the adhesion of the water molecules on the fiber surface decreases. Macroscopically, the droplet tends to spread over the surface, moving towards a more stable condition due to the increased adhesion force. As the water droplet (non-wetting phase) covers more surface area (the contact area), the apparent contact angle between the fiber surface and droplet decreases, as shown in Fig. 7-6. Note that the capillary pressure stems from the imbalance in pressure across the interface between two immiscible fluids. Therefore as the droplet approaches an equilibrium state (most stable state), the imbalance of molecular forces at the interface diminishes, yielding a lower capillary pressure.

In summary, the surface interaction between the phases and pore surface is greatly influenced by the temperature. Any increase in temperature is accompanied by an increase in the adhesion forces that reduce the surface tension and the intrinsic contact angle. This, in turn, decreases the capillary pressure of the DM as formulated in Eq. 7.1.

7.3.3 Modified Leverett Equation: Unified Approach

The capillary pressure-saturation relation of the fuel cell DM is of the utmost importance, especially for fuel cell modelers, to accurately predict the liquid saturation profiles within the operating PEFC. The inherent limitations and the ineffectiveness of
the traditional Leverett approach (given in Eq. 7.2) \[29\] for the highly heterogeneous thin-film fuel cell media have been addressed in detail in previous Chapters 4, 5 and 6. One of the main motivations of this specific study is to provide the most appropriate form of a modified Leverett approach (based on actual experimental data) for accurate prediction of the capillary pressure of the tested fuel cell DMs as a function of hydrophobic content and operating conditions, including compression and temperature.

The first two parts of this comprehensive study \[2,3\] were devoted to determining a proper empirical relationship that accurately correlates the capillary pressure as a function of liquid saturation, hydrophobic additive content and compression pressure of wide range of tested fuel cell DMs \[2\]. The final step includes the integration of experimentally observed temperature effects into the previous empirical correlation to deduce a unified description of capillary pressure incorporating the relevant material and operational effects. Previously, the modified form of the capillary pressure equation was introduced as \[3\]:

\[
P_c = \gamma \cos \theta \left( \frac{\varepsilon_c}{k} \right)^{1/2} J(s_{nw})
\]

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

\[7.2\]

\[
P_c = \gamma \cdot 2^{0.4C} \sqrt{\varepsilon_c} \cdot K(s_{nw})
\]

\[7.3\]

where $C$, $\varepsilon_c$, $k$, and $\gamma$ represent the compression pressure, compressed porosity, absolute permeability and surface tension, respectively. $K(s_{nw})$ represents the modified Leverett
function [2] correlating the capillary pressure as a function of liquid saturation and PTFE content of the DM. The reduction in effective pore size due to the compression of the DM was incorporated by the effective porosity parameter that was determined through the specific strain-stress relations of the DM described [3]:

\[ \varepsilon_c = \left( \frac{0.9}{1 + s_{TR}} + 0.1 \right) \cdot \varepsilon_o \]  

[7.4]

where \( \varepsilon_o \) and \( s_{TR} \) represent the uncompressed porosity and the compressive strain of the DM. The compressive strain, \( s_{TR} \), is a characteristic property of a specified DM and was experimentally determined as [3]:

\[
\begin{align*}
    s_{TR} &= -0.0083 \cdot C^2 + 0.0911 \cdot C & \text{SGL 24 series carbon papers} \\
    s_{TR} &= -0.0046 \cdot C^2 + 0.0843 \cdot C & \text{SGL 10BB carbon paper}
\end{align*}
\]  

[7.5]

Recognizing the fact that the surface tension of water is highly sensitive to the temperature, an appropriate approach, therefore, would be to impose the temperature effect into the surface tension term. The surface tension of water as a function of temperature is given by:

\[ \gamma = -1.78 \times 10^{-4} (T) + 0.1247 \]  

[7.6]

where temperature, \( T \) is in Kelvin. The benchmark capillary pressure-saturation measurements of SGL 24 carbon paper series were categorized according to the operating temperature and PTFE loadings of DM (ranging from 0 to 20% of wt.). The temperature sensitivity of the SGL 24 series carbon paper DM characteristics was taken into account by introducing a tunable parameter \( (293/T)^6 \), that is defined based on the wide range of
experimental data of the tested DM samples. Instead of the traditional standard Leverett $J$-function ($J(s_{nw})$), the modified Leverett function ($K(s_{nw})$) presented in the first phase [2] of this study was employed into the unified approach. Therefore, the general functional form of the capillary pressure in terms of PTFE content, temperature, compression pressure, effective porosity and liquid saturation becomes:

$$P_C = (293/T)^6 \cdot \gamma(T) \cdot 2^{0.4c} \left(\frac{c}{k}\right) \cdot K(s_{nw})$$

where $C$, $c_c$, $k$, and $\gamma$ represent the compression pressure, compressed porosity, absolute permeability and surface tension. The parameters in $K(s_{nw})$ namely; ($%\text{wt.}$) and $s_{nw}$ are PTFE weight percentage and non-wetting liquid saturation, respectively. The unique modified Leverett function ($K(s_{nw})$) is capable of correlating the capillary pressure as a function of liquid saturation and hydrophobic additive loading of the tested DM samples [2]. The PTFE parameter, ($%\text{wt.}$), embedded into the modified Leverett function ($K(s_{nw})$) adjusts the degree of hydrophobicity of the tested DMs. It also implicitly accounts for variations in internal contact angle, thus eliminating the need for the selection of a single (and unrealistic) surface contact angle.
Substituting all these sub-functions into the empirical framework, the representative empirical correlation describing the capillary pressure of *SGL 24 series* (SGL 24BC, CC and DC) carbon papers as a function of the relevant parameters is found as:

\[
P_C = (293/T)^6 \cdot \gamma(T) \cdot 2^{0.4C} \cdot \left[\frac{0.9}{1 + (-0.064 \cdot C^2 + 0.1661 \cdot C)} + 0.1\right] \cdot \frac{\varepsilon_o}{k} \cdot K(s_{nw}) \quad [7.8]
\]

Similarly, substituting the compression stress-strain relationship (given in Eq. 7.5) of SGL 10BB DM, the final form of the modified capillary pressure function for *SGL 10BB* carbon paper becomes:

\[
P_C = (293/T)^6 \cdot \gamma(T) \cdot 2^{0.4C} \cdot \left[\frac{0.9}{1 + (-0.0046 \cdot C^2 + 0.0843 \cdot C)} + 0.1\right] \cdot \frac{\varepsilon_o}{k} \cdot K(s_{nw}) \quad [7.9]
\]

**Validation and Comparison**

Figure 7-7 presents the capillary pressure predictions of modified Leverett approach (Eq. 7.8) and traditional Leverett approach along with the measured capillary pressure for SGL 24BC (5% PTFE) and SGL 24DC (5% PTFE) at 50 °C. As shown in Fig. 7-7, the standard Leverett approach is incapable of tracking the measured capillary pressure over the entire saturation domain, with the most significant deviation at high saturations, \(s_{nw} > 0.5\) (under-predicts more than 100% of the measured values). On the contrary, the modified approach more accurately predicts the measured capillary pressures (within the uncertainty of ± 14 % of the measured data) and captures the effect
of temperature while successfully tracking the complex shape of the measured curves over the entire saturation domain.

The present results emphasize that the Leverett approach in its original form (Eq. 7.2) can not appropriately describe the transport characteristics of a fuel cell DM. The significant deviation likely originates from the structural differences between the fuel cell DM and soil beds. The traditional Leverett approach was derived from the capillary pressure measurements of the various isotropic soil beds with uniform wettability. However, the fuel cell DM exhibits anisotropic internal architecture with mixed wettability. The existence of bi-modal pore size distribution in fuel cell DM bifurcate the transport paths, complicating the transport phenomena. On the other hand, the presented modified approach is generated from direct experimental measurements of fuel cell DMs. Thus the connection between the capillary pressure and relevant transport parameters is precisely linked to the operating conditions through the extensive experimental database. The generalized form of the modified approach, as given in Eq. 7.7, provides the flexibility to predict the capillary pressure by scaling the operating conditions and the governing DM parameters.

To further assess the prediction accuracy of the modified Leverett approach, the measured and predicted capillary pressure (using Eq. 7.9) of SGL 10BB carbon paper DM at 50 °C under 1.4 MPa compression were compared and are shown in Fig. 7-8. The capillary pressure predicted via standard Leverett approach is also presented in Fig. 7-8. Within the saturation range of 0 to 0.5 (Fig. 7-8-a), the modified approach successfully predicts the measured capillary pressure at the given conditions with an uncertainty of +7% of the measured value. On the other hand, the standard Leverett approach yields
much greater uncertainty of up to $+30\%$ of the measured value within this saturation range ($0<s_{nw}<0.5$). When the capillary pressure predictions were compared over the entire saturation domain ($0<s_{nw}<1$), the modified Leverett approach is much better able to track the complex shape of the measured capillary pressure, whereas the gap between the measured values and the prediction of the standard Leverett approach vastly increases, especially at high saturations ($s_{nw}>0.5$). These results also support that besides the mixed wettability characteristics of the DM, the standard Leverett approach in its original form is also insufficient to incorporate the coupled effect of temperature and compression, thereby failing to capture the corresponding changes in the capillary pressure of SGL 10BB (5% PTFE of wt.) carbon paper.

In order to validate the effects of temperature with the experimental observations, the capillary pressure of a DM coated with 5% PTFE over a wide range of temperatures was predicted by the present approach given for SGL 24 series (Eq. 7.8). Figure 7-9 depicts the predicted capillary pressures versus non-wetting saturation at different temperatures (20, 40, 60 and 80 °C). For a given saturation, the capillary pressure exhibits a decrease as a response to the increase in temperature due to the reduced surface tension. This trend is in good agreement with the previously discussed observations in Fig. 7-5, thereby supporting the effectiveness of the modified approach.
7.3.4 Features and Limitations

The final form of the capillary pressure equation given in Eq. 7.7 is comprised of three main terms, as shown in Eq. 7.10. The first term \((293/T)^6 \cdot \gamma (T)\) accounts for the effect of temperature. As described, any change in temperature influences the molecular interactions at the solid-liquid interface, therefore affecting the surface tension and wettability characteristics of the fuel cell DM. The corresponding change in surface tension is included in the analytical framework through both the surface tension term and the tunable parameter, \((293/T)^6\), deduced from broad set of experimental data. The second term, \(2^{0.4C} \cdot (\varepsilon_c/k)^{0.5}\), embodies the effect of compression on the morphological characteristics of the fuel cell DM. Any compression exerted on the DM causes substantial deformation of the fibers, leading to a reduction in the effective porosity [3]. The corresponding change in effective porosity (given in Eq. 7.4) is taken into account by an empirical correlation relating the compressive strain and compression pressure. It is worthwhile to emphasize that the compressive strain-stress relation is a characteristic property for each DM, and depends on the fabrication process and fiber types. Therefore it needs to be experimentally determined for each DM type.

\[
P_c = (293/T)^6 \cdot \gamma (T) \cdot 2^{0.4C} \left[ k \right]^{0.5} K(s_{nw})
\]

The final term includes the modified Leverett function \(K(s_{nw})\), which was derived from a wide range of capillary pressure measurements of various DM samples with different PTFE contents (0 to 20% of wt.). This function basically serves to account for
the mixed wettability characteristics of the DM, which is not properly treated in original Leverett $J$-function. The connection between the liquid saturation and the mixed wettability characteristics of the DM is linked to the capillary pressure by compilation of the extensive capillary pressure-saturation measurements. Adjusting the PTFE variable ($\%$ wt.) in the modified function, $K(s_{nw})$, enables successful determination of the capillary pressure as a function of hydrophobic additive loading of the DM. The variations in internal contact angle, a consequence of the mixed wettability characteristics of the DM, are implicitly embedded into the modified Leverett function, which in turn, eliminates the selection of a representative contact angle as an input. Overall, the inclusion of all these unique features into the modified approach enables more accurate modeling of capillary pressure over a wide range of PTFE loadings at different fuel cell operational environments.

In terms of limitations, it is important to emphasize that the final functional form of the empirical equation given in Eq. 7.7 is deduced from the capillary pressure-saturation measurements of SGL 10BB carbon paper (5% PTFE), E-TEK Elat 1200W carbon cloth (≥20% PTFE of wt.) and SGL 24 series carbon paper including: SGL 24BC (5% PTFE of wt.), SGL 24CC (10% PTFE of wt.) and SGL 24DC (20% PTFE of wt.). The experiments were performed at three different temperatures (20, 50 and 80 °C) under three compressions (0, 0.6 and 1.4 MPa). Therefore the presented unified approach is applicable to the tested DM samples within the temperature range from 20 °C to 80 °C for the compression range from 0 to 1.4 MPa. Among the tested DM samples, the unified form of the capillary pressure equation given in Eq. 7.7 can be modified to any of the tested DM by simply substituting the characteristics compressive strain ($s_{TR}$)-compression
pressure relation at a given temperature under any compression (within the specified ranges). The detailed description of the experiments, the corresponding results and the derivation steps of the unified approach (given in Eq. 7.7) are provided in previous Chapters 5 and 6.

Overall, the presented modified Leverett approach provides a reliable tool for the description of the capillary pressure in terms of accessible parameters, therefore representing an improvement in precision of PEFC DM multi-phase transport predictions.

7.3.5 Further Discussion: Temperature and PTFE Sensitivity

To further elucidate the significance of the temperature on the retention characteristics of the fuel cell DM, the changes in capillary pressure at a given saturation values were probed. Figure 7-10 depicts the calculated capillary pressure predicted by Eq. 7.8 of a DM tailored with 5% PTFE versus operating temperature at different saturation values (0.2, 0.3, 0.4 and 0.5), recalling that a PEFC typically operates in a saturation range of 0 to 0.5 [5,6]. At a given saturation, the capillary pressure is decreased with temperature, as expected. However, one distinctive observation can be drawn from this figure is that the decrease in capillary pressure with temperature is more pronounced at high saturation (\(s_{nw}=0.5\)), whereas at low saturation (\(s_{nw}=0.1\)), the temperature seems to have a relatively low impact. Physically, in a given pore, the capillary pressure is directly linked to the molecular imbalance at the interface of non-wetting and wetting phase. At high saturation, the imbalance between the interfacial forces is prone to be
more suppressed with increasing temperature, yielding a larger decrease in capillary pressure.

Finally, the governing parameters, namely operating temperature and PTFE content of the DM, were investigated jointly to assess the relative significance of these parameters on the capillary transport. The capillary pressure of SGL 24BC (5% PTFE) and SGL 24DC (20% PTFE) was calculated by means of modified approach (Eq. 7.8) for constant saturation values at different temperatures. Figure 7-11 shows the variation in predicted capillary pressure values of the DMs as a function of temperature. SGL 24 DC carbon paper appears to exhibit a larger decrease in capillary pressure (from 38 to 10 kPa at $s=0.4$) as the temperature is increased from 20 to 80 °C. On the other hand, for SGL 24BC (5% PTFE content of wt.%), the capillary pressure seems to be relatively less affected by the temperature. The capillary pressure is found to be increased from 2 kPa to 14 kPa as the temperature is increased from 20 to 80 °C at $s=0.4$. In other words, the effect of temperature on the capillary pressure within the pores of the DM appears to be amplified with rendering the DM more hydrophobic. This can be attributed to the fact that the reduction of surface tension with increasing temperature is more severe at the DM tailored with high PTFE loading.
7.4 Summary

The final part of this present study is aimed at explicitly investigating the effects of temperature on the multi-phase transport characteristics of the fuel cell DM. The benchmark data were generated from a wide set of capillary pressure-saturation measurements performed for various types of fuel cell DM at different temperatures, namely 20, 50 and 80 °C. Temperature is found to be an important factor affecting the transport characteristics of the fuel cell DM. The capillary pressure is observed to decrease with increasing temperature due to the reduced surface tension, therefore impeding the non-wetting phase transport from the pores of the DM. Any increase in temperature is also accompanied by the loss of hydrophobicity of the DM, indicating the possible formation of liquid film or connected conduits within the pores of the DM.

Experimentally observed temperature effects were integrated into the empirical correlation derived from the first phase of this study [1,2] to deduce a unified description of capillary pressure appropriate for the tested fuel cell DM samples as a function of the relevant material properties and operational environments. The final form of the modified Leverett approach (given in Eq. 7.7) well-predicts the capillary pressure as a function of liquid saturation, hydrophobicity, compression of the DM and operating temperature (within the uncertainty of ± 14% of the measured data).

Note that the presented unified approach is applicable to the tested DM samples (SGL 24 series, SGL 10BB and ETEK-Elat 1200W cloth) within the temperature range from 20 °C to 80 °C for the compression range from 0 to 1.4 MPa. Among the tested DM samples, the unified form of the capillary pressure equation (given in Eq. 7.7) can be
modified to any of the tested DM by simply implementing the characteristics compressive strain-compression pressure relation and the transport properties (porosity, permeability) of the DM. The key feature of the presented modified approach is that the non-uniform wettability characteristics of the fuel cell DM and the effects of fuel cell operating conditions are successfully embedded into the polynomial fit to incorporate the necessary changes in the capillary transport characteristics of the DM over a wide range of PTFE loadings (from 0 to 20% PTFE of wt.) at different operating environments, including at various temperatures and under different compressions.

The presented modified Leverett approach will help to close the loop between the fuel cell modeling studies and missing transport relationships for thin-film porous media, therefore it represents an improved step towards achieving an accurate two-phase transport model in fuel cell modeling studies.
7.5 Bibliography


### Table 7-1: Material Properties of tested DM samples.

<table>
<thead>
<tr>
<th>Material</th>
<th>Type</th>
<th>Thickness (µm)</th>
<th>PTFE (% of wt.)</th>
<th>Porosity</th>
<th>Permeability (cm³/cm²·s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SGL 24BC</td>
<td>Paper w/MPL</td>
<td>235</td>
<td>5</td>
<td>0.76</td>
<td>0.45</td>
</tr>
<tr>
<td>SGL 24CC</td>
<td>Paper w/MPL</td>
<td>235</td>
<td>10</td>
<td>0.76</td>
<td>0.45</td>
</tr>
<tr>
<td>SGL 24DC</td>
<td>Paper w/MPL</td>
<td>235</td>
<td>20</td>
<td>0.76</td>
<td>0.45</td>
</tr>
<tr>
<td>SGL 10BB</td>
<td>Paper w/MPL</td>
<td>420</td>
<td>5</td>
<td>0.84</td>
<td>3.00</td>
</tr>
</tbody>
</table>

All values are adapted from manufacturer technical specification sheets.

### Table 7-2: Measured connected hydrophilic porosity and hydrophilic surface area of the tested DM samples by MSP technique at different temperatures.

<table>
<thead>
<tr>
<th>Material</th>
<th>Connected Hydrophilic Porosity</th>
<th>Hydrophilic Surface Area (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>20 °C</td>
<td>50 °C</td>
</tr>
<tr>
<td>SGL 24BC (5% PTFE)</td>
<td>0.27</td>
<td>0.29</td>
</tr>
<tr>
<td>SGL 24CC (10% PTFE)</td>
<td>0.21</td>
<td>0.24</td>
</tr>
<tr>
<td>SGL 24DC (20% PTFE)</td>
<td>0.21</td>
<td>0.23</td>
</tr>
<tr>
<td>SGL 10BB (5% PTFE)</td>
<td>0.41</td>
<td>0.43</td>
</tr>
</tbody>
</table>
Figure 7-1: Hydrophilic pore distribution at 20, 50 and 80 °C of a) SGL 24BC (5% PTFE), and b) SGL 24DC (20% PTFE) carbon paper.
Figure 7-2: Hydrophilic pore distribution of SGL 24BC (5% PTFE), SGL 24CC (10% PTFE) and SGL 24DC (20% PTFE); a) at 20 °C, and b) at 80 °C.
For a given saturation, the measured capillary pressure in the connected hydrophilic pore space increases with temperature.

Figure 7-3: Measured capillary pressure versus wetting phase saturation for the connected hydrophilic pore network of SGL 24CC (10% PTFE) carbon paper at 20, 50 and 80 °C.
Figure 7-4: Schematic of air surrounded by liquid water in a *hydrophilic* pore.
Measured capillary pressure decreases as the temperature increases.

For DM coated with higher PTFE loadings, the effect of temperature on capillary pressure is more pronounced at low saturations ($s_{nw} < 0.4$).

Figure 7-5: Total (hydrophobic and hydrophilic) pore network non-wetting saturation versus measured capillary pressure at 20 and 50 °C of a) SGL 24BC, b) SGL 24CC and c) SGL 24DC.
Figure 7-6: Droplet shape in a hydrophobic pore of the DM at different temperatures
Figure 7-7: Comparison of modified Leverett approach (Eq. 7.8), standard Leverett approach (Eq. 7.2) and experimental data for, a) SGL 24BC, and b) SGL 24DC at 50 °C.
Figure 7-8: Comparison of modified Leverett approach (Eq. 7.9), standard Leverett approach (Eq. 7.2) and experimental data for SGL 10BB at 50 °C under 1.4 MPa over a saturation range of a) $0 < s_{nw} < 0.5$, and b) $0 < s_{nw} < 0.1$. 
An increase in temperature leads to a decrease in capillary pressure due to the reduced surface tension.

Figure 7-9: Predicted capillary pressure (by the modified approach given in Eq. 7.8) versus non-wetting saturation for a DM with 5% PTFE.
The capillary pressure decreases as the DM is exposed to higher temperature.

Effect of temperature is more pronounced at high saturations.

Figure 7-10: Predicted capillary pressure (by modified approach given in Eq. 7.8) versus temperature at constant saturations for SGL 24BC coated with 5% PTFE.
The decrease in capillary pressure due to the temperature at a given saturation is more pronounced at DMs with higher PTFE loading.

Figure 7-11: The predicted capillary pressure (by modified approach given in Eq. 7.8) versus temperature of SGL 24 BC and SGL 24DC at constant saturations.
Chapter 8

CONCLUSIONS AND FUTURE WORK

8.1 Conclusions

Proper tailoring of the water transport in the flow channel and porous diffusion media (DM) of a polymer electrolyte fuel cell (PEFC) has the potential to significantly increase stack power density, durability and performance stability under normal and cold-start operations. However, this challenging issue is multifaceted because of the extremely anisotropic internal architecture of thin-film fuel cell DM, minute length scales involved, and complex bi-modal pore configuration with mixed wettability characteristics. To date, state-of-the-art models of multiphase flow in the porous DM of PEFCs rely on transport relationships borrowed from soil science, where vastly different length scales, surface to volume ratios, pore size and wettability distributions exist. The applicability of these traditional approaches to accurately model the multi-phase flow is not validated and has so far yielded dubious guidance for the design of the next generation fuel cell systems.

This Ph.D. study was motivated by the need to develop a fundamental understanding of the multi-phase transport in thin-film fuel cell porous DM. A combined experimental and analytical study of multi-phase mechanism on and through the thin-film porous fuel cell DM was performed and the droplet behavior in the flow channel and the capillary transport mechanism through the DM were thoroughly investigated. A short summary and conclusions derived from this study are given below.
8.1.1 Droplet Instability and Removal in the Reactant Flow Channel of a PEFC

In the first phase of the study, the liquid droplet behavior and instability in a simulated model H₂ PEFC flow channel was investigated. A new visualization approach with an enhanced simultaneous optical access of side and top views was employed to probe the droplet deformation in the reactant flow channel. The effects of air flow rate, droplet size, DM surface PTFE coverage and channel geometry on the droplet deformation were elucidated in depth. An analytical model based on a macroscopic force balance was developed and validated by using the experimental data. The theoretical model was then utilized to predict the conditions leading to droplet removal. An empirical correlation, for the first time, relating the surface tension as a function of DM surface PTFE coverage was deduced. The results revealed that operational conditions, droplet aspect ratio, channel geometry and surface hydrophobicity of DM directly affect the level of droplet deformation and therefore influence the droplet instability and the removal mechanism. The important conclusions can be summarized as:

1. The growth of a droplet in a cross stream direction rather than in a streamwise direction is found to be more favorable and desirable for achieving effective water removal in the flow channel.

2. The influence of PTFE content on the droplet removal is determined to be more important in the high air flow rate regime ($Re \geq 600$). However, under a low air flow condition, droplet instability (and removal) is relatively unaffected by the surface PTFE content of the DM due to the diminished effect of interfacial adhesion of the DM.
3. The flow channel having the lowest channel height is found to be the most effective configuration for droplet removal due to the increased drag force acting on the droplet surface.

This fundamental study provides useful guidance regarding the optimal selection of the DM surface PTFE content and PEFC operating conditions for effective water removal in the PEFC flow channels.

8.1.2 Capillary Transport through the Porous DM

The second part of this Ph.D. thesis was devoted to delineating the effects of hydrophobicity, compression and temperature on the capillary transport characteristics of the fuel cell DM. The capillary pressure-saturation relationship in thin-film DM was experimentally determined over a wide range of realistic operating parameters including: DM hydrophobicity, compression pressure and operating temperature. Effects of these parameters on the capillary transport and morphological characteristics of the DM were investigated in depth. The important conclusions can be summarized as:

Effects of Hydrophobicity and Mixed Wettability Characteristics

1. Rendering the DM more hydrophobic is found to increase the measured capillary pressure, therefore promoting the liquid water transport within the pores of the DM.

2. The micro-porous layer is found to contain considerably fewer hydrophilic pores, and therefore is almost exclusively hydrophobic in nature. However
DM macro-substrate exhibits mixed wettability characteristics, containing hydrophobic and hydrophilic pores.

3. Spontaneous imbibition experiments reveal that the water retention capacity ($s_{wec}$) of a fuel cell DM decreases with an increase in PTFE content of the DM.

**Effects of Compression and Capillary Transport Mechanism**

1. The results show that the compression of the DM within the range from 0 to 0.6 MPa leads to an increase in capillary pressure. Any increase in compression above 0.6 MPa is found to have minor impact on the measured capillary pressures.

2. The connected hydrophilic porosity is observed to decrease with an increase in compression, leading to a reduction in water retention capacity.

3. From a physical perspective, inhomogeneous compression in fuel cell assembly creates distinct zones that have different capillary characteristics. The liquid transport in high compressed zone (high capillary zone) is expected to be mostly governed by the condensation of saturated gas streams underneath the landings. On the other hand, in the less compressed zone, water transport is hypothesized to be associated with the hydrodynamic liquid flow, which in turns, leads to the formation of the tree-like structure.
Effects of Operating Temperature

1. The capillary pressure is observed to decrease with increasing temperature due to the reduced surface tension, therefore impeding the non-wetting phase transport from the pores of the DM.

2. Any increase in temperature is also accompanied by the loss of hydrophobicity of the DM, indicating the possible formation of liquid film or connected conduits within the pores of the DM.

3. An increase in temperature enhances the water retention capacity of the DM due to the loss of hydrophobicity.

8.1.3 Modified Leverett Approach

The basic tools used to model multi-phase flow in the fuel cell DM are borrowed from soil science. The Leverett approach, indeed, is viewed as an indispensable tool for many modelers and serves as a useful starting point to model the liquid transport in the porous diffusion media (DM), however the applicability of the traditional Leverett approach in its original form to the highly anisotropic thin-film fuel cell DM has not been conclusively established.

\[
P_c = \gamma \cos \theta \left( \frac{e}{k} \right)^{1/2} J(s_{nw})
\]

\[
J(s_{nw}) = \begin{cases} 
1.417 \cdot (1 - s_{nw}) - 2.120 \cdot (1 - s_{nw})^2 + 1.263 \cdot (1 - s_{nw})^3 & \text{if } \theta < 90^\circ \\
1.417 \cdot s_{nw} - 2.120 \cdot s_{nw}^2 + 1.263 \cdot s_{nw}^3 & \text{if } \theta > 90^\circ 
\end{cases}
\] [8.1]
The present results in this study shows that the standard Leverett approach in its original form (Eq. 8.1) is not sufficient to describe the capillary transport characteristics of a fuel cell DM. The standard Leverett approach is found to be incapable of tracking the measured capillary pressure over the entire saturation domain, exhibiting a large deviation from the experimental data, especially at high saturation, $s_{nw}>0.5$ (under-predicts more than 100% of the measured values). The significant deviation likely originates from the structural differences between the fuel cell DM and soil beds. The traditional Leverett approach was derived from the capillary pressure-saturation measurements of a range of isotropic soil beds having uniform wettability. However, the fuel cell DM exhibits anisotropic internal architecture having mixed wettability characteristics.

Based on this motivation, the benchmark data gathered from the experiments were compiled and utilized to deduce a validated empirical relation (modified Leverett approach) that can precisely describe the multi-phase transport characteristics of thin-film porous fuel cell DM as a function of relevant transport parameters and operating conditions. The modified Leverett approach (Eq. 8.2) has been shown to be capable of determining the measured capillary pressure of the tested DM samples as a function of liquid saturation, hydrophobic additive content, uncompressed porosity, compression pressure of the DM and operating temperature. The modified approach predicts within an average uncertainty of ± 14 % of the measured capillary pressure over the entire saturation domain, showing considerable improvement over the traditional Leverett approach.
The salient features of the modified Leverett approach is:

1. Modified approach embodies both the non-uniform wettability characteristics of the tested DMs samples.

2. Modified approach incorporates the necessary changes in the governing transport parameters of the DM over a wide range of operating environments, including the temperature range from 20 °C to 80 °C and the compression range from 0 to 1.4 MPa.

3. Modified approach can implicitly resolve the change in internal contact angle caused by the anisotropic nature of the hydrophobic coating, therefore eliminating any ambiguity regarding the selection of a representative surface (unrealistic) contact angle.

The intellectual merit of this new approach is that it will help to close the loop between the modeling studies and missing transport relationships for fuel cell porous DM, and therefore provide key insights that will enable intelligent selection of design
parameters and empower the micro-fluidic management for next-generation fuel cell systems.

8.2 Recommendations for Future Work

Establishing effective micro-fluidic management in a PEFC requires an accurate understanding of the multi-phase transport characteristics of all the relevant components. Therefore, several related phenomena still need to be understood in depth. As a continuation of the present study, the following recommendations outlined below can be considered as the vital extensions of this thesis work.

8.2.1 Multi-phase Transport Characterization of Catalyst Layer

The catalyst layer, being the power-producing component, is considered as the most important component in a PEFC. It is made of platinum on carbon support, Nafion® ionomer and Teflon. The Nafion® ionic phase provides the ionic conductivity or pathways for the protons to migrate to and from the membrane electrolyte, whereas Teflon creates the hydrophobic gas region for reactant gas transport. Most importantly, catalyst layer is the region where water is generated through an electrochemical reaction.

The water transport mechanism with the minute pores of the catalyst layer still remains unclear. Often as simplification, these porous solids are assumed to be homogenous materials, and transport phenomena therein is assumed to be described by models developed for homogenous materials. Furthermore, given the variations in pore
characteristics, it is expected that not only the chemical nature of the surface but also the spatial distribution of the wettability can significantly affect the water transport mechanisms in the catalyst layer. A wide variety of water transport patterns may depend on the geometry of the porous space, the contact angle and the rate at which the penetrating fluid flows through the pores of catalyst layer. Therefore, it is necessary to first precisely define the complex interaction between the water transport mechanism and the material properties of the catalyst layer.

The characteristics water transport functions need to be developed and the effects of operating conditions and material properties should be precisely integrated into these functions. Using this appropriate fundamental understanding, a novel catalyst layer with well-defined and controlled structure can be developed to alleviate the catalyst layer flooding effects required for achieving high performance in PEFC operations.

8.2.2 Water Management and Component Design of Fuel Cell Stack

Using the modified Leverett approach developed in this study along with the appropriate catalyst layer transport functions describe above, a more accurate mathematical model for describing the water management in PEFCs can be developed. As it is equipped with the accurate physical descriptions, this model will be able to precisely incorporate the interaction between the two-phase transport and cell performance. This model can be further utilized as an optimization tool for determining the optimum electrode configurations suitable for different PEFC operations. The liquid water distribution and reactant gas phase distribution can be precisely probed and linked
to the overall cell performance. Based on the cell performance, morphological and surface properties of the electrode can be well-characterized for the design of next generation fuel cell materials to achieve the best micro-fluidic management during the operation.

Once the necessary design criteria for components are determined, *in-situ* fuel cell performance tests can be performed to validate the model output. This integrated approach can also be extended from single cell to stack design. A comprehensive stack modeling framework using the appropriate transport physics will enable to scale the fundamentals from a single cell to large stacks, thus providing insightful information regarding the transient characteristics, species and temperature distribution, especially for automotive applications.
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