INDIVIDUAL AND COUPLED EFFECTS OF FLOW FIELD GEOMETRY, INTERFACE AND MATERIAL PROPERTIES ON LIQUID WATER STORAGE AND FLOODING IN A POLYMER ELECTROLYTE FUEL CELL

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Ahmet Turhan

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The dissertation of Ahmet Turhan was reviewed and approved* by the following:

Matthew M. Mench
Associate Professor of Mechanical Engineering
Dissertation Adviser
Chair of Committee

Jack S. Brenizer
J. ‘Lee’ Everett Professor of Mechanical and Nuclear Engineering

Fan-Bill Cheung
Professor of Mechanical and Nuclear Engineering

John M. Regan
Associate Professor of Environmental Engineering

Karen Thole
Professor of Mechanical Engineering
Head of the Department of Mechanical and Nuclear Engineering

*Signatures are on file in the Graduate School
ABSTRACT

The existence of excess liquid water in the catalyst layer, diffusion media and flow channels of a polymer electrolyte fuel cell (PEFC), termed as “flooding”, results in major performance and durability limitations. Flooding, and the stored liquid water content, has adverse performance effects on operations at normal operating conditions as well as during start-up at sub-zero temperatures. In this study, the liquid water distribution, storage and flooding mechanisms inside a PEFC were thoroughly investigated using neutron imaging. For the first time, the individual effects of flow field design, land|channel interface and flow channel surface properties on liquid accumulation and distribution were analyzed. The flooded and non-flooded conditions were determined and results were used to develop a novel liquid filling and transport mechanism that better reflects the actual observed operation characteristics.

In the first part of this work, the impact of flow field geometry on liquid storage and flooding was investigated through in-plane neutron imaging experiments performed on seven different flow field configurations with land|channel (L:C) ratios ranging from 1:3 to 2:1. The stored liquid amount in each configuration was analyzed and a preferred land/channel ratio is suggested in terms of obtaining minimal residual water content in the fuel cell. For the configurations having same L:C ratio, the number of land|channel interfaces was found to have determining impact on liquid storage and flooding. The cell performance corresponding to each liquid storage value was also obtained for all configurations. The results revealed that at identical performance between two different cells, it is possible to significantly reduce the accumulated liquid water overhead by only tailoring the flow field design. This advance is important in terms of reducing the
parasitic losses required to purge the liquid after shutdown, and eliminating degradation experienced under freeze/thaw conditions.

In the second part of this work, the impact of land\channel interface surface energy on through-plane liquid accumulation, distribution and transport was analyzed with the use of high-resolution neutron imaging. Neutron images were taken with polytetrafluoroethylene (PTFE) coated and uncoated land\channel interface (flow channel walls). Anode to cathode liquid distribution was analyzed for each case at low and high current conditions over twenty minutes of operation. The form and amount of liquid water inside the channels and diffusion media (DM) were compared for hydrophobically coated channels and hydrophilic channels, and a primary liquid transport-flooding mechanism is suggested for each case. The location and value of maximum water storage in DM at low and high current operation were analyzed and slopes of water mass versus distance curve were calculated to compare the significance of capillary liquid flow and phase-change-induced flow within the diffusion media. A significant effect of CL|MPL and MPL|DM interfaces on liquid transport and flooding is found through the analysis of micro-porous layer (MPL) water content and saturation profile along the CL|MPL and MPL|DM interface region.

In the final part of this study, the nature of flooding and dry-out was investigated. In-plane neutron imaging was used to determine flooded, non-flooded and dry-out conditions in a PEFC and results were analyzed to identify the liquid mass responsible for the performance loss under flooding or dry-out. Results clearly indicate that common assumptions for liquid filling used in most computational studies are inadequate to represent the actual case. Based on the results, a modified liquid pore filling mechanism is suggested that is more appropriate.
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CHAPTER 1

INTRODUCTION

1.1 Fuel Cell Technology

The fuel cell is an electrochemical device which converts the chemical energy of a fuel and oxidizer into electrical energy through electrochemical reactions. A fuel cell typically consists of an electrolyte layer in contact with a porous anode side and a cathode side. Unlike a battery that must be recharged or disposed of after its finite amount of fuel or oxidizer is consumed, a fuel cell will produce electricity when the reactants are continuously supplied. The first known operating fuel cell can be traced to the year of 1839, when scientist William Robert Grove discovered the reverse electrolysis process of water. He combined hydrogen and oxygen gas by using separate platinum electrodes in a dilute sulfuric acid electrolyte solution to produce an electrical current. However, due to the limited catalyst active area and high electrolyte resistance, the electrical current obtained from the fuel cell was too small to be applied in a practical usage. Hence the early interest in Grove’s invention began to diminish.

The research and development of fuel cell did not get much attention until the 1960’s when General Electric developed the first low temperature polymer electrolyte fuel cell (PEFC) for NASA’s Gemini space program. Although some progress has been made since the 1960’s, only since the 1990’s have fuel cells become of high interest for stationary and portable power supplies, including automotive applications. It was apparent that a more efficient, environmentally friendly, renewable and petroleum-free power source was needed, especially in the automotive market. Due to the direct
conversion of chemical energy into electrical energy, the operating efficiencies of PEFC
are not limited by Carnot cycle. Hence they can approach an overall system efficiency of
50-60% which is much higher than the internal combustion engine efficiency of 25-35%.
This is shown in Eq. 1.1 [1] and Eq. 1.2 [2]. The schematic view of the two efficiencies is
shown in Figure 1-1.

\[ \eta_{PEFC} = 1 - \frac{T \cdot \Delta S}{\Delta H} \]  \hspace{2cm} 1.1

\[ \eta_{Carnot} = 1 - \frac{T_L}{T_H} \]  \hspace{2cm} 1.2

Figure 1-1: Comparison of the maximum thermodynamic engine efficiency for internal combustion engine and PEFC as a function of temperature[1].
In addition to potential high efficiency, fuel cells are also advantageous in terms of their quiet and emission free operation (except for emissions derived from production of fuel). Since there are no moving parts, besides pumps or blowers, involved in the fuel cell system, their operation is very quiet compared to other engines. Also, when hydrogen is used as a fuel, the only products are power and generally potable water. Therefore, pollutants such as nitrous oxides and particulate matter are eliminated, while carbon dioxide and carbon monoxide are reduced nearly to zero when hydrogen fuel is used. Thus fuel cells are a so called zero-emission engine. Furthermore, when obtained from electrolysis or from biomass and waste, hydrogen is a petroleum-free, renewable energy source, which makes fuel cells very advantageous, compared to other power sources.

There are several types of fuel cells, each being unique and typically characterized by the electrolyte used. The most popular fuel cells are listed in Table 1-1. Among these, the PEFC has the widest range of application area including the automotive industry, portable applications such as laptop power units and stationary power generation systems. The basic operation of PEFC is described in the next section.
The components and basic operation of a simple PEFC is shown in Figure 1-2.

Hydrogen, or other fuel, is supplied to the anode side of the fuel cell while the oxidant, usually the oxygen gas taken from the air, is delivered at the cathode side. The electrochemical oxidation reaction at the anode side occurs by the hydrogen gas splitting into hydrogen ions $H^+$, and free electrons $e^-$. The produced electrons flow through an external circuit connected to a load and produce electrical power. The hydrogen ions pass from anode side to cathode side through a semi-permeable polymer membrane which is not conductive to electrons but has high ionic conductivity. At the cathode side, the
electrons, hydrogen ions and oxygen gas are combined and oxygen reduction reaction takes place forming the product water. In order to help reduce the activation energy for the electrochemical reactions, a catalyst layer containing nano-size (2-4 nm) platinum particles is generally implemented on both anode and cathode sides. Since the earliest cells were constructed by General Electric, the platinum loading in the electrodes has been reduced substantially from approximately 28 mg/cm$^2$ to its present figure of 0.2-0.5 mg/cm$^2$ [1]. The tremendous achievement has resulted in a significant reduction in the fuel cell cost and has allowed for interest and development of the PEFC over the past decade.

Figure 1-2: Components and basic operation of a PEM fuel cell. [www.Ballard.com]
In the center of the diagram, there is the ion conductive polymer electrolyte membrane which usually varies between 25-175 μm in thickness. The electrolyte most commonly used by PEFC’s today is a polyperfluorosulfonic acid membrane. DuPont produces the industry’s most widely used membrane called Nafion®, although other similar products exist including Gore Technologies Primea® series of membranes. Nafion® contains a polytetrafluoroethylene (PTFE or Teflon®) backbone with sulfonic acid groups attached to the perfluorinated-vinyl-polyether side chains. In the presence of water, these highly hydrophilic sulfonic acid groups will absorb water and ionize to enable H+ ion transfer through the membrane [3-12].

On each side of the membrane, the catalyst layers are implemented which are typically consists of platinum powder roughly 2-4nm in size and supported by larger (~40nm) carbon particles. The electrochemical reactions take place in these layers; therefore they are also referred as the reaction sites. The total thickness of the catalyst layer is on the order of 10-30 μm [1]. The combined structure of membrane and two catalyst layers are usually referred as the membrane electrode assembly (MEA) or three layer structures. Outside the MEA structure, there are microporous layer (MPL) and/or diffusion media (DM). The main purpose of DM is for the transport of reactant gases from the flow channels to the catalyst layer. In addition, with the carbon structure of the DM, it allows the necessary electron conduction from the catalyst layer to the external load. Another important feature of this component is to remove product liquid and gas-phase water from the catalyst layer into the flow channel.

The flow channels, or bi-polar plates, are made of an electrically conductive material such as graphite or metal. They provide electron conductivity between the
electrodes and also provide robustness and strength to the whole fuel cell structure. Figure 1-3 shows various flow channel designs, the two common ones being serpentine and parallel flow channel designs. The advantage of serpentine flow channel is higher channel velocity and therefore easier liquid water removal from the channels under low flow rates, whereas advantage of parallel flow channel is decreased pressure drop and less parasitic loss. Most fuel cells use a combination of both patterns to provide optimal performance.

Theoretical molar flow rate of the reactant gases required to produce the desired current is termed as “stoichiometric” flow rate and defined by Eq. 1.3 and Eq. 1.4. The stoichiometric flow rate is the minimum value that should be supplied to obtain the desired current. This flow rate is basically calculated from the oxidation and reduction reactions of hydrogen and oxygen gases. In practical applications, the reactant gases are supplied at a higher rate than these theoretical values, usually at a ratio of 1.5 to 3. The purpose of this is to sustain enough flow even at the exit of the fuel cell in order to
improve the diffusion rate of the reactants. Otherwise, most of the fuel/oxidizer can be consumed near the exit of the fuel cell and there will be a drastic loss in the performance due to the diffusion limitation. The ratio of the actual flow rate and the theoretical flow rate is known as the flow stoichiometry and given in Eq. 1.5 and Eq. 1.6.

\[
\text{Anode : } \quad j_{H_2} = \frac{iA}{2F} \quad \text{Eq. 1.3}
\]

\[
\text{Cathode : } \quad j_{O_2} = \frac{iA}{4F} \quad \text{Eq. 1.4}
\]

\[
\xi_{\text{anode}} = \frac{j_{H_2,\text{actual}}}{j_{H_2,\text{theoretical}}} \quad \text{Eq. 1.5}
\]

\[
\xi_{\text{cathode}} = \frac{j_{O_2,\text{actual}}}{j_{O_2,\text{theoretical}}} \quad \text{Eq. 1.6}
\]

In the above equations, \( j \) represents the molar flow rate of the reactants [mole/s], \( i \) represents the desired current density [Amps/cm\(^2\)], \( A \) is the superficial electrode active surface area [cm\(^2\)], \( F \) is Faraday’s Constant = 96485 [Coulombs/electron-eq] and numbers two (anode) and four (cathode) are the number of electrons transferred per mole of reactant produced or consumed in the electrochemical cell reactions, hydrogen oxidation and oxygen reduction respectively.

The performance characteristics of a PEFC are generally defined by using a polarization curve, which is a graphical representation of the cell voltage output versus the operating current of the cell. In general, the polarization curve is a non-linear relationship between the voltage and current due to several over-potentials occurring in the fuel cell operation. In Figure 1-4, a typical polarization curve for PEFC is shown. Basic regions are labeled on the figure as; (I) activation polarization, (II) ohmic
polarization, (III) concentration polarization, (IV) crossover potential losses, (V) deviation from maximum thermal voltage due to entropy generation [1]. Each region is dominated with the potential loss described by the region; however, it also contains other potential losses at a smaller magnitude.

Although the operating point in which the cell functions (the voltage and/or current density of the cell) is quite arbitrary and up to the discretion of the system designer and/or operator, the maximum experimental operating voltage for a single PEFC is approximately 1.0 V at zero current, while operation with any appreciable power density reduces voltage below this starting point. These low values cannot satisfy large power requirements and therefore multiple cells are connected in electrical series to increase the overall voltage of the system to form a fuel cell stack. The current can be increased with additional reactive surface area.

Figure 1-4: Typical polarization curve for a PEM fuel cell with activation, ohmic, concentration and cross-over potential losses [1].
1.3 Motivation and Objectives

The polymer electrolyte fuel cell is a very promising clean and efficient energy producing technology as described in previous sections. However, there are some critical issues needed to be solved prior to the commercialization of this technology. Some of these issues are related directly to the fuel cell performance such as high temperature membranes and cost efficient catalysts, whereas others are related to the durability and long term usage of the fuel cell such as freeze/thaw and degradation issues. The most basic unresolved challenge in fuel cells is the water management phenomena, which is both related to performance and durability of the system. In most computational studies that model the two-phase flow inside fuel cell components, certain correlations were assumed for critical parameters such as effective diffusivity and relative permeability. These correlations were obtained mostly from soil science and their validity for an actual fuel cell operation is not proven. Therefore, the certainty of these studies on representing the actual liquid filling and transport mechanisms are questionable without experimental evidence. The motivation of the present study is to obtain experimental evidence on the liquid water accumulation and distribution in a PEFC and to reveal the liquid transport and flooding mechanisms in actual fuel cell operation under different design conditions. The main objectives can be listed as;

- Understanding the impact of flow-field geometry on water management by analyzing the liquid water storage and distribution with different land:channel (L:C) ratio flow field designs.

- Investigating the possibilities of passively reducing the liquid overhead in the cell through flow field design, without affecting the performance.
Revealing the preferred L:C ratio design in terms of obtaining minimal residual water content in the fuel cell.

Understanding the impact of land\channel interface (flow channel wall) on water management by obtaining the liquid storage and distribution under different number and surface energy conditions of land\channel interfaces.

Determining the liquid transport and flooding mechanisms inside the fuel cell with hydrophilic and hydrophobic land\channel interface.

Understanding the emphasis of generic water transport mechanisms in the fuel cell on through-plane liquid distribution and storage.

Understanding the nature of flooding and dry-out phenomena by analyzing the differences in performance and liquid storage between flooded, non-flooded and dry-out conditions.

Investigating the actual liquid-filling mechanism in the diffusion media pores by identifying the liquid mass responsible for the performance loss under flooding or dry-out.

Finally, coupling all these individual effects together and suggesting possible methods to obtain an effective water management in polymer electrolyte fuel cells.
CHAPTER 2

LITERATURE REVIEW ON WATER MANAGEMENT AND NEUTRON IMAGING

2.1 Water Management Phenomena in PEFC

2.1.1 Water Formation in PEFC

The fuel cell can produce electrical power while generating no hazardous byproducts such as nitrogen oxides, sulfonic oxides and carbon monoxide. Due to this feature, the fuel cell powered vehicles are also called as the zero emission vehicles (ZEV). Even tough it is not hazardous, there is a by-product generated at the end of the chemical reaction that has a crucial role on the fuel cell operation. This product is water. The formation and effective balance of water inside the fuel cell is tremendously important in terms of operational performance.

The basic mechanism of water formation is governed by two reactions given in Eq. 2.1 and Eq. 2.2, occurring at the anode and cathode catalyst layers respectively.

\[ \text{H}_2 \rightarrow 2\text{e}^- + 2\text{H}^+ \quad \text{2.1} \]

\[ \text{O}_2 + 4\text{e}^- + 4\text{H}^+ \rightarrow 2\text{H}_2\text{O} \quad \text{2.2} \]

The oxidation of hydrogen at the anode catalyst layer yields protons and electrons. The electrons pass from anode side to the cathode side through the bi-polar plates and supply the necessary power for the external load. The transport of the protons on the other hand is a more complex process involving proton movement through the
chemical structure of the ionically conductive electrolyte membrane. The electrolyte membrane was first created and used by Grubb and Niedrach of General Electric in 1960 by adding sulfonic side chains to cross-linked polystyrene and forming an ionically conductive structure when hydrated [1]. After that DuPont created a polymer electrolyte membrane named Nafion®, by replacing the hydrogen atoms in polyethylene with fluorine forming polytetrafluoroethylene (PTFE) or Teflon®. The PTFE is then sulphonated, producing side chains of SO$_3^-$ and H$^+$ ions when hydrated [1]. These highly hydrophilic structures tend to maintain water inside the membrane when it is hydrated and promote proton mobility. With the effect of hydration, the attraction between SO$_3^-$ and H$^+$ ions is weakened allowing mobility to the protons generated at the anode catalyst layer as shown in Figure 2-1.

![Proton transfer mechanism in Nafion®](image)

Figure 2-1: Proton transfer mechanism in Nafion® [6].
The ionic conductivity of Nafion® and related perfluorinated sulfonic polymers is excellent when fully hydrated, but decreases tremendously with lowered membrane water content $\lambda$, defined as the number of moles of water molecules per sulfonic acid sites. Also, the conductivity of the membrane changes with the equilibrated solvent phase such that it has a water content value of $\lambda \sim 14$ when equilibrated with water vapor whereas water uptake reaches to the levels of $\lambda \sim 21-22$ when equilibrated with liquid water [3]. This phenomenon is referred as Schroeder’s paradox and mainly related to the surface energy of the vapor-liquid interface that affects the chemical potential of the sorbed phase [4].

There are several theories in the literature investigating the membrane water content relation, ionic conductivity dependence and Schroeder’s paradox [3-14]. Springer et al. [3] proposed an experimental relationship of $\lambda$ with the water vapor activity as;

$$\lambda = 0.043a + 17.81a - 39.85a^2 + 36.0a^3 \quad \text{for} \quad 0 \leq a \leq 1$$

Depending on this membrane water content profile, the membrane resistance curve is obtained and an experimental curve fit was proposed, given in Eq. 2.4.

$$\sigma_{30} = 0.005139 - 0.00326 \quad \text{and} \quad \sigma(T_{cell}) = \exp \left( \frac{268}{303} \left( \frac{1}{273+T_{cell}} - 1 \right) \right) \sigma_{30}$$

Their results indicate that the membrane ionic conductivity in (ohm-cm)$^{-1}$ is a strong function of membrane water content. With a decrease in membrane hydration level, there occurs a significant increase in the membrane resistance. Also the water vapor activity at
the anode flow was found to be deterministic on the membrane hydration level such that, the membrane resistance is highly dependent on the anode flow inlet humidity value.

In Figure 2-2, the graph of equilibrium water content value of membrane with water vapor and liquid water is shown [5]. As it is seen, the water content increases from vapor side to liquid side in a non-linear fashion and shows a dual relationship at an activity of 1 for liquid or gas phase. As the membrane initially takes on water, the sulfonic acid groups are hydrated and dissociate, creating charged groups that participate in coulombic repulsions. When the membrane is placed in a liquid water reservoir the clusters swell and reorganize themselves, trying to minimize the total energy of the system. This reorganization results in an agglomeration of clusters such that they appear to be larger in X-ray analysis, therefore yielding a higher water uptake value. In other words, for a vapor-equilibrated membrane, the structure is that of ionic clusters in the shape of inverted micelles that are hydrophilic and they can be expanded by liquid water to form a liquid-filled channel. The figure indicates the uptake of water increases for the liquid-equilibrated membrane because it has enough pressure and energy to infiltrate and expand the channels.
The water content of the membrane is also closely related to the operating conditions of the fuel cell and the properties of the membrane. In their study, Sridhar et al. [7] investigated the water uptake by the inlet anode stream flowing over the membrane at different temperature, membrane surface area and membrane thickness. At low temperature (40°C) the water uptake rate was ~4 g/h at a flow rate of 1 slpm. As the temperature increased to 70°C, the water content of the membrane is increased almost 3 times. Also, it is observed that at 5 slpm, the water uptake rate at 50°C was 1.4 moles/h for Nafion 112 whereas this value drops to 1.05 moles/h for Nafion 115, which is a thicker membrane. The water pick-up was also found to increase with increase in membrane area because of a larger contact area.

The effect of membrane molecular structure on the membrane water content was studied by Weber et al. [8]. They developed a model that uses a degree-of-constraint parameter which simulates a membrane with higher deformation energy, smaller ionic cluster size and a more compact distribution of clusters. This is called a constraint

Figure 2-2: Water uptake curve for Nafion® 117 at 30 °C showing the Schroeder’s paradox [5].
membrane. The water uptake curves vs. water vapor activity was plotted and seen that at low activities, there is a small difference between the constraint membrane and free-swelling membrane. However, as water activity increases, such as saturated vapor-equilibrated membrane, the water uptake of constrained membrane is significantly lower than the free-swelling one. At fully-humidified inlet conditions, the results showed that membrane water uptake is reduced by 4 times with a constraint membrane compared to free-swelling membrane. The conclusion was made as it is beneficial to use a constraint membrane at these conditions to avoid flooding in the cell.

2.1.2 Gas Humidification

As described in the previous section, water content of the polymer membrane has a crucial role in the fuel cell operation. The low hydration levels of the membrane will result in a decrease in the proton conductivity and adversely affect the cell performance. Therefore, full saturation of the electrolyte is desired during operation. Especially at low current densities where the product water is not enough to hydrate the membrane, it is very difficult to maintain optimal water content in the electrolyte. For this reason, an external method to keep the membrane at a high hydration level is necessary. The most commonly used technique for this purpose is the humidification of inlet gas flow. There are several methods of gas humidification, one of them being the external humidification. In this method, inlet gases flow through a humidifier, which adds water vapor into the flow, before entering to the fuel cell. The water amount added by the humidifier determines the relative humidity of the flow, where relative humidity ($\Phi$) is given by Eq. 2.5.
\[ \Phi = y_v \frac{P_{\text{total}}}{P_{\text{sat}}} \]

In the above equation, \( y_v \) is the vapor mole fraction, \( P_{\text{sat}} \) is the saturation pressure of water and \( P_{\text{total}} \) is the cell pressure. High inlet relative humidities are typically desired for high performance especially at low current density operations since there is not enough water produced in the cell to hydrate the membrane. For high current density operations, however, low humidity or non-humidified flows can be used, especially at the cathode side, in order to balance and remove the excess water produced at the cathode catalyst.

Although external humidification is the most commonly used technique in PEFC, it has some disadvantages in terms of the high volume occupation and extra power consumption. Therefore, other techniques for humidification have also been developed [15-17]. Watanabe et al. [15] introduced a humidification method by dispersing platinum nanocrystals into the Nafion® film to catalyze the recombination of crossover \( H_2 \) with \( O_2 \). It was found that, the water produced in the Pt- Nafion® is all transferred to the anode gas flow providing the necessary anode humidification and also improved the cathode over-potential by preventing the reaction of \( H_2 \) with \( O_2 \) at the cathode side due to crossover. However, embedding small Pt particles in the polymer matrix causes significant degradation problems. Dong et al. [16] studied the performance of PEFCs at low humidity operation through a series of experiments at various anode and cathode humidity levels with high-frequency resistance data. Their results showed that the anode humidity has strong effect on the membrane resistance and therefore the cell
performance. Even tough there is more than twice the water content available at the cathode side, the anode water vapor activity still found to be the limiting factor on the cell performance. Their schematic of the local current distribution at under-humidified inlet conditions is given in Figure 2-3, to guide the water management systems for more efficient water injection, and serve as a validation for the computational studies.

Figure 2-3: Characteristic local current curve for under-humidified inlet conditions [16].

Williams et al. [17] performed polarization tests on a PEFC with no external humidification. Elimination of cathode external humidification only resulted in a performance loss of 33 mV at 0.4 A/cm$^2$ whereas this value increases to 159 mV when both the anode and cathode humidification removed. The ohmic resistance also increased almost 3 times. Similar to Dong et al., they concluded that the anode humidification level is dominant on the cell performance compared to cathode side.
2.1.3 Flooding Phenomena in PEFC

2.1.3.1 Water Transport Mechanisms

There are four different modes of water transport in the MEA of an operating fuel cell; electro-osmotic drag, thermo-osmosis, diffusion, convection or hydraulic permeation and. The first two modes of transport are solely from anode side to cathode side, whereas the latter two can be in both directions. In addition to these, there are also three different mechanisms of liquid and gas-phase transport inside the DM. All three modes of transport are shown in Figure 2-4 in detail.

Figure 2-4: Water transport mechanisms in PEFC
The diffusion of water between the anode and cathode sides is due to the concentration difference of water, $\Delta C_{\text{water}}^{c-a}$, that forms across the polymer electrolyte during the fuel cell operation. The diffusion rate is dependent on both the membrane thickness, $\Delta x$, the magnitude of the concentration gradient and the diffusion coefficient of the membrane. The amount of water transported per unit area by diffusion is referred as the diffusion flux and can be modeled by Fick’s law. The diffusion coefficient of several kinds of electrolyte is reported in the literature [18]. Diffusion dominated water transport can occur in both directions between the anode and cathode side, however, the water concentration at the cathode is usually higher during the operation due to the water production in cathode catalyst layer and electro-osmotic drag from the anode. Therefore, water transfer by diffusion is typically from cathode to anode side, referred as ‘back-diffusion’. Back-diffusion, given in Eq. 2.6, occurs mainly at high-current density operation and it is desirable to sustain a hydrated membrane at the anode side since the water concentration at the anode can be low at high current density due to the electro-osmotic drag.

$$j_{\text{diff}} = -DA \frac{\partial C}{\partial x} \quad 2.6$$

The second mechanism of water transport is the electro-osmotic drag as shown in Eq 2.7. When the positively charged $\text{H}^+$ ions migrate from anode to cathode side through the polymer electrolyte, they tend to attract polar water molecules via intermolecular forces. The average number of water molecules transported per proton is called the electro-osmotic drag coefficient, $\lambda_{\text{drag}}$, and in Nafion® membranes it ranges from 1-2.5
depending on moisture content [19]. In an operating fuel cell, the direction of the water transport due to electro-osmotic drag is always from anode to cathode side and it is directly proportional to the current density. Therefore, at high current densities, the rate of water removal from the anode side could be very high, resulting dehydration of anode. Back-diffusion can compensate for the depletion of water caused by this effect, especially for thin membrane.

\[ j_{\text{drag}} = \lambda_{\text{drag}} \frac{iA}{F} \quad \text{Eq. 2.8} \]

Water may also be transported through the membrane by hydraulic permeation, which is the result of pressure difference between anode and cathode gas flows. The rate of water transport is dependent on membrane thickness, current density and magnitude of the pressure difference. However, the gas-phase effect is usually negligible in practical applications since it is common in fuel cell operation to keep anode and cathode side pressures equal to prevent damage to the thin polymer electrolyte. Eq. 2.9

\[ j_{\text{hyd}} = \frac{\kappa \Delta P}{\mu \Delta x} \quad \text{Eq. 2.9} \]

Inside the DM, water transport may occur with diffusion similar to the membrane. In addition, the liquid accumulation inside the DM may cause pressure difference between the liquid and the gas phase, and result in capillary flow of liquid through the DM pores. Also, water may transport within the DM via evaporation and condensation of liquid due to the temperature differences inside the DM, which is called as phase-change-induced flow.
Acquiring high water content in the membrane is tremendously important in terms of effective ionic conductivity in the PEFC as described above. However, if excessive water forms in the cell, it may cover the surface of the catalyst layers, fill the pores of DM and even block the flow channels in the form of liquid water. The former case will prevent the electro-chemical reaction whereas the latter two cases will prevent the diffusion of reactant gases into the reaction sites. This phenomenon is known as ‘flooding’ which can drastically decrease PEFC performance. There are three types of flooding observed in PEFC; catalyst layer flooding, diffusion media (DM) flooding and flow channel flooding as illustrated in Figure 2-5. In the falling sections, the types and causes of flooding observed in the fuel cell structures are discussed.

Figure 2-5: Three types of flooding mechanisms
2.1.3.2 Water Management in Catalyst Layer and Diffusion Media

Catalyst layer flooding is a result of the reduction of active catalyst reaction area due to the accumulation of water in the pores of the catalyst layer. When liquid water accumulates over the surface of the nano-size Pt particles, a micro-layer of liquid film forms, through which the diffusion of reactant gases is decreased by ~5 orders of magnitude. This can be seen by Henry’s law for multi-phase transport across films, given by Eq. 2.10 [20].

\[ C_{\text{reactant}}^{\text{liquid}} = C_{\text{reactant}}^{\text{gas}} \left( \frac{RT}{H_o} \right) \]  \hspace{1cm} 2.10

where \( C_{\text{reactant}}^{\text{liquid}} \) and \( C_{\text{reactant}}^{\text{gas}} \) are the concentration of reactant gases after and before the liquid film and \( H_o \) is Henry’s constant given in Eq. 2.11 for oxygen in liquid water [21]. The reduction in active catalyst area causes an increase in the required reaction over-potential to obtain the same overall current, and may occur at both the anode and cathode of the cell.

\[ H_{\text{o}_2} = 5.08 \times 10^6 \exp \left( \frac{-498}{T} \right) \]  \hspace{1cm} 2.11

The second type of flooding occurs in the diffusion media (DM). DM is a porous structure allowing reactants to reach the catalyst layer and product water to be removed from the reaction sites. When the partial pressure of the product water exceeds the saturation pressure, condensation occurs and liquid water forms in the DM structure filling the available pores for reactant diffusion. Hence DM flooding can be defined as the obstruction of reactant diffusion due to the accumulation of liquid water in the pores.
of diffusion media. The paper-type and the cloth-type DM are most commonly used in PEFC applications. A scanning-electron microscope image of both types of diffusion media are shown in Figure 2-6.

![Figure 2-6: (a) SEM of a paper type DM (b) SEM of a cloth type DM [1].](image)

The reduction in reactant diffusion has been directly related to the saturation level of the membrane by the effective diffusion coefficient given by the modified Bruggeman relation [20]. This model of pore filling assumes an effective diffusivity calculated based upon the saturation level, given in Eq. 2.12. However, as this model is taken from soil sciences, it has a limitation on predicting the flooding amount in the cell i.e. it results higher water amounts at flooded conditions. Combined with the pore filling effect, formation of the micro layer liquid film due to the capillary action also contributes to the flooding in DM, as will be described in the following chapters of this thesis.

\[ D_{\text{eff}} = D(e - s)^{1.5} \]  

2.12
The water management and flooding issue in the catalyst layer and DM was investigated analytically [22-42] and experimentally [43-60] by several researchers. Baschuk et al. [22] investigated the flooding behavior in DM at different operating pressure and temperatures using a one-dimensional, steady-state, isothermal model. Performance curves was obtained for two different cell temperatures, 50 °C and 70 °C, and three different cell pressures, 1 atm, 3 atm and 5 atm, and for each case, the fraction of the cathode electrode flooded was calculated. The increasing pressure showed flooding on a greater fraction of the electrode at inlet gas humidities lower than 100%. It is suspected that the decreasing flow velocity in the channels is the major factor resulting in this behavior. The temperature found to have an inverse effect on flooding such that there is less electrode flooding for high cell temperature case. Also the cell efficiency and power density curves were plotted and the maximum cell efficiency for the entire operation range was obtained at 3 atm. Generally high cell pressure implies higher efficiency; however the increased flooding behavior at 5 atm increased the losses and resulted in a lower efficiency profile.

In their study, Lin et al. [30] developed a steady-state, isothermal water management model regarding the catalyst and DM flooding behavior. The model basically solves for the oxygen and water concentrations and liquid saturation level in these domains using basic transfer equations and appropriate boundary conditions. They analyzed the effects of inlet relative humidity of both anode and cathode flows, cell temperature and catalyst loading on flooding and found that excessive catalyst loading would not improve the overall cell performance by increasing reaction sites that are not covered with liquid water. Also they determined significant flooding in catalyst layer
under humidified flow conditions and the level of flooding in DM-backing layer was found to be lesser than that of inside catalyst layer. In their continuation work [31], they also analyzed the DM conductivity effect on flooding at three different values (200 S/cm, 20 S/cm and 2 S/cm). Due to an order of magnitude difference between the ionic conductivity of the catalyst layer and the electronic conductivity of the DM, there observed insignificant change at the cell performance even at the lowest electronic conductivity value. The importance of liquid water permeability values (in-plane and through plane) found to be deterministic on the liquid saturation distribution in DM. Performance curves for in-plane permeability values of $0.55 \times 10^{-9}$ cm$^2$ to $2.2 \times 10^{-8}$ cm$^2$ was plotted and improved mass-transport region was observed with increasing permeability values. At flooding conditions, it is reasonable to observe such a behavior since transport of liquid water from landing locations to flow channels becomes easier due to less flow resistance in lateral direction. It is important to note that, no difference was observed at the activation and ohmic region of the performance curves.

The liquid water accumulation and distribution in the catalyst layer and DM is also dependent on the thermal balance in the fuel cell. Ju et al. [40] coupled the heat transfer and water management effects in their single phase, non-isothermal model. Three important factors influencing the thermal balance in the fuel cell was considered; reversible heating due to the difference in the heat capacity of the chemical reaction and maximum work available determined by the second law of thermodynamics, the irreversible heating due to the difference in maximum voltage and operating voltage and the joule heating which is the heat generated due to the electronic resistances. The DM thermal conductivity values, inlet flow humidities and operating voltages were varied in
the study and resulting temperature and liquid water profiles were obtained. For low thermal conductivity of DM, the membrane hydration due to temperature difference was found to be dominating over water production resulting poor performance. Also at low inlet humidity values, average current density was decreased. This suggests using DM with high thermal conductivity (~3 W/mK) at low inlet humidity operation. Around 0.7 V, it is found that improved kinetics, due to the elevated temperature, is dominating the membrane hydration and therefore performance increases. However, as voltage drops to 0.6 V, the phenomenon is reversed and performance decreases. Also the temperature profile in the DM suggested that there are cold spots under the landings of the flow field which makes these locations the preferential water condensation sites.

Combined with DM, Weber and Newman [41] investigated the effect of microporous layer (MPL) on flooding in the fuel cell. In their model, the membrane, catalyst layer, DM and flow channels were constructed analytically and referred as the modeling sandwich. The model enables comparison between performances of fuel cells with and without MPL. The results showed that MPL improved the limiting current by decreasing the flooding level. MPL acts as a valve that pushes away water from the cathode DM through the membrane. Better membrane hydration and decreased DM flooding is achieved with MPL due to this reason. An important observation was that for DM having permeability within an order of magnitude of that of the MPL would be flooded. This is because the liquid pressure level calculated at the MPL zone is found to be much higher than the DM zone. They also analyzed the MPL effect on other performance regions such as the ohmic region. Using a MPL improved the ohmic loss in
the fuel cell due to better contact with DM, increased structural stability and better catalyst utilization.

The properties of the MPL applied on the DM have also important influences on the flooding of the fuel cell. Pasaogullari et al. [42] studied the effects of MPL properties such as average pore size, wettability, thickness and porosity, on water transport in a PEFC. A bilayer DM is analyzed using the M² model for different thicknesses, wettabilities and pore-sizes of MPL. The additional MPL layer enhanced the liquid water movement towards the anode compartment, decreasing the net water transport coefficient especially at low current density region where the electro-osmotic drag is not the determining transport mode. As the thickness of the MPL increases, the liquid pressure also increases. This increases the pressure driven liquid water flux to the anode side and decreases the level of flooding at the cathode compartment. The capillary or liquid-phase pressure difference between the MPL and the gas channel found to be as high as 80 kPa. It was also found that as the pore size gets smaller in the MPL, permeability also decreases and resistance to liquid flow increases. This builds-up the liquid pressure enhancing the liquid flow towards anode. Increasing the wettability of the MPL has a similar effect. It is seen that with increasing the contact angle of MPL from 95° to 120°, the net water transport coefficient decreased, almost 20% for 0.1 A/cm². The saturation level at the MPL DM interface was also studied, and a discontinuity was found. Due to the difference in pore sizes, and therefore capillary pressure, there is much lower liquid saturation at the MPL compared to DM under the same capillary pressure. This result showed that MPL also improves water removal from the DM-flow channel interface.
Modelling studies predicting the flooding behavior in CL and DM are useful in terms of understanding the physical phenomena inside the fuel cell components, however, experimental techniques are also required to measure the actual behavior of flooding during real operation. To measure the flooding in a conventional channel/land design fuel cell, Yamada et al. [43] used a pressure drop measurement technique. Their experimental evidence indicates that for a hydrophobic catalyst layer, flooding first occurred in the diffusion media and for a hydrophobic DM and hydrophilic catalyst layer, the initial flooding was determined in the catalyst layer. Li et al. [44] also used pressure drop measurements to develop a flow channel design procedure that will avoid channel flooding. Their design was based on determination of appropriate pressure drop that will evaporate all the liquid water accumulated in the channels.

An important factor determining the liquid water formation in DM is the pore size distribution in the carbon matrix. Kong et al. [48] investigated the influence of pore size distribution of the DM on flooding problems of PEFC. They performed different pore forming treatment to three diffusion medias, and obtained performance and impedance curves for each case. The total porosity value for all of the DMs was approximately same, however, the macropore (5-20μm) volume for first two cases was ~7% and for the third case it was ~15%. They found that the performance loss at high current density operations due to flooding significantly decreased for the higher macropore volume condition. A possible explanation was made that, in micropores having diameter smaller than a critical pore-size, capillary condensation will occur before the vapor pressure reaches saturation pressure, resulting severe flooding losses in the micropore GDL. The amount of macropore volume has also a limit since making pores larger decreases the
electronic conductivity in DM and results in ohmic losses. The optimum pore treatment loading, which basically enlarges the pores in DM, was found to be 140% wt. For this value, the impedance results also showed a minimal ohmic resistance in the fuel cell.

The flooding behavior inside the DM is highly related to the transport of liquid water via capillary flow. The capillary liquid flow is defined in terms of the relative permeability of the porous medium and the capillary pressure gradient which is related to liquid saturation via the Leverett function. Kumbur *et al.* [50-53] investigated the effectiveness of the Leverett function on describing the capillary liquid flow inside DM using a modified test cell. They measured the droplet detachment and capillary liquid flow in DM with different temperature, compression and DM PTFE content and proposed a modified-Leverett function. They developed a model based on the empirical correlation obtained from their data, and showed that this modified-Leverett function is more effective in describing capillary pressure-saturation relation in fuel cell porous medium compared to the original Leverett function which is directly embedded from the soil science.

**2.1.3.3 Water Management in PEFC Flow Field**

The last mechanism of flooding in PEFC is the flow channel flooding. When liquid water forms in the pores of the DM, it will be transported towards the flow channel/electrode interface by the capillary action arising from the pressure difference between the liquid and gas phases. As the liquid water reaches the interface, it will rise to the DM surface and form liquid slugs in the flow channel which will block the flow of reactant gases. This phenomenon is referred as the channel flooding and it adversely
affects the cell performance similar to the other modes of flooding. One of the major parameters determining the level of channel flooding is the flow rate of reactant gases. Hakenjos et al. [61] investigated the effect of reactant flow rate on channel flooding and they found there is a substantial decrease in flooding with increased reactant flow rate due to the removal of liquid slugs with high shear forces. Another important factor, the effect of the channel and landing width, was studied analytically by Lin et al. [31] At a fixed channel to landing ration, their modeling results showed that, fuel cell performance increased at small landing and channel widths. The liquid saturation under the landings found to be much higher than under the channels especially at large landing widths. Even tough at a constant channel/landing ratio, small channels perform better, for variable channel|landing ratios (3:1, 1:1, 1:3), they concluded that, large channel configuration is better for liquid water removal, which seems to be self-contradicting. This could be due to very small active area (1.2 cm$^2$) of the cell. Analyzing the effect of liquid layer formation under the channels could be difficult at very small electrode area and therefore results might be misleading. The isothermal assumption of the model might also be affecting the results negatively since at larger active areas, the heat generation effect could deviate the boundaries from isothermal conditions.

Similarly, Kumar et al. [62] performed a modeling work on the influence of the channel and landing sizes on cell performance by calculating the hydrogen consumption of the anode flow channel. Channel and landing sizes ranging from 0.5mm to 4mm were considered in the simulations. For a common hydrogen consumption range (~80%), results showed that channel width, landing width and channel height of 1.5mm, 0.5mm and 1.5mm respectively is the optimum design condition. The mass transport limitation
was observed for large landing widths, indicating excess amount of liquid formation under these locations. Also the hydrogen consumption was found to be below 70%. Therefore, it is thought to minimize the landing width by designing triangular or hemispherical flow channels. In terms of minimizing the liquid water accumulation and maximizing the hydrogen consumption, both designs performed better than the rectangular cross-section. Hydrogen consumption of ~93% was obtained with the hemispherical flow channels. However, limited electronic conductivity due to the minimized contact area still remains as a drawback of this type of design.

The flow configuration in the fuel cell is also an important factor affecting the performance together with the flow field design. Birgersson et al. [63] investigated both effects analytically by performing simulations on two different flow configuration, co-flow and counter-flow, with a parallel flow field, and two different flow field designs, foam and interdigitated. Simulations were carried out for six different cell potentials and three different stoichiometries, 1.5, 3 and 5. Simulated performance curves showed that interdigitated design significantly improved the mass-transport region. A limiting current of 4 A/cm² was obtained with this design whereas this value was 3.2 A/cm² for the foam case. The co-flow and counter flow arrangements had much higher polarization losses. Furthermore, the uniformity of current was also found for each scenario by calculating the standard deviation of local current density from the average current density. The interdigitated design has the most uniformly distributed current density profile since it forces the flow into the DM and enables more uniform reactant diffusion. A co-flow configuration was found to have the largest deviation from the average current density. Therefore, the water accumulation at the DM for the interdigitated design is more
uniform compared to the co-flow case. The pressure drop for each scenario was also calculated and highest pressure drop was found at the interdigitated design. This is a disadvantage of this design since the liquid water transfer into the inlet flow through evaporation decreases with increasing pressure drop.

An extensive review of flow field designs in PEFC was reported by Li et al. [64]. Four basic designs and their modifications were considered in the paper such as, pin-type flow field, straight (parallel) flow field, serpentine flow field and interdigitated flow field. The pin type design provides low reactant pressure drop. On the other side, reactants tends to flow through the least resistance path between the pins which yields to a non-uniform reactant distribution over the DM. Due to this disadvantage, pin type flow-field design is not commonly used in PEFCs. The straight flow field design enables more uniform distribution of reactants compared to pin type. However, the water droplet formation at the channel-DM interface is a problem at this design. The droplets easily spread over the walls of the parallel channels and form clogged channels that increase the performance losses. Another disadvantage is that, the overlapping parallel channels cause non-uniform compression stress on the DM and MEA structure. The high compression under the ribs might damage the MEA structure. Therefore it is recommended to uniformly distribute the parallel and perpendicular contact areas. This could be achieved by a serpentine flow field design in which the flow channels are continuous from inlet to the exit of the cell and also the anode and cathode compartment are skewed in opposite directions to avoid overlapping. This design eliminates the compression problems and also provides a better water removal from the channels compared to parallel design. However, high pressure drop along the continuous channels still remains as a
disadvantage of this design. The interdigitated design was also discussed in the paper. The effective reactant diffusion into the catalyst layer and high water removal rate makes this design advantageous over the previous ones. The most important issue with this design is high pump power required to overcome the high pressure drop from the forced convection through the DM.

Yi et al. [65] performed a modeling study to investigate water management along the flow channels of a PEFC. Three different channel lengths, 50 cm, 100 cm and 150 cm, were analyzed in the study. The liquid water flow rate were calculated for each case and results showed that for 100 cm case, the liquid water flux in the channels is almost two times higher than 50 cm one. This is because the amount of liquid water produced is linearly proportional to the channel length. However, for 150 cm case, a decrease in the liquid water flux is observed near the exit of the channels. The integrated effect of liquid formation with increasing channel length is compensated with the increased pressure drop for this case, and near the exit, due to high pressure drop, evaporation of liquid water occurred. The effect of pressure drop is so significant near the exit such that, a negative water flux was observed indicating membrane-electrode dry-out. It is concluded that the length of the channels has significant effect on water removal from channels.

There are also other studies reported in the literature investigating flow-field effect in PEFCs. Kulikovsky et al. [66] investigated the effect of flow-field structures on required catalyst loading. They reported that at high conductivity, catalyst loading under channels can be reduced up to 50% whereas for low conductivity, the catalyst loading under the landings can be removed in order to reduce the material costs. Wood et al. [67] studied the effects of interdigitated flow-field design on the fuel cell performance. Their
results indicated that the dead-ended flow channels in interdigitated flow field design could handle more liquid water in the anode compartment without causing severe transport losses. Also, they found that, when oxygen is used as the cathode gas, the pressure drop across the flow-field shoulders is minimal. In an other study, Chen et al. [68] performed modeling simulations with variable channel heights and concluded that larger channel height enables higher power density in a fuel cell.

2.1.4 Water Management during Shutdown and Cold-Start Conditions

The fuel cells are desired to be operated at temperatures above zero degrees Celsius. However, it is not always possible to obtain this condition, especially in automotive applications where outside temperatures can decrease below the freezing point of water. There is significant amount of liquid water accumulation in the fuel cell component and therefore, this temperature drop would result in ice formation inside the fuel cell components. The phase change from liquid to solid state will result in expansion of water and cause additional mechanical stresses inside the pores where liquid was accumulated. These mechanical stresses will damage the structure of CL and DM which cause performance loss and may even result in catastrophic failure. In order to avoid this problem, an effective water management which will minimize the liquid water storage during shutdown and cold-start of the fuel cells is required [69-76]. Alink et al. [69] showed that a fuel cell stack experienced less degradation when it is dried before cooling down. Tajiri et al. [70] proposed an equilibrium purge method to control the initial water distribution inside the fuel cell after shutdown in order to obtain a successful cold-start. He et al. [72-73] developed a one-dimensional, transient model based on frost heave
mechanism and found that under the channel CL|membrane and CL|DM interface locations may suffer exacerbated physical damage due to ice formation and their prediction was experimentally validated [74-75]. Khandelwal et al. [77] also developed a model describing water redistribution after shutdown by considering capillary and phase-change induced flow in DM and thermo-osmosis in membrane. They found that water at cathode can be controlled and freeze damage can be avoided through balancing phase-change induced flow in DM and thermo-osmosis and diffusion flux in membrane.

2.2 Characterization of Water Distribution with Neutron Radioscopy

2.2.1 Background Information

Neutron imaging is a powerful technique to observe and quantify the water distribution in an operating PEFC. It is the most realistic approach available today that has the ability of mapping near real time water distribution and quantifying the water amount in flow channels, gas diffusion media and membrane inside a test cell or an actual-stack-size fuel cell. The working principle of all neutron imaging methods are similar in that a neutron source passes through an object and the attenuation of the source’s initial intensity is measured [78]. The distinctive attenuation characteristics of different elements allow an image of the examined object under the exposition of radiation either in form of X-rays, gamma rays or neutrons. Using neutrons as the radiation source is advantageous in studying hydrogen concentrations, due to the fact that hydrogen has a large attenuation for neutrons. By placing a sample with varying concentrations of hydrogen, i.e. operating fuel cell in which there is liquid water accumulation, it is possible to observe the contrast in neutron transmission between areas
within the sample [79]. The neutrons are released from a collimated beam and the attenuation of the beam is recorded by a detective device, or camera, producing a two-dimensional image [80]. The ratio of the initial intensity to the intensity incident on a material for neutrons traveling through matter is given by Eq. 2.13 (ASTM E 748-95, 1995).

\[
\frac{I}{I_0} = \exp(-\mu \cdot x)
\]  

where

\[
\mu = \rho \frac{N \cdot \sigma}{A}
\]

In the above equation, \( \mu \) represents the attenuation coefficient of the element neutrons are traveling through and \( x \) is the thickness of the material. The attenuation coefficient of an element is a function of several parameters such as; density of the element (\( \rho \)), its cross-sectional area (\( A \)) and atomic weight (\( \sigma \)). The differences in the measured intensity ratio, such as liquid-vapor water and solid-liquid metal interfaces, permits two-phase flow to be visualized. In principle, neutron transmission radiography and radioscopy is analogous to X-ray radiography. However, the interaction mechanisms of neutrons and X-rays with matter are significantly different. X-rays interact with the electron cloud surrounding the nucleus of an atom whereas neutrons interact with the nucleus itself [81]. Therefore, neutrons have a higher interaction probability with light element such as hydrogen compared to X-rays. On the other hand, they have a longer penetration length through metals because of reduced interaction probability. This feature allows visualization of water in a normal fuel cell through the metal bi-polar plates. The
mass attenuation coefficients of thermal neutrons, low energetic and high energetic X-rays are given in Figure 2-7 for various elements [81]. Note the high attenuation for hydrogen, and the relatively low attenuation for aluminum, used as the flow-field plate in the fuel cells tested.

![Figure 2-7: Mass attenuation coefficients for several elements [81].](image)

As discussed in Pekula [82], there are two distinct methods in neutron imaging technique; neutron radiography and neutron radioscopy. The former method is commonly used for static objects of interest; therefore time-dependent processes can not be obtained using this method. The second method is neutron radioscopy, which is used in the present research, and is basically used for ‘real-time’ video imaging. Hence, neutron radioscopy is more suitable for time-dependent processes such as liquid water formation and depletion in a fuel cell. The basic advantage of radiography is its high spatial resolution
capability over a large imaging area. Processes with image quality as good as 30 μm pixel\(^{-1}\) are obtained with square imaging areas greater than 50 cm\(^2\), but require exposure times of several minutes. On the other hand, radioscopy technique has the advantage of real time imaging, usually at a rate of up to 30 frames s\(^{-1}\), with comparable spatial resolution (~15-30 μm) on much smaller rectangular imaging areas (5-10 cm\(^2\)) where the smaller side of the rectangle is typically between 0.5-2.5 cm. Mishima et al. [83] were successful at investigating the flow phenomenon of high velocity air-water two-phase flow in a metallic duct at recording speeds of 250, 500 and 1000 frames per second. The typical spatial resolution for a square 50 cm\(^2\) imaging area is ~ 100 μm with the radioscopy technique.

### 2.2.2 Neutron Radioscopy Technique in Fuel Cell Technology

In order to apply the neutron radioscopy technique to fuel cells, the neutrons generated from a nuclear reaction, such that inside a nuclear reactor core, has to be directed through a tubular or a rectangular section named as the beam collimator and released onto the surface of a fuel cell from a small hole named as the aperture. The neutrons that are not attenuated by the water molecules in the fuel cell hits on a special screen called the scintillator and releases photons. These photons then hits on a conventional charge coupled device (CCD) camera which converts them into a digital image that can be viewed from a personal computer (PC) [84]. As discussed in Trabold et al. [85], the ratio of the distance of test section from the aperture to the aperture diameter is referred as the L/d ratio and it is the most important factor determining the geometric sharpness of the resulting image. If the test object is placed too close to the beam
aperture, than the sharp edges on the object will appear as blurred lines on the image, which is called as “geometric unsharpness”, whereas if it is too far from the aperture than the resolution of the image may be significantly lower than the system resolution. The main limitation of the overall spatial resolution of a typical neutron imaging system is the deflection of the photons in the scintillator. This is called as “scintillator blooming”. As the neutrons hit the scintillation screen, they are “converted” to photons and these photons scatter in the order of couple hundreds of micron through the thickness of the scintillator. It is preferred to have a thin scintillation screen to reduce the amount of photon scattering, however, as the thickness of scintillator is reduced, the chance of neutrons being converted into photons also reduces which results in very long exposure times which results in a trade off between better system resolution and better observation of unsteady behavior in the cell. In their work, Trabold et al. [85] showed a detailed procedure to determine the scintillator resolution.

There are several studies reported in literature on the application of neutron radioscopy technique on fuel cells [78-110]. Bellows et al. [79] performed one of the initial studies of neutron imaging on fuel cells and measured the water gradient profiles qualitatively within Nafion® in an operating PEFC. Neutron radiographs of an extremely thick membrane (500 μm dry), processed by hot pressing of four layers of Nafion®, were obtained at different humidity conditions and water content through the thickness of the membrane was determined by evaluating the neutron intensity at each data location. Their results show that dry cathode inlet condition causes much more membrane drying than the dry anode inlet condition due to high flow rates. Even though they were successfully evaluated the qualitative distribution of water in the membrane, due to the
interface problems rising from extremely thick membrane, they were not able to calculate the water amount in the membrane with this technique. In another early neutron imaging study, Geiger et al. [81] presented neutron radiographs of an operating PEFC at different cell temperatures and current densities in order to observe the two-phase flow in the flow-channels during the start-up and shutdown periods of the fuel cell. The cell was heated from room temperature to elevated temperatures and condensation of water in the channels was observed with several radiographs. They found that there is liquid water condensation in the cell up to 55 °C cell temperature and then dry conditions were observed.

Satija et al. [86] used a curved guide for cold neutrons to have a uniform neutron intensity coming from the beam aperture that will significantly reduce the background radiation by eliminating the gamma rays and high-energy (fast) neutrons. They took 1000 images of a fuel cell with 160 μm/pixel spatial resolution and 1 second exposure time and revealed that, qualitatively, most of the water was formed in the center region of the cell. For each image, they also calculated the water mass in the cell; however, they did not explicitly mention the operating conditions, therefore, their water mass values are not useful in making quantitative analysis.

Pekula et al. [87] performed neutron imaging tests on an actual operating fuel cell at low current densities (0.05 A/cm2) and high current densities (1A/cm2) and investigated the liquid water distribution in the flow channels. The neutron radiographs were taken for 4.5 min with a maximum spatial resolution of 50-70 μm. The results at low current density showed that most of the liquid water is accumulated at the anode flow channels. This is explained by the condensation of water vapor in the humidified anode
inlet flow. Due to low flow rate, removal of this condensed water from the channels becomes very difficult at low current density condition. The high current density tests revealed that liquid water tends to accumulate at particular locations such that 90° and 180° turns in the flow channels.

Turhan et al. [88] studied the effect of fuel cell operating parameters on liquid water storage and distribution using neutron radioscopy and successfully quantified the liquid water amount inside the cell. They performed imaging tests at four different cathode flow rates (475 to 1188 sccm), three different cell pressures (0 to 0.1 MPag) and four different inlet humidity values (25% to 100%). At low flow rate values, the water accumulation at the flow channels found to be much higher compared to high flow rate case. Also, there was more water accumulation at low flow rate condition compared to high flow rate (155 mg to 106 mg). The increased flow rate mostly blows out the water in the flow channels and removes some water from DM also. The water amount in the cell was found to be increasing with decreasing cell pressure at over-humidified conditions. The neutron images of under-humidified conditions did not show a distinct difference in liquid water amounts, even though the cell performance at each case was significantly different from each other. This result indicated that the performance loss due to the electrolyte dry-out was a result of only a few miligrams in the 14.5 cm² active area cell.

Owejan et al. [90] also investigated the effect of cathode stoichiometry on the water accumulation by performing tests on a simulated fuel cell stack. They formed a bypass line in front of the inlet of a single cell and controlled the pressure drop across it until the water mass in the cell reaches a steady-state at 0.2 A/cm², 50/65% RH and 2.0/3.4 stoichiometry at anode and cathode respectively. Then they fixed the pressure
drop across the bypass line so that it will divert the flow as pressure drop across the cell increases due to any additional liquid water build-up. They monitored the cathode stoichiometry change by mass flow meter and oxygen sensor and measured the liquid water build-up in the cell by neutron radiography at the same time and found that water accumulation in the cell is proportional to the decrease in cathode stoichiometry. They suggested two modes for water build-up in the cell. The first mode is filling of GDL pores until a critical saturation is reached in which the liquid water mainly remains in the GDL and cell performance is unaffected. After this critical saturation level is reached, liquid water starts being rejected into the flow channels and slug formation occurs where these slugs reduce the cathode flow dramatically and yield in cell failure. From their data, they obtained an empirical relation for liquid water volume versus cathode stoichiometry as system reaches its critical saturation which might be a useful tool for fuel cell stack designs.

Water accumulation and distribution in PEFCs were also measured by Kramer et al. [91] using neutron imaging technique. They performed imaging tests with a serpentine flow field and interdigitated flow field fuel cells both having 100 cm² active areas. As a first observation, they stated that there is existence of liquid water in the cell even at 0.1 A/cm² current density condition. This suggests it is incorrect to evaluate the flooding behavior of the fuel cell only by measuring the performance curve since there is liquid water in the cell even at the kinetic region. The neutron images of the fuel cells indicated that above 0.4 A/cm², there is more liquid water at the interdigitated flow field design, most of it being at the dead ends of the channels. There is a sharp decrease in the performance for both cases at the high current density region. For serpentine flow, it is
suspected to be because of the high amount of liquid water in the DM. Hence from channel flooding view, it is suggested to use serpentine flow field design for high current density operations. The liquid water volume was also calculated in the study for dew-points of 55 °C and 65 °C at anode and cathode inlets (cell temperature is 70 °C). Results are shown in Figure 2-8. Liquid water amount at the inlet region was found to be higher for the high humidity case. Regardless of humidity, the maximum water volume found to be much less than open pore volume of the DM indicating it is not possible to completely fill the DM.

Owejan et al. [92] studied different flow field geometries by testing rectangular and triangular cross section, serpentine flow field designs and found that smaller droplets were formed and stored water amount in the cell is lowered with triangular cross section compared to rectangular design. They also studied three different DM materials; Toray 060, SGL 21BC and SGL 20BC, and found that lower in-plane permeability retains less water due to avoidance of bypass flow under the lands.
Hickner et al. [94] analyzed the water management phenomena in fuel cells in terms of local heating effects by performing several imaging tests at 40 °C, 60 °C and 80 °C cell temperatures. The 100% RH inlet humidity and 20 psig cell pressure is kept constant at all experiments. The 80 °C results showed that water content in the cell peaks around 0.65 A/cm² and then decreases with further increase in current density. At 40 °C condition however, liquid water and current density increases linearly. They explained...

Figure 2-8: Polarization curves and total mass of water under ribs for two different humidities, 55°C (a) and 65 °C (b). Cell temperature is 70 °C [91].
that the difference in liquid water trends is due to the non-linear behavior of saturation pressure of water with temperature. There could be up to 10 °C local temperature variations in the electrolyte during the fuel cell operation. Due to this fact, at 80 °C case, a 10 °C variation in the cell could increase the liquid evaporation into the inlet flow more than that of 40 °C case. They also studied the transient behavior and observed that there is ~ 100s delay in response of liquid water accumulation to a step change in current density. The basic reason behind this is suspected to be the time constant of capillary water diffusion in DM.

In most of NR studies to date, planar images of the fuel cell were analyzed and therefore, it was not possible to differentiate anode and cathode water accumulation. This limitation was eliminated with the use of micro-channel plate (MCP) based detector [95]. For a 0.3 mm thick scintillator, the spatial resolution limit is ~250 μm and thermal neutron detection efficiency is ~ 20%. However, this limit is almost an order of magnitude lower in a micro-channel plate (MCP) based detector which basically is a glass structure with open channels that has center-to-center separation of ~10μm [95]. The walls of the a few micron thick glass is loaded with neutron absorbing material, such as boron or gadolinium, that emits charges particles when hit by neutrons. To amplify the emitted particles, a high voltage (5kV) was applied to the MCP stack which creates an electron cloud amplified by order of $10^6$. This method results in detector resolution of ~ 2 times the separation of open channels which is adequate to differentiate the anode and cathode GDL and flow channels via cross-sectional imaging [95]. This technique is first used by Hussey et al. [95] by imaging a fuel cell at 50, 75, 100% RH conditions; 0.01, 0.02, 0.05 and 0.2 A/cm² current densities. They plotted the total optical density through
the cell and showed that this technique is adequate to detect the water thickness in through plane direction with high resolution. Hickner et al. [96] analyzed cross-sectional water profile using this technique in a 2.1x7.7 cm active area, single-pass serpentine channel fuel cell at 40, 60 and 80 °C cell temperatures and low to high current densities. They found significant liquid water residue in the anode gas channels and surprisingly, at current densities above 0.75 A/cm², the residual water in anode gas channels was found to be 1.2-1.8 times higher than the cathode gas channels. Weber et al. [97] developed a computational model based on these results and estimated the through plane saturation in fuel cell components at different operating conditions. Boillat et al. [98] developed a vertical slit aperture, which greatly increases the L/D ratio (object-aperture distance) in horizontal direction while sacrificing little from the neutron flux compared to circular aperture case and obtained a resolution of 2.5 µm per pixel. They tested a 0.5 cm² cell at 1 A/cm² with cathode-anode relative humidities of 90-90, 110-110, 110-90 and 75-110 %. At under-humidified cathode flow, they found that water tends to accumulate under the ribs more than the channels, however, this is reversed when cathode is fully-humidified.

2.2.3 Other Visualization Techniques in Fuel Cell Technology

In addition to the neutron imaging technique, there are also other methods developed as a visualization tool for fuel cells. One of the most common methods is using transparent fuel cell backing plates which enables direct visualization of two-phase flow in flow channels. Tuber et al. [111] observed the flooding behavior on DM flow channel interface at different air flow rates and diffusion media properties. A cathode side
transparent fuel cell with an active area of 62 mm x 6.5 mm was used in the experiments. Tests were performed at constant voltage of 0.5 V with dry hydrogen and 60% RH air. Formation of liquid droplets was observed after 3 minutes of operation for almost each flow rate condition. A sharp decrease in the current density occurred at this time. However, for 150 ml/min and 225 ml/min air flow rates, a second drop at the current density was observed whereas for 450 ml/min, current density was constant. They calculated a threshold current density value before liquid water starts to form in DM for different air flow rates. The value of 175mA/cm² for 450 ml/min air flow rate was found to be consistent with the experimental observations. The effect of DM hydrophobicity was also investigated in the study. Hydrophobic, standard and hydrophilic DM were tested and for 30°C cell temperature, images showed that minimum water formation in the channels occurred at the hydrophilic case. Also, current density was higher for this case compared to the others. The low temperature operation and under-humidified conditions suspected to be the reason of this fact since the hydrophilic DM can distribute the liquid water uniformly providing a hydrated MEA structure. This improves the cell performance. However, the effect of DM characteristics at higher cell temperatures and fully-humidified inlet conditions still has to be investigated.

A combined experimental and analytical study was performed by Zhang et al. [112] on liquid water removal from a fuel cell. Experiments were conducted using a transparent fuel cell under operating conditions of 80 °C cell temperature, 2 atm absolute pressure, and the liquid distribution in the flow channels was observed. For a flow velocity of 1.43 m/s, high liquid condensation on the DM surface was observed, resulting in a mist flow in the flow channels. As the velocity was increased to 7.43m/s, almost all
of the liquid disappeared from the DM surface and an annular flow (liquid film on the channel walls) was observed. The liquid removal from the DM surface basically related to two opposing forces as drag force on the liquid droplet and the surface adhesion force (surface tension). Based on a simple force diagram on the liquid droplet and using appropriate correction parameters, a detachment diameter was calculated analytically at which the drag force overcomes the surface tension and liquid removal occurs. The main reason of observing two different flow regimes in the flow channels highly depends on this detachment diameter such as, at low flow velocity, detachment diameter is small and capillary interactions with the channel surfaces is not possible. Therefore, mist flow regime is observed. However, as the velocity increases, the detachment diameter grows gradually becoming comparable with the channel size. Due to the capillary interactions, this size of a droplet directly spreads on to the channel walls, resulting in an annular flow regime. The removal of water via the inlet flow was also studied in the paper. Results showed that, for fully humidified inlet flow, it is necessary to use stoichiometries higher than 7 in order to sufficiently remove the product water. This value drops to 3-4 for a 75% inlet relative humidity flow.

Chen et al. [113], proposed a similar study regarding the droplet instability regimes in the flow channels. Rather than investigating the flow regimes in the flow channels, they developed macroscopic force balance models for spherical and cylindrical droplet shapes that would predict the necessary conditions for droplet instability. In their model, basic parameters were the drag force exerted on a partially grown droplet and the total surface tension force on the droplet mainly determined by the contact angle hysteresis. At the equilibrium state, these forces must be equal to each other and solving
the appropriate equations will yield the contact angle hysteresis at this condition. According to their results, for a fully grown spherical droplet, the channel length to height ratio by the capillary number greater than $\pi/12$ will prevent channel blockage. This value drops to $1/6$ for a cylindrical droplet. This indicates it is easier to remove the cylindrical droplets than spherical ones. They also predicted an instability region for partially developed droplets and compare the results for different channel geometries, solid state contact angles and flow velocities. Lengthening the flow channel, increasing the flow velocity and using a more hydrophobic DM (contact angle $>110^\circ$) will enlarge the droplet instability region. Their results were validated by a visualization experiment performed on a simulative transparent fuel cell, in which the actual operating conditions were simulated by a flow velocity of 5 m/s, liquid water production of 0.3 $\mu$l/min and solid state contact angle of 110$^\circ$. The comparison curves are shown in Figure 2-9.

Other experimental visualization techniques such as magnetic resonance imaging [114-116] and x-ray tomography [117-119] also measure the real time liquid water accumulation in a fuel cell. An excellent comprehensive review of the visualization techniques in fuel cells is given by Bazylak [120]. The drawback of all of these techniques is they have to use an experimental fuel cell with unconventional bipolar plate material, such as plexi-glass or other non-metal materials, which is not used in real operation. The neutron imaging solves this problem by enabling use of actual-stack-size fuel cells and therefore it is a very powerful diagnostic tool.
Figure 2-9: From top to bottom; effect of air-velocity, channel length and DM properties on droplet stability [113].
CHAPTER 3

METHOD OF APPROACH

In this study, in-plane and through-plane neutron imaging techniques were used to determine the water accumulation in the fuel cell both qualitatively and quantitatively. Basic steps of the data collection processes are described in the following sections for the in-plane neutron imaging technique developed in The Pennsylvania State University Breazeale Nuclear Reactor. First, the neutron images were collected with a data acquisition system. Then the qualities of the images were improved using image post-processing techniques. Finally, the liquid water distribution and quantification was performed with using the water quantification system. The high-resolution, through-plane imaging developed in National Institute of Standards and Technology (NIST) is briefly described in this chapter. For the details, author is referred to Hussey et al. [95].

3.1 In-plane Neutron Imaging Data Acquisition System

The images of the fuel cell located in front of the neutron beam source were recorded by a charge-coupled device (CCD) camera. A video capturing software program, Streampix, collects and records the fully digital video signal produced by the CCD camera system on a customized PC. The individual frames taken by the camera were sent to the computer in digitized form. The images were stored on a date and time-based file structure with each image containing a time stamp for which it was recorded. This feature allows single images of interest or multiple sequential images to be easily located and analyzed.
The Streampix software has a user-friendly interface that controls several parameters of an experiment. The system’s maximum frame grab rate is 30 frames per second and the number (sampling rate) can be changed by the user from 1 to 30 frames per second. A lower frame grab rate requires less disk space on the computer’s hard drive, and should be utilized when a lower temporal resolution is sufficient. The length of an experiment is also controlled by the software.

### 3.1.1 Image Post-Processing

Several post-process image enhancement techniques, developed in-house, by A. Kevin Heller, Ph.D. Candidate in Nuclear Engineering, were used to increase the overall image quality and accuracy of the water quantification process. Fluctuations in the reactor power level are minor, but can be 1% and result in changes in the neutron beam flux and consequently the corresponding measured pixel luminance values. By monitoring a static reference location on each image that was recorded, such as the fuel cell backing plate, the beam intensity between each frame was determined and the entire image is normalized accordingly. This procedure is referred to as Reactor Power Normalization. \( L_{x,y,t=0} \) represents the pixel luminosity value of the reference location at \((x, y)\) within the pixel array. The value \( t \) refers to the frame number, where \( t=0 \) is the initial frame. A correction value, \( Z_t \), is created for each following image \( (t=1, 2, 3, \ldots) \) and creates a corresponding normalized image. The variables \( M \) and \( N \) represent the entire pixel array and are 640 and 480, respectively.
The intensity of the neutron beam is not perfectly uniform across the fuel cell image plane. This results in different pixel luminance values even where material attenuation characteristics and thicknesses are identical. Each image recorded during an experiment is divided by a blank image (only the uninterrupted neutron beam) and then multiplied by the average pixel intensity of the blank image. This produces a “flattened” image making the initial beam intensity uniform on the fuel cell. It was assumed that the neutron beam shape is constant for each experiment.

\[
L_{x,y,1} - L_{x,y,t=0} = Z_1
\]

\[
\begin{bmatrix}
L_{11} & L_{12} & \ldots & L_{1N} \\
L_{21} & \ldots & \ldots & \ldots \\
\vdots & \ddots & \ddots & \ddots \\
L_{M1} & \ldots & \ldots & L_{MN}
\end{bmatrix}
- 
\begin{bmatrix}
Z_1 & Z_1 & \ldots & Z_1 \\
\vdots & \ddots & \ddots & \ddots \\
Z_1 & \ldots & \ldots & Z_1
\end{bmatrix}
= 
\begin{bmatrix}
L_{11} & L_{12} & \ldots & L_{1N} \\
L_{21} & \ldots & \ldots & \ldots \\
\vdots & \ddots & \ddots & \ddots \\
L_{M1} & \ldots & \ldots & L_{MN}
\end{bmatrix}_{\text{Normalized}}
\]

\[
L_{\text{avg}} = \frac{1}{MN} \sum_{1}^{M} \sum_{1}^{N} L_{MN}
\]

\[
\begin{bmatrix}
L_{\text{avg}} & L_{\text{avg}} & \ldots & L_{\text{avg}} \\
L_{\text{avg}} & \ldots & \ldots & \ldots \\
\vdots & \ddots & \ddots & \ddots \\
L_{\text{avg}} & \ldots & \ldots & L_{\text{avg}}
\end{bmatrix}
\begin{bmatrix}
L_{11} & L_{12} & \ldots & L_{1N} \\
L_{21} & \ldots & \ldots & \ldots \\
\vdots & \ddots & \ddots & \ddots \\
L_{M1} & \ldots & \ldots & L_{MN}
\end{bmatrix}
= 
\begin{bmatrix}
Q_{11} & Q_{12} & \ldots & Q_{1N} \\
Q_{21} & \ldots & \ldots & \ldots \\
\vdots & \ddots & \ddots & \ddots \\
Q_{M1} & \ldots & \ldots & Q_{MN}
\end{bmatrix}
\]

\[
\begin{bmatrix}
L_{11} & L_{12} & \ldots & L_{1N} \\
L_{21} & \ldots & \ldots & \ldots \\
\vdots & \ddots & \ddots & \ddots \\
L_{M1} & \ldots & \ldots & L_{MN}
\end{bmatrix}
\begin{bmatrix}
Q_{11} & Q_{12} & \ldots & Q_{1N} \\
Q_{21} & \ldots & \ldots & \ldots \\
\vdots & \ddots & \ddots & \ddots \\
Q_{M1} & \ldots & \ldots & Q_{MN}
\end{bmatrix}
= 
\begin{bmatrix}
L_{11} & L_{12} & \ldots & L_{1N} \\
L_{21} & \ldots & \ldots & \ldots \\
\vdots & \ddots & \ddots & \ddots \\
L_{M1} & \ldots & \ldots & L_{MN}
\end{bmatrix}_{\text{Flattened}}
\]
Random noise and noise caused by the analog to digital conversion process can cause time varying error. To account for this, the luminance value of corresponding pixels within sequential images can be averaged together. This process improves image quality and makes liquid water accumulation and movement more discernible.

\[
L_{\text{avg},MN} = \frac{1}{t} \sum_{0}^{t} L_{MN}
\]

### 3.1.2 Water Quantification System

The ability to store individual images digitally allows for easy post-process analysis including ascertaining pixel luminance values within the fuel cell. Consequently, the determination of water content within the cell as a function of time is attainable by referencing a pre-generated calibration curve which correlates water thickness to pixel luminance. This curve is generated using a water-filled wedge, constructed of aluminum (Al alloy 6061-T6) as shown in Figure 3-1.

![Figure 3-1: Aluminum water-filled calibration wedge.](image)
It has the exact same through-plane dimensions to duplicate the neutron attenuation and scattering effect of the cell. The water wedge is connected to the fuel cell during experiments. The wedge contains a water filled void of continuously varying thickness. The steady and gradual decrease in pixel luminance from the bottom to top of the wedge is representative of the increasing water thickness level within the wedge. Through statistical analysis of the wedge, pixel luminance values were recorded at the known water thickness levels producing a correlation curve as seen in Figure 3-2.

![Figure 3-2: Typical calibration curve for water thickness vs. neutron attenuation.](image)

This curve can then be referenced to assign water thickness values to areas within the cell. The mass and volume of water in the cell can then be computed for finite instances or as a varying function of time. The anode and cathode side inlet and exit portions of the flow field were not included in water quantification process. The portion of the flow field where the heaters are placed also removed in order to eliminate the artifact of heater. The quantification of liquid water within the cell is comprised of line-averages of water through the entire fuel cell assembly (i.e., gas flow channels, MEA,
and gas diffusion media). Therefore, it is not possible to determine the difference in cathode and anode side water quantitatively. This could be achieved by looking to the real-video where the liquid water motion can be detected. Since the cathode and anode flow directions are known, it is then possible to determine which side the water accumulated. This is only a qualitative analysis. A correlation curve is generated for each experiment to account for differences in the neutron beam flux and reactor power level between an experimental run. This method works well in this application because the water thicknesses are at most 1 mm, and they are typically less than 250 μm. Thus, there are essentially no multiple neutron scatters.

Prior to the operation of the fuel cell, an image was taken in which there was no liquid water. This image is called the dry-image. Then, a total of 60 images, at 5 frames per second for 12 seconds, were taken for all data shown. All 60 frames were averaged together into a single image to reduce instrument noise and pixel variance. After that, every averaged image was divided by the dry-image. This method produces an image of only liquid water in the cell. Then the liquid water was quantified using the calibration curve, as described above. To improve qualitative analysis and the presentation of single images or video, false colorization technique was applied to the liquid water in the fuel cell. Pixels pertaining to liquid water were assigned a shade of red while the remaining pixels within the fuel cell were remained on a gray scale.

### 3.1.3 Water Quantification Capability

The minimum detectable water thickness in the current system was measured by subsequent experiments with an in-house constructed water calibration channels. The
results proved that the observable limit of liquid water is \( \sim 12.7 \) \( \mu \)m. Liquid water thicknesses (e.g. total accumulated liquid water in the line-of-sight of the neutron beam including anode and cathode) less than \( 12.7 \) \( \mu \)m are below the current detectability limit of the imaging system. For example, the total water content in the vapor-phase is not observable, since the equivalent liquid thickness of the moist gas is well below \( 10 \) \( \mu \)m. Thus, our imaging system only observed liquid water (\( > 12.7 \) \( \mu \)m thickness) in this application, and is not affected by variations in the gas-phase humidity. It is possible to determine the amount of water under the landings and in, or under the flow channels, using a masking technique developed at PSU.

3.2 In-plane Neutron Imaging Experimental Setup and Design

3.2.1 Neutron Imaging Facilities at Penn State University

The neutron radioscopy system and thermal neutron beam from the Breazeale Nuclear Reactor at the Penn State Radiation Science and Engineering Center was utilized in this study. Specialized image processing hardware was developed for the analysis, storage and presentation of the collected images. The Penn State Breazeale Nuclear Reactor (PSBR) is located at the Penn State Radiation Science and Engineering Center (RSEC). The pool-type reactor utilizes a Training Research Isotope production General Atomics (TRIGA) core. The core operates at a maximum steady-state power level of 1000 kW. Using a \( \text{D}_2\text{O} \) tank to thermalize neutrons and a graphite reflector, a well-collimated beam of thermal neutrons is available for transmission to one of seven beam ports located in the facility. At a maximum reactor power level of 1000 kW, the neutron flux at the port aperture is approximately \( 3 \times 10^7 \) neutrons/cm\(^2\)sec. The current temporal
and spatial resolution for radioscopy is approximately 30 frames · sec\(^{-1}\) and 129 μm · pixel\(^{-1}\) in the 50 cm\(^2\) active area. Continuous digital radioscopy can be recorded for up to 45 minutes.

### 3.2.2 Experimental Setup

An integrated fuel cell test station at the NBL was necessary in order to control and monitor the operating parameters of the cell while neutron imaging was conducted. The NBL Test Station (NBLTS) was designed user-friendly so that it was isolated from the neutron beam source by a thick concrete enclosure, protecting the operator and station components from radiation poisoning and contamination. The layout of the station is illustrated in Figure 3-3.

---

**Figure 3-3:** Schematic of experimental setup and picture of the fuel cell used in the experiments.
The station can accommodate various sized fuel cells, from 14 cm\(^2\) to 250 cm\(^2\), for neutron imaging processes. Several operating conditions can be controlled through this station, i.e. inlet gas flow rates, inlet gas temperature and inlet relative humidity of anode and cathode side, fuel cell temperature, fuel cell voltage and operating current, and cell pressure. The NBLTS performance was validated against the performance of other well established test stations at the Penn State Fuel Cell Dynamics and Diagnostics Laboratory (FCDDL). The anode and the cathode gas flows are controlled by digital mass flow controllers (MKS Technologies, M100B) that utilize a thermal sensor design for accurate flow measurement. To ensure better accuracy across a wide range of flow rates, a low-flow rate (50 sccm) and a high-flow rate (10000 sccm) controller were incorporated for both the anode and the cathode. The flow controller set points are established and monitored using a “Power Supply and Readout System” (MKS, 247D). The 4-channel unit has a digital LED display with a sequentially selectable single readout. The NBLTS is also equipped with a nitrogen purge option which allows the operator to exhaust reactant gases from the fuel cell and the test station gas lines at any time. This feature is especially important for freeze-thaw applications where the residual liquid water inside the fuel cell has to be removed before shut-down in order to avoid freezing inside the diffusion media.

The fuel cell control system utilizes a 1kW electronic loadbank (Fideris, Inc.). The anode and the cathode gas flows are controlled by calibrated digital mass flow controllers (MKS Technologies, M100B). The relative humidity of the reactant gases is controlled through a calibrated active feedback control humidification subsystem. Due to the significant amount of water exiting the cell from the humidified flow and water
produced at the cathode, condenser units were designed and installed at the cell exits. The unit removes and collects the water in the flow by rapidly cooling the gas flow temperature. This process eliminates the blockage of gas flow down stream of the fuel cell by water that may condense in the long exhaust lines. The fuel cell operating pressures are individually controlled by back-pressure regulators (Tescom Corp., 44-2361-24). The regulators are positioned down stream of the cell, and the pressure is monitored using standard 0-100 psig dial gauges. In addition, voltage output-pressure transducers (Omega Engineering, PX213-060G5V) are capable of measuring and recording in real-time the gas flow pressures. All of the temperature control processes are managed using PID temperature controllers (Omega, CN9300). The fuel cell temperature is monitored from the cathode backing plate. Two 6.3 mm diameter cartridge heaters, one in each fuel cell backing plate, provide heat, while small fans operate to convectively remove excess heat. The gas flow lines and humidifiers are heated using resistive heat tapes (BriskHeat, BSAT051010/BSAT101010).

Fideris Inc.’s Electronic Loadbank Fuel Cell Test System is a MOSFET variable resistance loadbank unit with a maximum power dissipation of 1 kW. Located on the NBLTS, the system allows for full-user programmable operation of the fuel cell using the accompanying FC Power™ Software. The operator can choose from constant current, constant voltage, or constant power modes of operation. In addition, the unit is also equipped with current ramp and pulsed current modes; where ramp rate, amplitude, duty cycle and frequency are adjustable. The maximum current rating of the loadbank is 1000 Amps and the maximum voltage rating is 20 Volts.
3.2.3 Fuel Cell Design

A 50 cm$^2$ active area fuel cell with seven different flow field patterns was used for testing. The channel and landing sized were varied between 0.5 mm to 2.0 mm. The related properties of each configuration, along with the detailed test matrix are shown in Chapter 4. A 25 μm thick, 0.4/0.4 mg/cm$^2$ Pt loading Gore 5510 MEA and a 210 μm thick, 70% porosity, Johnson-Matthey diffusion media were used in all configurations. In all configurations, fully humidified inlet conditions at the cell temperature were maintained with 7.35 psig cell pressure and anode/cathode stoichiometries of 2 / 2. A counter-flow arrangement was utilized at each test configuration.

In order to reduce the overall attenuation and scattering of the neutron beam, special design considerations are applied to many of the fuel cell components. The graphite flow field plates found in a standard PEFC were replaced with aluminum plates in order to decrease the neutron attenuation of the bi-polar plates. The aluminum plates were coated with a very thin layer of gold for conductivity purposes. The attenuation and scattering of neutrons caused by the gold layer was negligible due to its very small thickness. The cell compression plates and current collectors were also constructed of aluminum (Al Alloy 6061-T6). Thicknesses of the components of fuel cell are also reduced in order to minimize the neutron attenuation.

3.3 Through-plane High Resolution Neutron Imaging

The neutron imaging facility at the National Institute of Standard and Technology (NIST) was used to perform through-plane neutron radiography tests. The details of the
test facility were given in Hussey et al. [95]. The main difference from the in-plane imaging technique is the use of micro-channel plate (MCP) based detector which basically is a glass structure with open channels that has center-to-center separation of \(\sim 10\mu\text{m}\). The walls of the a few micron thick glass is loaded with neutron absorbing material, such as boron or gadolinium, that emits charges particles when hit by neutrons. To amplify the emitted particles, a high voltage (5kV) was applied to the MCP stack which creates an electron cloud amplified by order of \(10^6\). This method results in detector resolution of \(\sim 2\) times the separation of open channels which is adequate to differentiate the anode and cathode GDL and flow channels via cross-sectional imaging. The main challenge for this method is the electronic readout limitations which are currently 200kHz with a 1% dead time. This limitation results in imaging of small areas with \(\sim 2\text{cm}\) diameter.

In all tests, each neutron image has 54 seconds of total integration time and 15.4 x 15.4 \(\mu\text{m}\) pixel resolution. The fuel cell used in all of the tests has an active area of 17.2 cm\(^2\) and was machined out of 6061 aluminum with a gold plated, single serpentine design flow channels having 1 mm width and 1 mm depth. The width of the landings was also 1 mm. A Gore Primea 5710 MEA and two SGL 10BB diffusion media were used in all experiments at a cell temperature of 65 \(^\circ\text{C}\), and a cell pressure of 1 atm. Anode and cathode flows were fully humidified with stoichiometric ratios of 1.5 and 2.0, respectively.

Two different channel wall surface conditions were used in the experiments. In the first set of experiments, an imaging area consisting of 4 channels and 3 landings at the bottom of flow field centerline, as shown in Figure 3-4, was selected and a PTFE coating
was applied to the cathode flow channel walls only. The uncoated gold-plated walls are naturally hydrophilic. The through plane water distribution data were obtained for 0.2 A/cm$^2$ and 1.0 A/cm$^2$ current density conditions at various times. For the second set of experiments, a PTFE coating was applied only to the anode flow channel walls of an imaging area of 4 channels and 3 landings at the top of flow field centerline. The neutron images were taken at the same current conditions as the first set of data to compare the effect of PTFE coating on channel wall surface. For both sets of experiments, the fuel cell was purged with dry nitrogen for 5 minutes prior to applying current, to ensure similar initial conditions.

Figure 3-4: Schematic of test cell and imaging area used in all through-plane imaging tests.
CHAPTER 4

IMPACT OF FLOW FIELD DESIGN ON LIQUID WATER STORAGE AND CELL PERFORMANCE

In this chapter, the effect of the flow-field design on water accumulation and distribution in the fuel cell is presented. Seven different flow-field configurations were tested and in each configuration, a distinct landing to channel (L:C) ratio was used, ranging from 1:3 to 2:1. The neutron images and water mass values were analyzed to understand the impact of channel and landing dimensions on liquid storage inside the DM and flow channels. The liquid transport and flooding behavior were also investigated based on flow field configuration. Furthermore, the differences in water amounts between the configurations were explained in terms of the interface effects and mass-transfer characteristics. Finally the cell performance of different flow field designs were recorded and compared with the corresponding liquid storage levels to investigate the possibility of a passive water management method through flow field design without sacrificing from the cell performance.

4.1 Impact of Channel Size on Liquid Water Storage, Distribution and Flooding.

The effect of flow field channel width on the liquid water accumulation and residual liquid water content was analyzed by performing the tests listed in Table 4-1. Table 4-2 and Table 4-3 show the geometric parameters and resulting calculated water mass values respectively.
Table 4-1: Test matrix followed in the experiments.

<table>
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<tr>
<th>Cell Configuration</th>
<th>Current Density (A/cm²)</th>
<th>Cell Temp. (°C)</th>
<th>Cell Pressure (kPa)</th>
<th>Inlet Relative Humidity</th>
<th>Stoichiometry</th>
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<td>80</td>
<td>150</td>
<td>100%</td>
<td>2 / 2</td>
</tr>
<tr>
<td>0.5 x 1.5</td>
<td>0 --&gt; 1.5</td>
<td>80</td>
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<td>100%</td>
<td>2 / 2</td>
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<tr>
<td>1.0 x 0.75</td>
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<td>100%</td>
<td>2 / 2</td>
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<tr>
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<td>80</td>
<td>150</td>
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<td>2 / 2</td>
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</tr>
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<td>150</td>
<td>100%</td>
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Table 4-2: Cell configurations and corresponding channel/landing ratios.

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<th>L/(C:L) Ratio</th>
<th>#Channel-DM interfaces</th>
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Table 4-3: Calculated water mass values under the landings and in, or under the channels are shown together with the flow velocities.

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Among those experiments, two representative conditions were selected to illustrate the difference in liquid water content in the fuel cell at different channel sizes. In Figure 4-1 (a) and (b) neutron images of cell configurations 1.0x1.5 and 1.0x0.75 (L:C) are shown.

![Neutron images of cell configurations](image)

**L/C: 1.0x1.5 Cell**
- Total Liquid Water Mass = 361 mg
- Land DM Liquid Water Mass = 151 mg
- Channel Liquid Water Mass = 210 mg

**L/C: 1.0x0.75 Cell**
- Total Liquid Water Mass = 515 mg
- Land DM Liquid Water Mass = 281 mg
- Channel Liquid Water Mass = 234 mg

**Figure 4-1:** Neutron images of 1.0x1.5 and 1.0x0.75 cell configurations at 10 A, 100% RH, 150 kPa (7.35 psig) operating conditions are shown together with the calculated water mass values. The total water mass and channel water mass is greater in small channel case.

The total water content calculated for the large channel (Figure 4-1a) configuration (361 mg) is almost 50% smaller than the small channel configuration (Figure 4-1b, 515 mg). For the small channel case, a significant increase (86%) was observed in the liquid storage under the landings and a relatively small difference (11%) was observed for liquid storage in or under the channels compared to the large channel size. In Figure 4-2a and 4-2b, cell configurations 0.5x1.5 and 0.5x0.5 are shown. Similar
trends were also observed between the smaller and larger channel patterns. The total residual water in the small channel configuration was 468 mg, which is ~66% greater than the larger channel case. There was also more channel water accumulation in the small channel cell as indicated in the figure. These results clearly suggest that the water distribution and the residual water content in the cell strongly depend on the flow field geometry, and they are not just a function of DM properties. They also indicate that a strong interaction is present between the DM|land interface since different flow field dimensions directly results in different number of DM|land interfaces as shown in Table 4-2.

![Figure 4-2: Neutron images of 0.5x1.5 and 0.5x0.5 cell configurations at 40 A, 100% RH, 150 kPa (7.35 psig) operating conditions are shown. Similar trends to previous configuration were also observed in this case.](image)
The different channel and landing widths of each cell configuration results in different landing and channel areas and the differences found in residual water content might be simply due to this fact which may not reflect a true geometry effect. Therefore, it is required to standardize the water mass values obtained with the images such that the results will not reflect the effect of different landing and channel areas. In order to achieve this, the calculated water mass values from the neutron images were normalized according to the corresponding geometry and these normalized values were compared to understand the generic effect of flow field design on residual water content. In this calculation, the channel and landing area of each design, calculated using Table 4-2, was taken as the normalization parameter and calculated water mass values were divided by these areas. Then the effective liquid storage levels under the landings and in, or under the channels were calculated to determine the geometry effect. The liquid storage values per unit surface area are called “specific water storage” values. In Figure 4-3, the normalized water contents of 0.5x1.5 and 0.5x0.5 configurations are shown. The difference in liquid storage amounts for the small channel and large channel cases can be clearly seen from the figure. For example, at 0.8 A/cm² and 100% RH, the water amount in or under the channels for 0.5x1.5 cell is 193 mg and the channel area of this configuration is 38.2 cm² (based on Table 4-2, there are 11 landings and 12 channels). Hence, the specific water storage in or under the channels for this configuration is ~5.0 mg/cm². The 0.5x0.5 cell on the other hand, has 223 mg water in or under the channels with its channel area being 25.5 cm² (based on Table 4-2, there are 23 landings and 24 channels) which increases the specific water storage in or under the channels to ~8.7 mg/cm². It is seen that even though the effect of larger channel area in 0.5x0.5
configuration is eliminated from the results, there is still ~75% more water storage in or under the channels in this design compared to 0.5x1.5 case. These results clearly show that the flow channel size has significant impact on liquid storage with larger channel widths resulting in lower liquid storage in or under the channels.

![Graph showing water mass values for 0.5x0.5 and 0.5x1.5 configurations.](image)

Figure 4-3: Normalized water mass values for 0.5x0.5 and 0.5x1.5 configurations. Larger channels tend toward lower liquid saturation, lands generally carry more water.

The differences in liquid water accumulation and storage due to channel size effect also have important consequences on cell performance. The cell performance data of 0.5x0.5 and 0.5x1.5 configurations are shown in Figure 4-4. The kinetic and ohmic regions for each configuration are almost identical, however, the polarization region of the performance curves shows significant difference. The performance of the fuel cell with smaller channel width deviates from the linear behavior at the high current region,
starting from 1.2 A/cm² which indicates significant flooding losses in the cell. This was not observed with the larger channel width. The specific water storage values in or under the channels were analyzed to understand the reason of this difference. For the 0.5x0.5 case, the specific water storage in or under the channels at 1.2 A/cm² is 6.5 mg/cm² and for the 0.5x1.5 case, it is 4.0 mg/cm², which corresponds to a 60% more liquid storage in smaller channel width case. To be consistent, the difference in specific water storage under the landings between the two cases was calculated, and 0.5x0.5 configuration was also found to have more liquid storage (~60%). These differences explain the observed flooding losses with the smaller channel widths since both under the landings and in or under the channels contain more liquid to block the diffusion pathways and prevent sufficient reactant transport to the reactions sites that will result significant decrease in the cell performance.
In Figure 4-5, a possible liquid water accumulation scenario in the DM is given that is consistent with the results shown. For the small channel configuration, the accumulated liquid water under the landings can easily be connected within the DM pores under the channels and block reactant access through the DM. This could decrease the reactant diffusion drastically yielding to severe flooding losses. For the large channel case, although there is still some liquid water in the DM, due to absence of saturated and connected DM structure, performance at high current region is much better compared to the small channel case.

Figure 4-4: Polarization curves for cell configurations 0.5x0.5 and 0.5x1.5. Performance loss due to flooding behavior is observed for the small channel configuration indicating the effect of channel size on cell performance.
Data presented in Table 4-3 were further analyzed in Figure 4-6. Water mass values at each current density were plotted against the cell configuration. At the horizontal axis of the plot, landing size over channel/landing ratio of each configuration is shown. The purpose is to differentiate the three configurations with L:C ratio being unity *i.e.* 0.5x0.5, 1.0x1.0 and 2.0x2.0. In Table 4-2, the configurations corresponding to these values are given. From the figure, it appears as there are three distinct ratios where the residual water in the cell is minimal. The first two have small L:C ratios, *i.e.* 1:3 and 2:3 respectively, and a small landing size. The third minima is a large channel configuration with the L:C ratio being unity *i.e.* 2.0x2.0 configuration. When compared
to other configurations where this ratio is also unity, 2.0x2.0 configuration has significantly less residual water at all current density conditions. An important observation is made from these regions such that, effect of water distribution and storage basically depends on two different flow field scenarios; 1) L:C ratio is unity, 2) landing / channel ratio is different than unity. In the following paragraphs, each scenario is discussed in detail.

![Figure 4-6: Water mass values calculated at different channel/landing ratios. There are three configurations with L:C ratio being unity. To differentiate those configurations, water mass values are plotted against landing size divided by channel/landing ratio.](image)

Water mass values of three configurations with L:C ratio being unity are plotted at Figure 4-7. The 0.5x0.5 and 1.0x1.0 cases have considerably higher water mass values compared to the 2.0x2.0 cell. It is important to note that landing and channel areas and
flow velocities of all three configurations are identical. Therefore, the difference in the calculated water mass values is suspected to be due to the DM|channel interface effects in the cell.

The number of interfaces between the channel and DM is calculated for all the cell configurations and shown in Table 4-2 to investigate this phenomenon. As it is seen from the table, there are 12 interfaces at the 2.0x2.0 configuration which has the lowest water mass and 48 interfaces at the 0.5x0.5 configuration which has the highest water mass values. This definitely indicates that with the decreasing number of interfaces, the water storage in the cell also decreases. It is expected to have more liquid suction from

![Figure 4-7: Water mass values for configurations that have unity landing to channel ratio are shown.](image)
DM with larger number of interfaces which seems to be a contradiction with our results. However, there is another factor effecting the liquid removal from the channels which is the liquid film layer formation on the channel walls as a function of channel wall surface energy. This subject is investigated extensively in the following chapter of this thesis, however, a very brief explanation is given here without the detailed analysis. As the liquid suction at the DM|channel interface increases, depending on the channel wall surface energy, a thin liquid film on the channel walls can easily be formed. This is also called as the annular flow regime and once this regime is formed, it is difficult to remove the water from the channels. In our case, all of the configurations have the identical channel wall surface energy. Therefore, the configuration with the highest DM|channel interface will have more liquid film formation on the channel walls which will result in more residual water for 0.5x0.5 case. This can also be observed from the neutron images shown in Figure 4-8. This figure will be explained in detail in the following chapter through the analysis of channel wall surface energy condition. At this point, only the conclusion is made such that larger number of interfaces for the same L:C ratio results in more liquid water with the channel wall surface energy condition used in these tests.
Figure 4-8: The effect of DM|channel interface number on channel liquid film formation is shown. 0.5x0.5 cell has the highest DM|channel interface and in all current conditions, it has more liquid film in the channels.
In the second scenario, the L:C ratios are different than unity. In Figure 4-9, water mass values of 0.5x1.5, 1.0x1.5 and 1.0x0.75 are shown. Corresponding L:C ratios and number of interfaces are listed in Table 4-2. The interface effect explained above is not observed in this scenario. As seen from the table, number of interfaces is almost same for 0.5x1.5, 1.0x1.5 and 1.0x0.75 cases; 24, 18 and 26 respectively, but there is much less liquid water in 0.5x1.5 configuration compared to 1.0x0.75 case. This behavior is explained through the L:C ratio effect. It is seen from Figure 4-9 that as L:C ratio increases, water mass in the cell also increases. A simple single-phase mass transfer calculation is performed, for 1:3 and 4:3 L:C ratios assuming laminar, fully-developed, steady flow in the channels. The calculation is shown in appendix. The results showed that mass transfer in the 1:3 case is 1.6 times higher than the 4:3 case, which is suspected to be the reason of difference in water mass values. In global sense, this suggests it is better to design L:C ratios smaller than 2:3. This result is in general agreement with the modeling study of Natarajan et al. [33] in which they have performed performance simulations with L:C ratios of 1:3, 1:1 and 3:1 and concluded that, cell performance increases with decreasing L:C ratio. It is suggested to design flow fields with L:C ratios closer to 1:3. Furthermore, they found that liquid saturation under the landings is always higher than that of under the channels which is also found in our tests.

In summary, the residual water content in the fuel cell DM and channels strongly depends on channel size and landing to channel ratio. For smaller channel size (and L:C ratio), the residual water in both the channels and the entire DM increases drastically. Furthermore, this configuration yields significant performance loss due to flooding behavior.
The second effect investigated in this study is the flow field landing size effect on liquid water accumulation and distribution. In Figure 4-10a and 4-10b, neutron images of two different flow-field configurations, 2.0x1.0 and 1.0x1.0 (L:C), are shown.

Figure 4-9: Water mass values for configurations that have landing to channel ratio different than unity are shown.

4.2 Impact of Landing Size on Liquid Storage, Distribution and Flooding

The second effect investigated in this study is the flow field landing size effect on liquid water accumulation and distribution. In Figure 4-10a and 4-10b, neutron images of two different flow-field configurations, 2.0x1.0 and 1.0x1.0 (L:C), are shown.
The calculated water mass value under the landings for 2.0x1.0 case is 428 mg, 40% greater than that in, or under the channels. This result was also seen in previous images and was a general trend for the other test conditions. Hence, for the fuel cell used, it can be said that water preferentially accumulates under the landings. This is expected for a couple of reasons; 1) thermal effects, such that condensation of water vapor on landing surfaces due to high heat removal rate, and 2) inability for water removal from these locations. The water content in both configurations was compared and it is observed there is more residual water in the large landing configuration (735 mg) than small (584 mg).

The total water mass values were plotted at each current condition and illustrated in Figure 4-11. At each cell configuration, the behavior of water content in the cell is
similar when plotted against the performance. After a peak in water content at \( \sim 20 \text{ A} \), water removal from the cell due to increased flow rate is dominant over water production in the cell due to increased current. The non-monotonic relationship between liquid water and current could be due to the competing forces of increased channel shear with current density that tends to remove water, and increased production of water with current density, and the thermal boundary conditions (\textit{i.e.} heater operation).

![Graph showing total water mass curve for 2.0x1.0 and 1.0x1.0 conditions.]

Figure 4-11: Total water mass curve for 2.0x1.0 and 1.0x1.0 conditions.

The specific water storage values for 2.0x1.0 and 1.0x1.0 configurations were plotted in Figure 4-12. Similar to the results obtained for channel size effect, the liquid saturation levels for each configuration were observed to be different indicating there is an independent landing effect on water accumulation and storage. From the figure, it is
observed that there is higher specific water storage in the larger landing case. This is also consistent with the results obtained from the neutron images.

The cell performance comparison for each configuration was also made. Performance data of each cell were recorded and plotted in Figure 4-13. In addition to analyzing the effect of landing size on cell performance, an important conclusion was also derived from these plots. The performances of both cells are almost identical at low current although the residual water contents are very different. For example, at 0.2 A/cm² condition, both configurations have ~0.8 V performance. However, in the small landing case there is 20% less liquid water compared to the large landing case (525 to 631mg).

Figure 4-12: Normalized water mass values for 2.0x1.0 and 1.0x1.0 configurations are shown. Results indicate there is a geometric effect. Larger landings tend toward higher liquid saturation especially as current increased.
Hence, it is clear that, operating current is not the only criterion determining the water accumulation in the cell. Due to different flow field geometries, there could be different residual water contents in the cell even though electric power output is identical. This result has important implications on freeze thaw and other degradation issues. The second observation from the figure is the difference in flooding behavior between two configurations. In large landing case, there occurs a significant performance drop due to flooding losses whereas for the small landing case, an improved polarization performance is observed. Hence, in terms of obtaining best performance with sustaining residual water amount at a minimum level, it is better to design small landing size flow-fields.
Figure 4-13: Cell performance for (a) 2.0x1.0 and (b) 1.0x1.0 configurations. There is 20% less water storage in 1.0x1.0 case with identical performance at 0.2 A/cm$^2$. 

Flooding due to concentration loss

Improved performance, less flooding
In the literature, several studies mentioned that increasing the channel velocity reduces the residual water content in the cell although it is not preferable due to high parasitic power consumption and high operation cost. This is valid for a distinct flow field configuration. However, in this study, it is seen that, the effect of flow field geometry has a deterministic role in water accumulation, more so than the channel velocity. In Figure 4-14, for conditions 1.0x1.0, 2.0x1.0, 0.5x0.5 and 0.5x1.5, the water mass values and cathode channel velocities were plotted at each current density condition. Conditions 1.0x1.0 and 2.0x1.0 emphasize the landing size effect. At 0.4 A/cm² condition, the velocity graph shows that cathode velocity for the large landing configuration is ~4.1 m/s whereas small landing velocity is ~2.7 m/s. That is large landing configuration has ~52% higher channel velocity. However, residual water in this configuration is ~26% greater than small landing case (735 mg and 583 mg, respectively). The behavior is similar for the different channel configurations also. Moreover, this trend is observed at all the current density conditions revealing the strong effect of landing and channel interface on water storage and accumulation in the cell. The larger landing size prevents removal of water from the cell even though channel velocity is relatively high. Similarly, small channels tend to retain more water even at high channel velocities. Thus, increasing the parasitic power and operation costs to obtain better water management in the fuel cell is not necessarily the only solution and instead it might be more efficient to re-design the flow field geometry.
The results obtained in this chapter can be summarized as follows;

- The liquid water storage and the corresponding cell performance data were obtained for seven different flow field geometries with L:C ratio ranging from 1:3 to 2:1. The results may serve as validation data for the models predicting the liquid saturation inside fuel cell components.

- The liquid water mass data obtained for different channel and landing dimensions were normalized by the corresponding channel and landing areas to obtain the

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**Figure 4-14:** Cathode velocity and water amount is plotted at each current density condition for 0.5x0.5, 0.5x1.5, 1.0x1.0 and 2.0x1.0 cell configurations.

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**4.3 Summary**

The results obtained in this chapter can be summarized as follows;

- The liquid water storage and the corresponding cell performance data were obtained for seven different flow field geometries with L:C ratio ranging from 1:3 to 2:1. The results may serve as validation data for the models predicting the liquid saturation inside fuel cell components.

- The liquid water mass data obtained for different channel and landing dimensions were normalized by the corresponding channel and landing areas to obtain the
“specific water storage” values. This way, the effect of different channel and landing area is eliminated.

- For different channels size configurations, the liquid water distribution were analyzed and significantly more channel liquid accumulation was observed in flow fields with smaller channel width.

- The liquid mass data and the specific water storage values for different channel size configurations were compared. The results showed that channel size has significant impact on the liquid storage. The specific water storage in smaller channel width configuration was found to be ~75% more than that in larger channel width case.

- The cell performances of two different channel size configurations were compared. The results showed significant mass transport (flooding) losses in smaller channel size cell at high current. The specific water storage at high current operation in small channel cell was found to be ~60% higher than larger channel cell which is the reason of the observed flooding losses.

- A flooding mechanism is suggested depending on the channel size.

- The number of land|channel interfaces found to be the determining factor in liquid storage, especially inside the flow channels, for the configurations having L:C ratio of unity. As the number of interfaces increase, more liquid storage inside the channels was observed at every current.

- For L:C ratios different than unity, the liquid storage was found to decrease with decreasing L:C ratio. The reason was explained through a single-phase mass transfer calculation between a small and a large L:C ratio case.
• The effect of landing size on liquid storage and flooding was also analyzed. The specific water storage in larger landing case found to be significantly higher than smaller landing configuration.
• Significant flooding loss was observed at high current region for the larger landing configuration compared to the smaller landing case.
• At identical cell performance, 20% less liquid storage was found in the small landing case.
• The common procedure to reduce the liquid storage in the cell was taken as increasing the reactant flow velocity. However, the liquid storage results for different channel velocity configurations showed that the effect of flow field design on reducing the liquid storage is the determining factor compared to the reactant flow velocity.
• Overall, it is suggested that, passively reducing the liquid storage and improving the performance of the cell is possible by only tailoring the flow field geometry. Designs with smaller landing and larger channel sizes (L:C ratio smaller than 2:3) result in minimal liquid storage and better cell performance.
CHAPTER 5

IMPACT OF SURFACE ENERGY ON THROUGH-PLANE LIQUID DISTRIBUTION AND FLOODING

The analysis of in-plane neutron images of different flow field designs showed preliminary evidence that the land|channel interface and its surface properties might have a major impact on liquid transport and storage. To further investigate this phenomenon, the cross-sectional view of the fuel cell is necessary, where the DM|channel (and land|channel) interface can be clearly visualized. The in-plane imaging resolution, however, is not adequate to capture the cross-sectional (through-plane) view of the fuel cell. In this chapter, the through-plane liquid accumulation, distribution and transport inside the fuel cell components were analyzed as a function of land|channel interface (channel wall) hydrophobicity with the use of high-resolution neutron imaging. The details of this technique were described in Chapter 3. Based on the neutron images taken with polytetrafluoroethylene (PTFE) coated and uncoated flow channel walls, anode to cathode liquid distribution was analyzed for each case and the form and amount of liquid in the channels and DM were compared for hydrophobic and hydrophilic land|channel interface. Based on the results, liquid transport mechanisms were suggested for both cases. The significance of capillary liquid flow and phase- change-induced flow within the diffusion media were analyzed. Also a significant effect of CL|MPL and MPL|DM interfaces on liquid transport and flooding is found through the analysis of micro-porous layer (MPL) water content and saturation profile along the CL|MPL and MPL|DM interface region.
5.1 Effect of channel wall surface hydrophobicity on liquid water distribution

The neutron images of hydrophilic-anode/PTFE-coated-cathode and PTFE-coated-anode/hydrophilic-cathode channel walls at 0.2 A/cm² operation are shown in Figure 5-1, to illustrate the water build-up mechanism in the flow channels based on surface treatment. In all of the images, liquid water thickness at each pixel is represented by different colors (color online) where water thickness increases from dark blue to red, as shown in the color scale. In PTFE coated channels, it is observed that the liquid water formed as droplets on the side walls, whereas on the uncoated channels, water spreads from DM to the entire wall surface forming a liquid film layer. This observation is consistent with the planar neutron imaging results of Owejan et al. [92] where they found large slugs of water without PTFE coating and discrete droplets with PTFE coating. To better understand the characteristic through-plane water profile with and without PTFE coating, the through-plane distribution of liquid water is plotted with respect to time in Figure 5-2. In Figure 5-2a, the water content inside the anode channel peaks around through-plane position of zero. This corresponds to the anode channel back wall which indicates a thin film formation formed at this location. The anode channel is uncoated, which is naturally hydrophilic, and therefore it is consistent to have liquid film formation around the channel walls. For the cathode channel however, peak water content is observed near the center of cathode channel, at a through-plane position of ~2.1 mm, a result of droplet formation on the side walls due to PTFE coated channels.
Figure 5-1: Neutron images of tests with 0.2 A/cm² operation and (a) anode channel hydrophilic / cathode channel PTFE coated and (b) anode channel PTFE coated / cathode channel hydrophilic. In all the images, left side is anode and right side is cathode. The color scale is appropriate for all of the images in this article.
Figure 5-2: Through-plane water distribution for 0.2 A/cm$^2$ operation with (a) anode channel hydrophilic / cathode channel PTFE coated and (b) anode channel PTFE coated / cathode channel hydrophilic.
A similar trend is also observed in Figure 5-2b, where water mass peaks around center for the coated anode channel and near the end for the uncoated cathode channel. The PTFE coating also has an effect on water removal from the channels with respect to time. On the hydrophobically coated cathode channel, the accumulated droplets on the walls are purged at 11th minute of operation whereas, without the coating, no sudden drop in channel water content is observed during testing. The PTFE coating on the walls seems to retain more water in the channels on average, but at the same time, the sporadic droplet purge is more frequent due to discrete droplet formation rather than liquid film layer.

The total normalized water mass in the cathode side for 0.2 and 1.0 A/cm² cases are shown in Figure 5-3. The liquid water mass values in each component are shown per unit volume of that component to normalize the results. At 0.2 A/cm², the total water mass on average inside the PTFE coated cathode channels were 100% greater compared to water in the uncoated cathode channels at the same condition over the entire twenty minutes of operation. As current density increased to 1.0 A/cm², this average difference dropped to 70%. When the transient behavior is analyzed, the water mass values in the PTFE coated channels show more frequent fluctuation, especially at low current density after ten minutes of operation, indicating a high frequency of water build-up and sudden removal compared to uncoated channels. When the total liquid inside the cathode DM is considered, at the initial minute of operation, the coated cathode channel case has ~150% more DM water for 0.2 A/cm² and ~100% more for 1.0 A/cm². This initial difference decreases with time and at the end of 20 minute operation, for 0.2 A/cm², there was only ~7% more water in the cathode DM with the hydrophobically coated channel walls. At
1.0 A/cm$^2$, this difference was found to be ~15%, with the coated channel having more liquid water.

Figure 5-3: At every minute of operation, total water mass values inside the cathode DM and the cathode channel are plotted for (a) 0.2 A/cm$^2$ and (b) 1.0 A/cm$^2$. 
These total water mass results suggest that surface energy of channel walls significantly effects the water accumulation, back-diffusion and removal. This will have an impact on net transport coefficient which should be included in water transport models. The effect of surface energy of the channel walls seems to be more significant at high current operation; however, the smaller impact at low current is still important especially at idling conditions of cold-start operation. The higher DM water content in hydrophobically coated channels may not be beneficial during initial start-up at sub-zero temperatures. The through-plane neutron imaging results also reveal significant evidence that water discharge mechanism from DM in to the flow channels is coupled to the land|channel interface, and its hydrophilic-hydrophobic nature might have important implications on performance loss due to DM flooding. In Figure 5-4 neutron images of both hydrophobically coated and uncoated cathode channel conditions are shown for 0.2 A/cm², from the start of operation to the point where significant channel water accumulation was observed.

For the first two images in both Figure 5-4a and 5-4b, the liquid water accumulation was observed mainly in the DM, under the landings, which was expected from Chapter 4. From the third to last image, increasing liquid water mass under the landings moves within the cell in two directions; 1) in vertical (through-plane) direction such that from DM-under-the-landing into the flow channel through the DM-channel wall intersection, 2) in lateral (in-plane) direction within the DM such that from DM-under-the-landing to DM-under- the channel location. The water accumulation under the landing and removal of water through the 90° interface is common for both cases. The major difference is with a hydrophobic surface, water tends to form large droplets on the wall, with a negative
suction of water into the channels. This enhances the lateral movement of water inside DM, and lead to a liquid connectivity under the channels which can promote flooding losses. In Figure 5-4a, the DM-under-the-channel locations of the hydrophobic land|channel interface filled with liquid water much faster compared to hydrophilic land|channel interface in Figure 5-4b. Also, after significant water built-up in the channels, as shown in the last images of both Figure 5-4a and 5-4b, more liquid accumulation was observed in DM-under-the-channel locations with hydrophobic channels. Both of these observations suggest that with the hydrophobically coated channels, more connectivity of liquid in DM under-the-channel locations occurs compared to uncoated channels. This also results in more water storage inside DM and a peak water mass near the DM|channel interface. The through-plane liquid distributions in Figure 5-5 and Figure 5-6 for both current conditions and channel PTFE coatings show this difference more clearly.

The hydrophobic coating on the walls slightly increased peak water mass in 0.2 A/cm$^2$, as shown in Figure 5-5, and significantly increased (~15%) peak water mass in 1.0 A/cm$^2$, as shown in Figure 5-6. The location of cathode DM peak water mass is also different between the two cases. In the 1.0 A/cm$^2$ operation of uncoated cathode case, the peak water mass was observed at 0.524 mm whereas in the coated channel case, the peak shifted towards DM|channel interface, to a distance of 0.554 mm. In the anode side, it was also observed (Figure 5-6b) that the hydrophobically coated anode channel walls caused a peak in DM water storage near the DM|channel interface (~0.04 mm) having ~30 % more water storage than hydrophilic channel case, as shown in Figure 5-6a.
These results indicate the land-channel interface is critical in removal of water from DM. It is suggested that the hydrophilic interface enhances the capillary suction from DM and results in lower water storage whereas, the PTFE coated interface suppresses the liquid in DM due to the water repellent nature of the surface. Based on

Figure 5-4: Neutron images of water build-up in DM and water discharge into channels for (a) cathode PTFE coated channel (b) cathode uncoated channel.
these results, a schematic of water accumulation and removal mechanism is suggested for both hydrophobic and hydrophilic channel cases and shown in Figure 5-7. The figure starts with similar initial water accumulation for both cases, and as water built-up increases with time, more suction into channels is observed with hydrophilic channels and more liquid connectivity is observed in DM under the channel for PTFE coated channel walls. In the last images, the actual results for each case are shown, which are in agreement with the proposed transport mechanism.

The in-plane neutron imaging results shown in Chapter 4 were also very consistent with these through-plane results. Revisiting Chapter 4, the in-plane imaging results of configurations with unity L:C ratio (0.5x0.5, 1.0x1.0 and 2.0x2.0) showed that configurations with higher number of land\channel interface store more liquid water compared to lower number of land\channel interface design. The flow fields used in these tests have gold plated surface which is naturally hydrophilic. According to the suggested transport mechanism given in Figure 5-7, this means that there will be more liquid suction from the DM into the flow channels with higher number of land\channel interfaces. The main mechanism to remove this liquid water from the channels is by the drag of the reactant flow. Since all three configurations have the same flow velocity, the drag force applied by the flow will be almost the same in all cases. Therefore, with more land\channel interface, there will be more liquid stored in the channels, which was exactly the case observed in Chapter 4, from Figure 4-8.
Figure 5-5: Through plane water distribution inside DM and MEA at 0.2 A/cm² for (a) anode channel hydrophilic / cathode channel PTFE coated and (b) anode channel PTFE coated / cathode channel hydrophilic.
Figure 5-6: Through plane water distribution inside DM and MEA at 1.0 A/cm² for (a) anode channel hydrophilic / cathode channel PTFE coated and (b) anode channel PTFE coated / cathode channel hydrophilic.
Finally, it is important to note that for the discharge of liquid water from diffusion media into the flow channel, many of the studies consider droplet emergence on diffusion

Figure 5-7: Schematic of water transport and removal with coated channels (left) and uncoated channels (right) at (a) start-up, (b) after couple minutes of operation, (c) after significant liquid build-up and (d) real-time neutron images for each case.
media surface as the main discharge mode, without consideration of the role of the channel|land interface. In our results, however, there is almost no droplet accumulation observed directly on the DM surface. Instead, liquid directly accumulated on the channel walls which strongly indicates that continuous discharge of liquid water from DM occurs mainly from under-the-landing location into the flow channel through the land|channel interface. This does not imply that droplet emergence directly on to DM surface is not possible. In fact, there are studies in literature that visualized this behavior [112, 121]. However, our results imply that the liquid water discharged from DM-under-the-channel location is easily removable, and may not be accumulated on the DM surface long enough for detection by the 54 seconds exposure of the neutron image, compared to liquid discharge onto channel walls from land|channel interface. Hence, it can be effective to engineer the water storage in the cell by tailoring the geometry and the surface energy of the land|channel interface.

5.2 Generic through-plane liquid distribution and significance of capillary versus phase change induced flow inside the DM

In this section, the common trends observed in the through-plane water distribution for both of the channel wall surface energy conditions are analyzed to understand the generic water transport mechanisms inside the DM. The through-plane water mass profiles of only the hydrophobically coated cathode tests are shown for the sake of simplicity, however, the same trends are also valid for the hydrophobically coated anode case. The liquid distribution of 0.2 A/cm² and 1.0 A/cm² are represented in two different formats. In the first format, normalized liquid water mass in the entire fuel cell
(total water mass) and in each of the fuel cell components (flow channel, DM and MEA) are plotted over twenty minutes of operation, starting at open circuit voltage condition. Note that the total liquid water mass values in the entire fuel cell are shown for unit surface area of the cell. This format enables comparison of total water mass between components at transient and steady conditions, as well as at low and high current. In the second format, water mass values at each pixel location along the through-plane direction are shown to analyze the water transport mechanisms inside DM and MPL.

In both Figure 5-8a and 5-8b, a significant difference in liquid water accumulation between anode and cathode DM was observed at constant current operation. At low current density (0.2 A/cm²) the water mass per unit cathode DM volume was 84% higher than that of anode DM during the first minute of operation. After steady state was reached, this difference increased to 120%. For the 1.0 A/cm² condition, however, cathode DM water was only 86% higher than that of anode DM at steady state. Based on this observation, a 1:1.8 to 1:2.2 for the anode to cathode DM liquid water ratio may be a good range to assume for basic calculations depending on the current condition. At 1.0 A/cm², the liquid water built up in the channels was removed by the gas flow, and the water mass fluctuated only ~10% from an average (steady-state) value. In 0.2 A/cm² case, however, the first water removal was observed after 10 minutes of operation and even at twenty minutes of operation, a true steady-state was not observed. A similar trend in steady-state behavior was also observed in MEA and DM water content between the two conditions. At 1.0 A/cm², the steady state is reached in DM water storage within 4 minutes of operation, whereas at 0.2 A/cm², 10 minutes was required for steady state.
Figure 5-8: At every minute of operation, the total water mass values in the cell components for anode channel hydrophilic / cathode channel PTFE coated case at (a) 0.2 A/cm², (b) 1.0 A/cm².
The five times greater water generation in 1.0 A/cm² case as well as the higher channel shear explains this difference, but in order to better compare the differences in water mass accumulation between two current conditions, the percent increase of water mass in each component from 0.2 A/cm² to 1.0 A/cm² is shown in Figure 5-9. Here, a negative value represents a lower water amount in 1.0 A/cm² case compared to 0.2 A/cm².

Figure 5-9: The difference of water mass values between 0.2 A/cm² and 1.0 A/cm² at every minute of operation for each cell component.

The first difference was observed in channel water accumulation between the two conditions. There was consistently more channel water in 0.2 A/cm² throughout the entire operation, except the first couple minutes. This is consistent with observed low-power instability in stacks, and is a result of low channel shear flow. The average channel
water accumulation at 0.2 A/cm\(^2\) was found to be 57\% higher in the cathode side and 47\% higher in the anode side compared to high current density operation. It is also important to note that there was significant anode channel water in both current conditions.

For the DM and MEA water content, the commonly expected result would be a greater water mass accumulation at high current due to more water generation. This behavior is seen in Figure 5-9 for the first 10 minutes of operation where steady state was reached for 1.0 A/cm\(^2\) but not for 0.2 A/cm\(^2\) case. After 10 minutes, where both conditions reached steady state, there was ~20\% more water in anode DM and ~10\% more water in MEA at 1.0A/cm\(^2\) compared to 0.2 A/cm\(^2\). On the other hand, the water accumulation difference in cathode DM was almost zero (±3\% fluctuation). In other words, even though there is five times more water generation at 1.0A/cm\(^2\) condition, the water storage at cathode DM is almost same as 0.2 A/cm\(^2\), while the anode DM water does increase.

In order to understand this interesting result, the liquid water mass distribution with respect to the through-plane position for 0.2 and 1.0 A/cm\(^2\) current density conditions were shown in Figure 5-10. In the graph, initial value of x-axis corresponds to anode DM|flow channel interface and final data point corresponds to cathode DM|flow channel interface. The water mass distribution is similar in both conditions, with a peak value near the middle of cathode DM. At 0.2 A/cm\(^2\) condition, increasing liquid accumulation in cathode DM from 77 mg/cm\(^3\) to 115 mg/cm\(^3\) for the first 10 minutes can be clearly seen. After this point, the water mass values do not fluctuate, indicating a pseudo steady-state is reached. For the 1.0 A/cm\(^2\), there is almost no fluctuation in the
water mass values and steady state is reached in the first few minutes. The peak water mass value in the anode DM for 1.0 A/cm$^2$ is ~20% greater than that of 0.2 A/cm$^2$ case, as expected due to higher water generation. However, the graph clearly shows that, at steady-state, peak water mass values in cathode DM are the same (115 mg/cm$^3$) for both current conditions, despite the significant difference in water generation. This result might indicate an important water transport mechanism inside the DM. It is shown in literature that liquid water transports from hot to cold side by vapor diffusion and condensation in the existence of a temperature gradient across the DM; a transport mode named as phase-change-induced (PCI) flow [77, 122-123]. It is also known that a temperature gradient occurs in the cathode DM during operation due to heat generation at the reaction sites. The through-plane results presented in Figure 5-10 show that there is water transport within DM via PCI-flow. For a solely capillary flow, the distribution should be monotonically decreasing from CL|DM to DM|channel interface following a Darcy law relationship for one-dimensional flow in porous media, as shown in Eq. 5.1

$$\dot{n}_w^x = \left( \frac{K_w}{\mu_w} \frac{\partial P_c}{\partial s} \right) \frac{\partial s}{\partial x}$$

where $\dot{n}_w^x$ is the liquid flux, $K_w(s)$ is the permeability depending on liquid saturation ($s$), $\mu_w$ is the liquid viscosity, and capillary pressure ($P_c$) is defined in terms of saturation via the Leverett function. Many two-phase models assuming isothermal conditions show this behavior in their saturation plots where condensation of water vapor is neglected. However, the existence of a source term for liquid water inside DM, which is the vapor
condensation due to PCI flow, is seen in Figure 5-10 with a peak of liquid water mass near the center of DM where temperature is lower than the cathode catalyst layer.

Figure 5-10: Water mass distribution with respect to through plane distance at (a) 0.2 A/cm² and (b) 1.0 A/cm².
The slope of water mass curve between the peak value and the cathode DM|channel interface is calculated for both current conditions, to better explain this mechanism. Note that the liquid flux due to capillary flow is directly related to saturation gradient. Through the same DM material, the saturation gradient is exactly the same as liquid water mass gradient; therefore, by calculating the slope of water mass curve, the magnitude of capillary liquid flow from cathode DM into cathode flow channels can be qualitatively compared for both current conditions. The slopes are found to be 0.670 and 0.924 for 0.2 A/cm² and 1.0 A/cm² cases, respectively. This shows that the increased rate of capillary removal at 1.0 A/cm² overcomes the increased rate of PCI flow due to greater temperature gradient and water generation at this condition, and results in same liquid storage in cathode DM compared to 0.2 A/cm² case. Hence, the PCI flow is not normally the dominant water transport mechanism compared to capillary flow in the cathode DM of an operating fuel cell. The fundamental physical reason behind this fact can be explained through transition from pendular to funicular regime in DM water accumulation [77]. For a short duration after start-up, the water generated at the CL accumulates in DM as isolated droplets, which is called as the pendular regime. In this regime, the liquid moves in DM due to the temperature gradient. As the fuel cell operates and more water is generated, water storage in DM exceeds a certain level of saturation and the isolated droplets get connected. This is called the fenicular regime and in our case, this corresponds to the time where steady-state is reached. Once the transition from pendular to fenicular regime is established, the capillary flow becomes dominant over phase-change induced flow and therefore, for both 0.2 A/cm² and 1.0 A/cm², the peak water mass value and stored water content in DM do not change. The only difference
occurs in the time to reach that transition, which is seen from Figure 5-10. This result is in agreement with model predictions of Khandelwal et al. [77] where they showed that magnitude of the temperature gradient through DM does not affect the steady-state liquid distribution after shutdown but it greatly changes the time required to reach steady-state.

Finally, it is important to mention that there is a significant amount of water in the MPL, and the water mass curve is continuous through the MPL|DM and MPL|CL interfaces such that there is no abrupt change or jump from DM to MPL or from MPL to CL. In two-phase flow models predicting the saturation curve through MPL and DM, an increase in saturation at MPL|DM interface is commonly suggested based on capillary pressure equilibrium, with a much higher saturation on the DM side. The MPL saturation is normally predicted to 40-60% smaller than the DM saturation at the interface depending on the MPL porosity. These saturation predictions can be converted into water mass values using the DM and MPL porosities. For SGL 10BB DM, the uncompressed porosity is given as 0.84 by the manufacturer [124], however the MPL porosity is not clearly stated. Gostick et al. [125] calculated the MPL porosity of SGL 10BB as 0.72 whereas Nam et al. [126] used a value of 0.5. For both cases, the MPL porosity is smaller than DM porosity. Therefore, using the definition of saturation, it can be shown that models predict much less water storage in the MPL compared to water storage in the DM at the interface. In other words, there should be a jump in the water mass curve at the MPL|DM interface based on many capillary flow based model predictions. However, the continuous water mass curve in our results suggests this is not the case, and in fact, there is another effect to be considered other than capillary pressure equilibrium between the pores of MPL and DM. This might be the effect of surface morphology at this interface.
It is shown that there are significant number of cracks (up to 5-7% of surface area) at MPL|CL and MPL|DM interface which have much larger size compared to pores in MPL and DM [77, 127-129]. As shown in Figure 5-11a, these can be in the form of isolated holes or connected and elongated cracks at the interface. Significant liquid flow may occur inside the connected cracks via capillary action as well as condensation of water vapor may cause liquid accumulation inside the isolated holes. Both of these cases will result in significant liquid water mass through the MPL layer which will explain the liquid water in MPL and continuous water curve through MPL|CL and MPL|DM interfaces obtained from the actual through-plane liquid mass profile. Other published evidence from Hartnig et al. [130], as shown in Figure 5-11b, also shows the existence of high water accumulation next to the MPL that can only be reasonably explained by these interfacial effects. Therefore, interface surface morphology effects also have to be considered in two-phase flow and flooding analysis.

The models predicting the saturation curve uses the porosity values and capillary pressure equilibrium by considering each component separately and do not consider their combined and compressed structure in the fuel cell, which involves the interfacial effects. The liquid water mass values shown in Figure 5-10 are converted into saturation values using the same approach where all interface effects are neglected. The MPL porosities were taken as 0.72 and 0.5, as mentioned earlier, and the results were plotted in Figure 5-12. As opposite to model predictions, the water saturation decreases (a reverse jump) from MPL to DM since MPL have smaller pores and lower porosity value compared to DM when they are considered separately. The same is valid for MPL|CL since the CL porosity is between 0.4-0.6, which is lower than MPL porosity [1]. This difference also
shows the interfacial effects plays an important role in saturation distribution and may have important effect on flooding at these locations.

Figure 5-11: (a) Isolated holes and connected cracks on MPL surface [129] (b) Liquid water mass peaks around MPL|DM interface [130].
Figure 5-12: Through plane liquid saturation inside DM at 0.2 A/cm$^2$ current density for (a) MPL porosity of 0.72 and (b) MPL porosity of 0.5. In both cases, there is a reverse jump at MPL|DM.
5.3 Summary

The results obtained in this chapter can be summarized as follows:

- The through-plane liquid storage, transport and flooding mechanism inside a PEFC was investigated as a function of channel wall hydrophobicity.
- The liquid removal from under the lands into the channels via land|channel interface is found to be a significant water transport mechanism and the hydrophilic-hydrophobic nature of this interface affects the water storage in DM and channels.
- The PTFE coating on the land|channel interface (channel wall) resulted in discrete droplets on the channel walls with a higher water removal frequency.
- The uncoated channels have less water on average, and liquid forms a film layer around the walls which promotes steadier operation, but is more difficult to purge.
- Hydrophilic land|channel interface enhances the liquid suction from under-the-land locations whereas PTFE coated land|channel interface suppresses the liquid inside DM resulting more water storage in DM, ranging from 7-15% depending on the current.
- The PTFE coated interface was also found to increase the liquid connectivity in DM under-the-channel location. Based on these results, a DM-liquid transport mechanism is suggested depending on surface PTFE coating.
- Overall it is suggested that, to obtain lower amount of liquid storage inside the DM after shutdown, it is desirable to have hydrophilic land|channel interface, where a short gas purge is necessary to remove high channel liquid observed with this surface condition.
• A highly non-linear behavior with a peak near the center of DM was found for the water mass distribution regardless of channel wall surface energy, suggesting phase-change-induced (PCI) flow exists in DM as a significant source term.

• The steady-state water mass storage inside anode DM was determined to increase with increasing current; however, significant difference in water storage was not observed inside the cathode DM. The peak water mass location in cathode DM also did not change with increasing current.

• Based on this and the slopes of the water mass curves, it is suggested that after a critical liquid saturation is reached in DM, liquid removal from the DM via capillary flow dominates phase-change-induced flow.

• Liquid water storage was observed in the MPL and the water mass curve through MPL|CL and MPL|DM interfaces was found to be continuous.

• The liquid saturation curves obtained using different MPL porosities suggest a reverse saturation jump at the MPL|DM interface which indicates MPL surface cracks and interface morphology have an important impact on liquid storage and distribution.
CHAPTER 6

NATURE OF FLOODING AND IMPACT OF LIQUID STORAGE ON FLOODING AND DRYOUT LOSSES IN A PEFC

The most important problem caused by the existence of liquid water in the fuel cell is the performance loss due to flooding. The through-plane imaging analysis revealed insightful knowledge on the generic liquid transport modes and their balance inside the fuel cell components; however, relating the liquid storage and transport directly to the flooding losses will not be accurate since it is not possible to visualize the entire fuel cell with this technique due to resolution limitations. The width of the imaging area with high-resolution neutron radiography is limited to couple centimeters, and therefore only a ratio of the total area can be viewed. As a result, analyzing the performance loss in the entire cell with the liquid storage results of a certain ratio of the total area will not be an accurate and reliable analysis. Therefore, the use of in-plane imaging, where the entire fuel cell can be viewed, is essential. In this chapter, the in-plane neutron radioscopy experiments were conducted with two different cell configurations to analyze the flooding mechanism and understand the impact of liquid water storage on performance losses due to flooding or dryout. The experiments performed under flooding, dryout, and normal operating conditions are explained in the first part of the chapter and based on the results obtained at these conditions, possible flooding mechanisms inside the DM are discussed in the second part, in terms of the liquid storage in DM and flow channels. The current approach of models in predicting the flooding losses found to be inadequate in describing the actual case, and an improved approach is suggested based on the results.
6.1 Flooding Conditions

The first set of experiments was performed with a 50 cm$^2$ active area fuel cell with two different flow field patterns. Fuel cell #1 is a parallel serpentine combination with a 0.5 mm channel width, and a 0.5 mm landing width. Fuel cell #2 has a 1.0 mm channel and landing width. All fuel cells used have a channel depth of 0.5 mm. The polarization curves and neutron radioscopy images of fuel cell #1 are shown in Figure 6-1 and Figure 6-2, respectively.

![Figure 6-1: Polarization Curves for non-flooded and flooded conditions for Fuel Cell #1. For both cases, RH is 100% set at 80°C.](image-url)
At 1.34 A/cm², 80°C operating condition, there was virtually no departure from linearity of the polarization curve, and thus flooding losses were insignificant. At this operating condition (0.511 V, 1.34 A/cm²) the total fuel cell liquid water content in the diffusion media and flow channels (anode and cathode sides) was determined to be 317 mg. From this non-flooded operating point, the cell temperature was decreased until fairly significant voltage deterioration was observed, at 76°C. The resulting cell voltage of 0.480 V at 1.32 A/cm², dropped 31 mV from the condition at 80°C, and the liquid water content in the diffusion media and flow channels increased to 350 mg. It is important to note that, in both cases, the inlet gas was fully humidified at 80°C, and only the fuel cell operating temperature was changed. A 33 mg increase in liquid water content resulted in a 31 mV voltage loss (~1.0 mg/mV for the 50 cm² fuel cell), assuming insignificant kinetic and ohmic effects for the 4°C reduced operating temperature. That this slight temperature change results in such a performance variation illustrates the

Figure 6-2: Neutron Images for Fuel Cell #1 at Conditions of (a) Flooding and (b)Non Flooding.
tenuous balance between saturation and condensation in the fuel cell. This 4°C temperature change represents a ~15% change in saturation pressure from 47.7 kPa to 40.5 kPa. At the fuel cell output pressure (150 kPa), the calculated fully saturated water vapor mole fraction is reduced from 0.32 to 0.27 between temperatures of 80°C and 76°C, respectively. The maximum output water mole fraction is closely related with flooding of the cell, since it determines the amount of water that can be removed in vapor form. Therefore, a lower maximum equivalent water vapor mole fraction is more likely to suffer flooding losses.

From the neutron images shown in Figure 6-2, it can be seen that the water distribution in the DM under normal operation is highly-bimodal, and a majority of the liquid water accumulation is in the DM under the lands, not in, or under, the channels. The total amount of liquid under the lands (anode and cathode combined) was determined to be 183 mg and 195 mg for the 80°C and 76°C cases, respectively. Measured liquid water content for all cases discussed is summarized in Table 6-1. The total amount of liquid in the channels, and diffusion media under the channels, was determined to be 134 mg and 155 mg for the 80°C and 76°C cases, respectively. As the fuel cell goes toward a more flooded condition, there is an increase in liquid water content in both the diffusion media under the landings, and in, or under, the flow channels.
Figure 6-3 and Figure 6-4 show the polarization curves and neutron radioscopy images, respectively, for fuel cell #2. The channel-level gas-phase velocities of this cell and fuel cell #1 are identical for the same current density and stoichiometry due to their flow field design.

Table 6-1: Measured Water Mass and Distribution

<table>
<thead>
<tr>
<th>Fuel Cell Water Location</th>
<th>DM Under Land (mg)</th>
<th>Channel Flow path and DM (mg)</th>
<th>Total (mg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5 mm x 0.5 mm</td>
<td>195 / 183</td>
<td>155 / 134</td>
<td>350 / 317</td>
</tr>
<tr>
<td>1.32 A/cm²</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(100% RH @ 80°C,</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fuel cell 76°C/80°C)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.0 mm x 1.0 mm</td>
<td>211/123</td>
<td>170 /83</td>
<td>381/206</td>
</tr>
<tr>
<td>1.5 A/cm²</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(100% RH @ 80°C,</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fuel cell 80°C/85°C)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.0 mm x 1.0 mm</td>
<td>N/A</td>
<td>N/A</td>
<td>141/140</td>
</tr>
<tr>
<td>1.5 A/cm²</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(50% RH @ 80°C,</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fuel cell 80°C/85°C)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure 6-3: Polarization Curves for non-flooded and flooded conditions for Fuel Cell #2. For both cases, RH is 100% set at 80°C.

Figure 6-4: Neutron Images for Fuel Cell #1 at Conditions of (a) Flooding and (b) Non Flooding.
In Figure 6-3, under fully humidified inlet operating conditions at 80°C, there was significant departure from linearity of the polarization curve at 1.5 A/cm² attributed to the cathode flooding. At this operating condition (0.509 V, 1.5 A/cm²), the total liquid water content in the fuel cell diffusion media and flow channels (anode and cathode sides) was determined to be 381 mg. From this flooded operating point, the cell temperature was increased until the voltage deviation from linearity in the polarization curve was mostly eliminated, at 85°C. The resulting cell voltage of 0.624 V at 1.5 A/cm² is a significant increase (115 mV) from the condition at 80°C. The total liquid water content in the fuel cell diffusion media and flow channels concomitantly decreased from 381 to 206 mg. Thus, a 175 mg decrease in liquid water content resulted in a 115 mV voltage increase (~1.5 mg/mV for the 50 cm² fuel cell), assuming insignificant kinetic and ohmic effects for the 5°C increased operating temperature. The 5°C difference in cell temperature represents a change in maximum equivalent water vapor output mole fraction from 0.32 to 0.39, as shown in Table 6-2. Increased maximum output water mole fraction at 85°C cell temperature is consistent with the reduced flooding losses.

<table>
<thead>
<tr>
<th>Cell Configuration (LxC)</th>
<th>Cell Temperature(°C)</th>
<th>Cell Back Pressure(psig)</th>
<th>Stoic. A/C</th>
<th>Maximum output water mole fraction (y_{water})</th>
</tr>
</thead>
<tbody>
<tr>
<td>#1: 0.5 mm x 0.5 mm</td>
<td>80</td>
<td>7.35</td>
<td>2/2</td>
<td>0.32</td>
</tr>
<tr>
<td>100% RH @80°C</td>
<td>76</td>
<td>7.35</td>
<td>2/2</td>
<td>0.27</td>
</tr>
<tr>
<td>#2: 1.0 mm x 1.0 mm</td>
<td>80</td>
<td>7.35</td>
<td>2/2</td>
<td>0.32</td>
</tr>
<tr>
<td>100% RH @80°C</td>
<td>85</td>
<td>7.35</td>
<td>2/2</td>
<td>0.39</td>
</tr>
<tr>
<td>#2 1.0 mm x 1.0 mm</td>
<td>80</td>
<td>7.35</td>
<td>2/2</td>
<td>0.32</td>
</tr>
<tr>
<td>50% RH @80°C</td>
<td>85</td>
<td>7.35</td>
<td>2/2</td>
<td>0.39</td>
</tr>
</tbody>
</table>
The total amount of liquid under the lands was determined to be 211 mg and 123 mg for the 80°C and 85°C at 1.5 A/cm², respectively. The total amount of liquid in the flow channels, and diffusion media under the flow channels was determined to be 170 mg and 83 mg for the 80°C and 85°C cases, respectively. With increasing temperature and decreasing flooding losses, it was again observed that the liquid water content at both the channel and land locations decreases.

For perspective, the 175 mg decrease for a 5°C temperature increase in fuel cell #2 represents a volume of about 0.18 cm³. Thus, the total liquid water volume increase between flooded and non-flooded conditions is modest. Yet, there is a quite significant effect in both the limiting current density obtainable, and the steady state voltage under flooding limitation. Many models of two-phase effects in PEFCs account for the voltage decrease through a segregated phase pore-filling model. As discussed, the calculated liquid water saturation in the diffusion media is used to adjust the effective porosity in the media by implicitly assuming a segregated-phase filled pore, as shown in Figure 6-5, reducing mass flux of reactant to the catalyst through a modified effective diffusivity where the effective diffusivity is defined through Bruggeman relationship as:

\[ D_{\text{eff}} = D^o \varepsilon^n \]  \hspace{1cm} 6.1
However, using the liquid water content in the diffusion media under the lands determined from neutron imaging, the change in effective porosity, and thus additional diffusion restriction predicted from this approach, can be calculated. With known landing/channel dimensions, the active area under the landings can be calculated as:

\[ A_L = A_T \cdot \frac{\ell}{c + R \cdot c} \]  \hspace{1cm} 6.2

where \( A_T \) is the total active area, \( R \) is the channel/landing width ratio and \( c \) is the number of channels in parallel and \( \ell \) is the number of lands. Knowing the dry DM porosity (0.625 after compression), the maximum liquid volume in one DM (one side only), and maximum liquid volume under the landings only can be calculated as:

\[ V_{\text{liq}}^{\text{max}} = \varepsilon \cdot V_{\text{DM}} \]  \hspace{1cm} 6.3
\[ V_{\text{liq, landing}}^{\text{max}} = \varepsilon \cdot V_{\text{landing}} \]  \hspace{1cm} 6.4

Figure 6-5: Physical model of (left) the Bruggeman Relationship and (right) a more realistic physical possibility with greater diffusive transport limitation.
After determining the maximum water mass in DM under the landing, we can use the measured water amount under the landings (assuming a worst case scenario, where all liquid water accumulates only in the cathode DM), the modified effective porosity can be calculated through Eq. 6.5.

$$\varepsilon^{\text{eff}} = \left(1 - \frac{m_{\text{measured}}}{m_{\text{Max}}^{\text{liq.landing}}}\right) \cdot \varepsilon$$  \hspace{1cm} (6.5)

Effective diffusivity in porous media can be defined by modification of the standard diffusivity via the Bruggeman relation. Therefore, the diffusivity ratio between flooded and non-flooded cases, based on the Bruggeman model, can be calculated by using the initial and modified porosities as given in Eq. 6.6.

$$\frac{D_{\text{eff, wet}}^{\text{wet}}}{D_{\text{eff, dry}}^{\text{dry}}} = \left(\frac{\varepsilon^{\text{eff}}}{\varepsilon}\right)^n$$  \hspace{1cm} (6.6)

where the coefficient $n$ on Eq. 6.6 is typically chosen to be 1.5. However, as the level of saturation increases, the tortuosity should also increase by physical reasoning, so that a value of up to 1.8 has also been suggested. If all water measured under the lands occupied only the cathode side of the ~168 μm thick diffusion media, the effective porosity under the lands for the flooded, 76°C case would change from 0.625 to 0.138 for the flooded case. For the non-flooded condition (80°C), the effective porosity under the lands would change from 0.625 to 0.168. The effective diffusivity for $n = 1.5$ under the land through the diffusion media for the flooded and non-flooded cases (calculation via Eq. 6.6.) would thus decrease by 89.7% (93.4% for $n = 1.8$) for flooded conditions and 86.1% (90.7% for $n = 1.8$) for non-flooded conditions, respectively. For fuel cell #2, the changes in diffusivities under the lands for $n = 1.5$ would be 95.0% (97.3% for $n = 1.8$)
and 65.1% (71.7% for $n = 1.8$) for flooded and non-flooded conditions respectively. While it is not appropriate to make a similar calculation for water under the channel in the diffusion media, since the neutron imaging cannot distinguish water in the channel from under the channel, the effect would clearly be even less, since there is less water in the channel locations at these conditions. Because there is less overall water in the channel and diffusion media under the channels, it is obvious there is significantly less saturation of the diffusion media under the channels.

The maximum saturation level under the channels can be found by taking the measured channel liquid water content and assuming it is completely under the channels in the diffusion media. For fuel cell #1, it is calculated a minimum under-channel effective porosities (maximum possible saturation) of 0.254 and 0.304 under flooded and non-flooded conditions, respectively. For fuel cell #2, this value is 0.226 and 0.430 under flooded and non-flooded conditions, respectively.

It seems doubtful that the relatively small differences in diffusivity under the lands or channels calculated via the Bruggeman approach accounts for the observed loss. For fuel cell #1, there is only around a 4% difference in the effective diffusivity between flooded and non-flooded conditions under the land, and for fuel cell #2, the difference is larger, but still only 30%. Although this is a significant difference, a purely segregated phase modified diffusivity approach is generally inadequate to account for all of the flooding loss observed.
6.2 Flooding Mechanisms

6.2.1 Segregated Phase Pore Filling Model

As discussed, modification of diffusivity or porosity with the water saturation implicitly assumes that even at very high saturation level, a continuous gas-phase pathway exists for mass transport of reactants. The relatively small differences in effective diffusivities between the flooded and non-flooded conditions found from measured data imply that this pore filling model is inadequate to completely describe the performance loss resulting from flooding. That is, significantly less water is responsible for the flooding losses than predicted. Additionally, it is clear from the images that the water distribution is bimodal, and favors accumulation under the lands, where our calculation was only for a liquid distribution under the lands. Thus, less diffusive resistance in DM under the channels is expected than that in under the lands. In order to obtain a deeper insight into DM-level flooding, the order of magnitude of liquid water responsible for the acquired voltage loss (115 mV) was calculated for fuel cell #1 and #2, using the Bruggeman approach. The ratio of the electrode surface concentrations of oxygen gas for flooded and non-flooded cases can be calculated from the voltage loss:

\[
\Delta V = \frac{RT}{2F} \cdot \ln \left[ \frac{C_{o_2,\text{non-flooded}}}{C_{o_2,\text{flooded}}} \right] + \frac{RT}{F} \cdot \ln \left[ \frac{C_{o_2,\text{non-flooded}}}{C_{o_2,\text{flooded}}} \right]^\gamma
\]

where the first term on the right hand side accounts for the thermodynamic effect of oxygen concentration on voltage (the Nernst Equation), and the second term accounts for the affect of oxygen mole fraction on the kinetics. The value for \( \gamma \), the oxygen reduction reaction elementary reaction order for constant overpotential, has been estimated from
several studies to lie between 0.6 and 0.75. Here, this value is assumed to be 0.75 for calculation. Above equation also assumes the same hydrogen and water mole fraction for each case. Then, using Fick’s Law for diffusion of gases and Faraday’s Law for oxygen consumption, the electrode surface concentration of oxygen in non-flooded case can be approximated.

\[
\frac{i \cdot \delta_{DM}}{4F \cdot D_{eff}} = C_{i} - C_{o_{2},non-flooded}
\]

The effective diffusivity for a non-flooded case is calculated through the Bruggeman relation, taking the initial compressed porosity as 0.625. Then, knowing the voltage loss between the flooded and non-flooded case (31 and 115 mV for fuel cell #1 and #2, respectively), the ratio of oxygen surface concentrations for flooded and non-flooded cases is calculated. Finally, oxygen surface concentration for the flooded case can be determined. Using Fick’s Law and Bruggeman relation together, the corresponding effective porosity in the DM for the flooded case \((\varepsilon-s_{w})\) for fuel cell #1 and #2 was calculated to be 0.132 and 0.130, respectively, for \(n=1.5\) (0.178 and 0.183 for \(n = 1.8\)). This effective porosity value is the equivalent of ~400 mg of liquid water in one diffusion media for \(n = 1.5\) and ~360 mg of water in one diffusion media for \(n = 1.8\). For fuel cell #1 and #2, the total water content in the cell was 350 and 381 mg. Since this calculation was made for a worst-case scenario where all the water was distributed in a single diffusion media (i.e. none of the observed water is in the channels or anode DM), the Bruggeman model generally overestimates the liquid required for the observed flooding losses, and falls on the boundary of predicting the actual water content required.
only for $n = 1.8$. Hence, for $n = 1.5$, in the Bruggeman model, 2.75 and 1.71 mg/mV (1.56 and 1.34 mg/mV for $n = 1.8$) of liquid water corresponds to the losses observed for fuel cell #1 and #2, respectively. However, the observed ratio from the neutron images is only 1.06 and 1.52 mg/mV for fuel cell #1 and #2, respectively. Since the experimental and calculated values represent worst-case scenarios (some water is almost positively in the anode-side DM and channels), it is unlikely that the concept of a Bruggeman approach with a continuous gas-phase pathway is solely responsible for the sharp decay in voltage upon flooding, especially considering the sharply bimodal nature of liquid accumulation observed between channels and landings. This also illustrates the relatively large sensitivity of the exponent chosen for $n$, which represents tortuosity. This variable should be more precisely defined for various diffusion materials to provide accurate simulation results, and the variance with saturation level should be included.

If the same calculation is considered for the area only under the channels, the effect would be even less, since the overall water content is generally lower in these areas. We conclude that this segregated phase pore filling model, used alone, generally overestimates the water required to cause flooding loss, and an additional film effect should be considered in analysis.

**6.2.2 Thin Film Model**

The segregated-phase pore-filling model over-predicts the water required to suffer flooding loss. If instead of pore-filling, a thin-film layer, connected through a small region of the diffusion media, on the catalyst, or along the DM/catalyst layer interface, is considered, the severe effects of flooding can be explained with a minimal amount of
water. This film resistance model can also represent a locally flooded catalyst layer or interface. In this physical flooding model, a micro layer of liquid film connected in a direction perpendicular to gas-phase transport is considered. If the total water measured in the channels and lands were assumed to be uniformly distributed in the diffusion media (which is not the case but assumed for the purpose of discussion here), the thickness of the resulting liquid film layer can be found from Eq. 6.9.

\[
t = \frac{m_{\text{measured}}^{\text{liq.}}}{\rho_{\text{water}} \cdot A_f}
\]

The corresponding equivalent thin film thicknesses calculated under the designated flooded conditions for the total measured liquid in fuel cell #1 and fuel cell #2 are 72 µm and 78 µm, respectively. Note that these are the minimum thickness values, since liquid water is assumed for comparison purposes to be uniformly distributed over the entire 50 cm², and not actually what occurs, since only local blockage of a fraction of catalyst area is needed to cause performance loss. The liquid water distribution actually observed demonstrates this model used alone underpredicts DM water, but it illustrates the extreme case where the smallest amount of liquid possible causes flooding. This order of magnitude thickness of liquid film, if covering the cathode, would essentially stop oxygen penetration to the catalyst, when calculated considering interfacial diffusion via Henry’s Law. Consequently, film coverage represents the minimum amount of total liquid water in the fuel cell possible to obtain flooding losses. If instead of a uniform film, a portion of the fuel cell is connected with a thin layer, flooding losses can also be extreme. The presence of even micro-layer thicknesses of locally connected liquid film blocking access to the catalyst can effectively shut down reactant transport at a given
location, forcing the remaining active area to carry the total current, and increasing the overpotential.

A simplified calculation for the thin film model is performed here in order to estimate the order of magnitude of liquid water corresponding to the measured voltage losses. The mole fraction of oxygen gas in the liquid layer is related to the free stream oxygen mole fraction via Henry’s Law:

\[ y_{o_2, \text{liquid}} = \frac{y_{o_2, \text{fs}} \cdot P}{H} \]  \hspace{1cm} (6.10)

where \( H \) is the Henry’s constant which is a known function of temperature. Knowing the mole fraction of oxygen in the liquid water, the thickness of the equivalent uniform micro layer can be evaluated through the diffusion law, assuming the electrode surface concentration of oxygen to be zero due to the flooding conditions.

\[ \delta_{\text{aq}} = \frac{C_{o_2, \text{aq}} \cdot 4F \cdot D_{o_2-\text{water}}}{i} \] \hspace{1cm} (6.11)

In the above equation, \( C_{o_2, \text{aq}} \) is obtained from the mole fraction of oxygen in liquid water (computed by Eq 6.10) and \( D_{o_2-\text{water}} \) is the diffusivity of oxygen in liquid water. From the above equation, the equivalent thickness of liquid water required to result in the observed voltage loss is calculated as on the order of 10 nm for both fuel cells, which is much smaller than the total water observed with neutron imaging, and would actually be under the detectability limit of the present neutron imaging system. If we assume a uniform 10 nm layer of water is present, then the total liquid water content responsible for the voltage decay is only 0.05 mg total water. We are not suggesting a uniform film exists, or a uniform film would be required for voltage loss, but the calculation is shown
to illustrate that the thin film model vastly under-predicts the amount of liquid water responsible for the voltage loss attributed to flooding, while a segregated phase model generally over-predicts the liquid water observed for voltage losses.

**6.2.3 Connected Pore Filling Model**

A continuous thin film is not observed in practice. Instead, a highly bimodal distribution is observed, with high liquid accumulation under lands and relatively little accumulation in and under the channels at high current density. The calculations were shown to emphasize that if any continuous thin film covers portions of the cell, severe flooding losses would be observed, even for very low total liquid content. It is likely that the DM pores that are partially filled will achieve connectivity with each other only in certain locations, beginning with the nearly saturated land DM, and extending into the tree-like structure of the DM pore network under the channel, as capillary pressure increases with increasing saturation. Based on the experimental data, the Bruggeman segregated phase model generally over-predicts the liquid water required for flooding losses, whereas a thin film model under-predicts water saturation required for flooding, as shown in Figure 6-6. A hybridization of the Bruggeman and thin-film physical models falls in between the two extremes, and allows reconciliation between liquid saturation level measured and flooding losses, and is thus in agreement with observed data.
If some filled pores in the diffusion media establish a continuous connectivity with other open pore network structures across the surface or interface of the diffusion media, a film resistance effect would occur, as shown schematically in Figure 6-5. Not all the pores in the DM would need to be filled, and overall DM liquid saturation level could be quite low. It is conjectured that local connectivity and concomitant flooding losses would occur at locations directly under the channel, growing first from the high capillary pressure, highly saturated pore network under the lands, and reaching through the pore network tree-like structure into the diffusion media under the channel, until a connectivity between adjacent lands is established. This concept cannot be established

Figure 6-6: Liquid water mass responsible for unit voltage loss at flooding conditions plotted for each model.
based solely on 2-D neutron imaging, although it is consistent with all observations, including an increased propensity for flooding for fuel cells with smaller channel and wider landing widths, as will be described in the second part of this chapter. PSU is developing a 3-D computed tomography to resolve this question, and is the subject of further study.

### 6.3 Dry-out Conditions

Figure 6-7 and Figure 6-8 show the polarization curves and neutron radioscopy images for the fuel cell #2 operating at an inlet relative humidity of 50% at 80°C. At this underhumidified condition, operation at constant cathode backing plate temperature of 80°C resulted in only a slight departure from linearity of the polarization curve at 1.5 A/cm² (calculated total cell exit relative humidity at this condition is 95% at 80°C. At this operating condition (0.573 V, 1.5 A/cm²), the total fuel cell liquid water content in the diffusion media and flow channels (anode and cathode sides) was determined to be 141 mg. Note that at full humidity operation at 1.5 A/cm², there was 381 mg of liquid water in this configuration. At 50% RH at 80°C, this decreased to 141 mg, but is still many times greater than that needed to hydrate the electrolyte. The fuel cell voltage under full humidity conditions was lower (0.573 compared to 0.509 V for the 50% and 100% RH at 80°C conditions, respectively, due to flooding).
From this operating point, the cell temperature was increased to 85°C, where the voltage deviation from linearity in the polarization curve was significant, and attributable to anode dry-out and not flooding, since performance decreased with increased temperature (calculated total cell exit relative humidity at this condition is (86% at 85°C). The resulting cell voltage of 0.504 V is a 69 mV decrease from operation at 80°C. However, the liquid water content in the fuel cell diffusion media and flow channels remained almost identical (140 mg), indicating the change in performance can be attributed to a small relative water content in the electrolyte. This also illustrates the difficulty to remove residual liquid water in the diffusion media, since a half an hour was waited between the flooded and non-flooded images to ensure a steady-state has been achieved. The total liquid water content for a fully moisturized electrolyte in the anode

Figure 6-7: Polarization Curves for Conditions of Anode Dryout and No Dryout for Fuel Cell #2. For both cases, RH is 50% set at 80 °C.
catalyst layer of the 50 cm$^2$ active area is estimated to be 9 mg, and in the main electrolyte as 72 mg, so that dry-out in the catalyst layer can be the result of an exceedingly small amount of H$_2$O. Thus, it is not surprising that an exceedingly small amount of water is responsible for dry-out voltage loss.

![Images](image1.png)

**Figure 6-8**: Neutron Images for Fuel Cell #2 at Conditions of (a) Anode Dryout and (b) No Dryout.

### 6.4 Summary

The results obtained in this chapter can be summarized as follows;

- The total liquid water mass and corresponding cell performance values were obtained for two different fuel cell configurations under flooded, non-flooded and dry-out conditions with identical current density and slightly different temperature.
- Relating the observed losses to the liquid storage values revealed that for high current operation with the catalyst and diffusion media utilized, flooding is a highly localized
phenomenon with changes in the mass of liquid water in the DM amounting to 1-1.5 mg/mV.

- The Bruggeman relation based segregated-phase pore filling model was found to over predict the liquid water mass responsible from the measured flooding losses. A single liquid film layer formation inside the DM or CL was also found to be unrealistic.

- Based on the results, a connected pore-filling model inside the DM is suggested, where the liquid interfacially connects within some of the pores and completely blocks the reactant diffusion pathways.

- A very small amount of liquid was found to be responsible from the performance loss at dry-out conditions. This is attributed to the loss of water inside the electrolyte of the anode CL.
CHAPTER 7

CONCLUSIONS

Flooding, in the fuel cell catalyst layer, diffusion media and flow channels, is one of the most important unresolved problems in PEFC operation. It is one of the major performance limiting factors and therefore gathered extensive attention from the researchers studying in fuel cell area. Most of the computational studies modeling water management and the two-phase flow of liquid water in the catalyst layer, diffusion media and flow channels assume correlations for important parameters such as effective diffusivity and relative permeability that mostly based on soil science studies. The modeling study results were generally validated by obtaining polarization curves of an operating fuel cell and the liquid saturation and flooding predictions were than made based on this performance curve validation. However, the validity of these correlations for fuel cell operation is questionable and, to the knowledge of the author, there has not been any experimental work validating these predictions by measuring the actual liquid accumulation amount during operation. The presented work in this manner is a unique approach since the real-time liquid water storage and cell performance under flooded, non-flooded and dry-out conditions were analyzed at the same time and based on the results, the adequacy of the assumptions of existing models were discussed. The impact of flow-field geometry and land-channel interface surface properties on both the in-plane and the through-plane liquid water distribution and storage were also investigated for the first time with quantifying the water amount in the cell. Furthermore, the generic liquid transport modes in the DM were identified and the balance between different transport
mechanisms was investigated with the use of high-resolution neutron radioscopy. The results are believed to be highly valuable to the modeling studies conducted in this area, as a feasible validation to their results. The summary of the conclusions can be made as follows:

- The liquid water tends to preferentially accumulate under the landings rather than in, or under the channels.
- Normalized results (specific water mass) showed that water storage is not only a function of diffusion media properties, but also strongly dependent on the flow field geometry. Specific water mass levels are higher under the landings for both flooded and non-flooded conditions.
- Based on the analysis of the liquid storage values and the performance curves for each cell configuration, it is suggested that the optimum condition is the large channel - small landing flow field design in terms of minimum residual water content and maximum performance.
- For the unity landing/channel ratio, the number of land|channel interface have an important influence on water accumulation. Higher number of land|channel interfaces results in more liquid storage, especially in the flow channels, for the same gas flow velocity. On the other hand, if the landing/channel ratio is different than unity, the liquid water in the cell is found to be strongly dependent to landing/channel ratio rather than the number of interfaces. As this ratio gets smaller, less amount of liquid water was found to be stored in the cell.
- Based on the flow field design, there can be large differences in the stored water content between the two different fuel cells with nearly identical cell performance.
This result has important implications on freeze thaw and degradation issues. The residual liquid in the cell after shutdown can be minimized, without any parasitic power consumption, by tailoring the flow field geometry.

- The liquid removal from under the lands into the channels via land|channel interface is a significant water transport mechanism and the hydrophilic-hydrophobic nature of this interface affects the water storage in DM.

- Hydrophilic channel walls enhance the liquid suction from under-the-land locations whereas PTFE coated land|channel interface suppress the liquid inside DM resulting in more water storage in DM, as high as 15% at high current condition.

- The PTFE coating on the channel surface results in discrete droplets on the channel walls with a higher water removal frequency. The hydrophilic channels have less water on average with a steadier operation, but liquid forms a film layer around the walls which is more difficult to purge.

- The PTFE coated interface increase the liquid connectivity in DM under-the-channel location. Based on these results, a DM-liquid transport mechanism is suggested depending on surface PTFE coating.

- Overall it is suggested that, to obtain lower amount of liquid storage inside the DM after shutdown, it is desirable to have hydrophilic land|channel interface, where a short gas purge is necessary to remove high channel liquid observed with this surface condition.

- A highly non-linear behavior with a peak near the center of DM was found for the water mass distribution regardless of channel wall surface energy, suggesting phase-change-induced (PCI) flow exists in DM as a significant source term.
- The steady-state water mass storage inside anode DM was determined to increase with increasing current; however, significant difference in water storage was not observed inside the cathode DM. The peak water mass location in cathode DM also did not change with increasing current. Based on this and the slopes of the water mass curves, it is suggested that after a critical liquid saturation is reached in DM, liquid removal from the DM via capillary flow dominates phase-change-induced flow.

- Liquid water storage was observed in the MPL and the water mass curve through MPL|CL and MPL|DM interfaces was found to be continuous. The liquid saturation curves obtained using different MPL porosities suggest a reverse saturation jump at the MPL|DM interface which indicates MPL surface cracks and interface morphology have an important impact on liquid storage and distribution.

- For high current density operation, flooding is a highly localized phenomenon with changes in the mass of liquid water in the DM amounting to around 1 mg/mV.

- The actual change in DM saturation is generally lower than predicted by a worst-case Bruggeman segregated phase filled pore model, and much greater than that predicted by a thin film transport resistance model.

- A connected pore-filling physical model, where liquid water is connected interfacially or through the tree-like structure of the pore network in the diffusion media, is more consistent with the results to resolve the effects of flooding on voltage.

- An exceedingly small liquid water (on the order of 0.1mg/cm²) is found to be responsible for the reduction in ionic conductivity and anode dry-out. There is more than enough water available in the diffusion media to fully hydrate the electrolyte, but it is isolated enough from the anode and ineffective to prevent performance loss.
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APPENDIX

Calculation of single-phase mass transfer of liquid water into the reactant flow:

\[ D_h = \frac{4 \cdot A_c}{P} \]  

where \( D_h \) is the hydraulic diameter, \( A_c \) is the flow cross-sectional area and \( P \) is the wetted perimeter.

\[ h_m = \frac{Sh_d \cdot D_{AB}}{D_h} \]  

where \( Sh_d \) is the Sherwood number, \( D_{AB} \) is the diffusivity of molecule A in B.

For steady, laminar, fully-developed flow with uniform surface temperature, the Sherwood number is constant and given as:

\[ Sh_d = 3.08 \]

The mass transfer rate of liquid water can be determined from:

\[ \dot{m} = h_m \cdot A_c \cdot (\rho_f - \rho_\infty) \]  

where \( A_c \) is the surface area.

Cell Configuration (L/C):

a) \( 1.0 \times 0.75 \)

\[ D_{h,a} = \frac{4 \cdot 0.75 \times 0.5}{2 \cdot (0.75 + 0.5)} \approx 0.6 \]

\[ A_{s,a} = 0.75 \times 1 = 0.75 \]

where channel length is taken as unity.
b) 0.5x1.5

\[ D_{h,b} = \frac{4 \cdot \eta_{5} \cdot 0.5}{2 \cdot (1.5 + 0.5)} \approx 0.75 \]

\[ A_{s,b} = 1.5 \times 1 = 1.5 \]

where channel length is taken as unity.

Calculating the mass transfer of liquid water as a ratio of configuration in (a) to (b).

\[
\frac{\dot{m}_a}{\dot{m}_b} = \frac{h_{m,a} \cdot A_{s,a} \cdot \eta_{s,a} - \rho_{\infty}}{h_{m,b} \cdot A_{s,b} \cdot \eta_{s,b} - \rho_{\infty}} \quad \text{A.4}
\]

where concentration terms cancel out since both cases have the same operating conditions and reactant flow.

\[
\frac{\dot{m}_a}{\dot{m}_b} = \left( \frac{Sh_d \cdot D_{AB}}{D_{h,a}} \right) \cdot \left( \frac{A_{s,a}}{A_{s,b}} \right)
\]

\[
\frac{\dot{m}_a}{\dot{m}_b} = \left( \frac{D_{h,b}}{D_{h,a}} \right) \cdot \left( \frac{A_{s,a}}{A_{s,b}} \right) = \left( \frac{0.75}{0.6} \right) \cdot \left( \frac{0.75}{1.5} \right)
\]

\[
\frac{\dot{m}_a}{\dot{m}_b} = 0.625
\]

Hence

\[
\dot{m}_b = 1.6 \cdot \dot{m}_a
\]
VITA

AHMET TURHAN

EDUCATION


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