PHYSICAL DAMAGE OF POLYMER ELECTROLYTE FUEL CELLS SUBJECT TO FREEZING

A Dissertation in
Mechanical Engineering
by
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ABSTRACT

One of the remaining technical challenges for polymer electrolyte fuel cell (PEFC) commercialization is to achieve shutdown to a frozen state, and rapid start from frozen conditions without damage. PEFCs generate water as reaction product, so when PEFCs are subjected to sub-freezing environments without removal of residual water, they can experience irreversible damage. There exist conflicts in the literature regarding freeze-damage, and the particular damage modes are not clearly understood. This work is designed to elucidate freeze-damage modes of fuel cell materials, and to investigate temperature-gradient driven water transport phenomena as a potential to mitigate freeze-damage.

Freeze-damage modes were identified through ex-situ and in-cell freeze/thaw (F/T) cycling experiment. Three primary damage modes were discovered: 1) interfacial delamination, 2) ice expansion damage, and 3) pore level damage. The effect of interfacial delamination, which was diagnosed as a main damage mode on fuel cell performance, was also investigated by developing a two-dimensional anisotropic current disruption model.

Extensive ex-situ material F/T cycling testing was conducted under the worst case conditions of liquid water submersion to identify the key factors leading to physical damage. Specifically, the membrane electrode assembly, porous media, and electrolyte were found to be sources of water that can damage the catalyst layers under freeze/thaw conditions. Damage was found to occur almost exclusively under the channel, and not under the land. Conceptually, the best material to mitigate freeze damage in a PEFC was found to be a crack-free virgin catalyst layer, and a thin reinforced membrane with a stiff hydrophobically treated diffusion media.

The in-cell study affirmed that significant damage can occur for a single cell with no purge, indicating that water removal from the cell, especially from the catalyst layer pores, during shutdown is critical for robust PEFC operation in frozen conditions.
A two-dimensional anisotropic model was developed to investigate the impact of local delamination on PEFC performance. Localized interfacial delamination of the membrane | catalyst layer and catalyst layer | diffusion media were found to significantly increase ohmic resistance. The in-plane resistance and in-plane-to-through-plane resistance ratio of PEFC components adjacent to the delamination were determined to be the key controlling parameters for increase in ohmic resistance.

Temperature-gradient induced water transport phenomena were explored in PEFC materials because of a potential for non-parasitic water drainage at shutdown. Two different modes were identified: 1) thermo-osmosis, and 2) phase-change induced flow.

Direct thermo-osmotic experiments on different polymer membrane types (non-reinforced Nafion® and two different commercial reinforced membranes) show that thermo-osmotic flow was observed in all membranes, and the water flow direction in the membrane was determined to always flow from the cold to the hot side, as anticipated for a small pore hydrophilic porous medium. The water flux was found to be proportional to temperature gradient and to increase with average membrane temperature. The dependency of the thermo-osmotic diffusivity on average temperature showed predictable Arrhenius-type behavior. True interfacial temperatures of the membrane were estimated using a two-dimensional thermal model, and empirical relations for the thermo-osmotic diffusivity for the membrane types tested were developed. These can be of use to design engineers concerned about achieving optimal water balance during steady and transient operation.

Contrary to thermo-osmotic flow in fuel cell membranes, a net flux of water was found to flow from the hot to cold side of the full membrane electrode assembly. The key to this is the existence of some gas phase in the catalyst layer or other porous media. This mode of transport is a result of phase-change induced flow. The measured water transport through the membrane electrode assembly is the net effect of mass diffusion as well as thermo-osmosis in the membrane,
which moves counter to the direction of the phase-change induced flow. Arrhenius functions that are dependent on material set, temperature gradient, and average temperature across the materials were developed that describe the net flux. In addition to direct quantification, phase-change induced flow was visualized and confirmed using high resolution neutron radiography.
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### Standard subscripts

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<tr>
<td>A</td>
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<td>C</td>
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### English Symbols

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<tr>
<td>$k_{r,j}$</td>
<td>relative permeability of phase j</td>
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<td>$n$</td>
<td>(a)number of delamination site</td>
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<td>$n$</td>
<td>(b)stoichiometric number of electrons involved in an electrode reaction</td>
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<td>$n_d$</td>
<td>electro-osmotic drag coefficient</td>
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<td>$p_a$</td>
<td>air pressure</td>
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<tr>
<td>$p_b$</td>
<td>bubbling pressure</td>
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<td>Meaning</td>
<td>Unit</td>
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<td>$p_c$</td>
<td>capillary pressure</td>
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<td>$Pe$</td>
<td>Pelet number</td>
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<td>pressure of non-wetting phase</td>
<td>Pa</td>
<td>2.2</td>
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<tr>
<td>$P_0$</td>
<td>reference pressure</td>
<td>Pa</td>
<td>2.3</td>
</tr>
<tr>
<td>$P_{orb}$</td>
<td>overburden pressure</td>
<td>Pa</td>
<td>2.3</td>
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<tr>
<td>$P_w$</td>
<td>water pressure</td>
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</tr>
<tr>
<td>$p_{nw}$</td>
<td>pressure of non-wetting phase</td>
<td>Pa</td>
<td>2.2</td>
</tr>
<tr>
<td>$r'$, $r''$</td>
<td>principal radii of interface</td>
<td>m</td>
<td>2.2</td>
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<tr>
<td>$r$</td>
<td>mean radius</td>
<td>m</td>
<td>2.2</td>
</tr>
<tr>
<td>$r^*$</td>
<td>mean radius of capillary tube</td>
<td>m</td>
<td>2.2</td>
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<td>$R$</td>
<td>areal ohmic resistance</td>
<td>$\Omega \cdot m^2$</td>
<td>6.2, 6.3</td>
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<tr>
<td>$R_b$</td>
<td>areal ohmic resistance of baseline (non-interfacial delamination case)</td>
<td>$\Omega \cdot m^2$</td>
<td>6.2, 6.3</td>
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<tr>
<td>$R_{ct,i}$</td>
<td>charge transfer resistance of three phase boundary, i, in the catalyst layer</td>
<td>$\Omega$</td>
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<td>$R_{el/i}$</td>
<td>electronic resistance of component i</td>
<td>$\Omega$</td>
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<tr>
<td>$R_{el/j}$</td>
<td>electronic interfacial resistance between component i and j</td>
<td>$\Omega$</td>
<td>6.2</td>
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<tr>
<td>$R_{H^+/i}$</td>
<td>protonic resistance of component i</td>
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<tr>
<td>$R_{H^+/j}$</td>
<td>protonic interfacial resistance between component i and j</td>
<td>$\Omega$</td>
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<td>$R_{ohm}$</td>
<td>total ohmic resistance, high frequency resistance</td>
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<td>$R_x$</td>
<td>through-plane resistance</td>
<td>$\Omega$</td>
<td>6.3</td>
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<tr>
<td>$R_{x,i}$</td>
<td>through-plane resistance of component, i</td>
<td>$\Omega$</td>
<td>6.3</td>
</tr>
<tr>
<td>$R_y$</td>
<td>in-plane resistance</td>
<td>$\Omega$</td>
<td>6.3</td>
</tr>
<tr>
<td>$R_{y,i}$</td>
<td>in-plane resistance of component, i</td>
<td>$\Omega$</td>
<td>6.3</td>
</tr>
<tr>
<td>$RR_M$</td>
<td>ratio of in-plane and through-plane resistance of membrane</td>
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<td>6.3</td>
</tr>
<tr>
<td>$RR_{CCL}$</td>
<td>ratio of in-plane and through-plane resistance of cathode catalyst layer</td>
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<td>Symbol</td>
<td>Meaning</td>
<td>Unit</td>
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<td>---------</td>
<td>------</td>
<td>--------------------</td>
</tr>
<tr>
<td>( \Delta S )</td>
<td>entropy change in a chemical process</td>
<td>( kJ / mol \cdot K )</td>
<td>1.2</td>
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<tr>
<td>( s_j )</td>
<td>saturation of fluid ( j ) in the porous media</td>
<td>dimensionless</td>
<td>2.2, 2.3</td>
</tr>
<tr>
<td>( S_{m,j} )</td>
<td>mass source term for phase ( j )</td>
<td>( kg / m^3 \cdot s )</td>
<td>2.2</td>
</tr>
<tr>
<td>( S_h )</td>
<td>heat source term</td>
<td>( W / m^3 )</td>
<td>2.2</td>
</tr>
<tr>
<td>( S_{h,j} )</td>
<td>heat source term for phase ( j )</td>
<td>( W / m^3 )</td>
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<tr>
<td>( s_w )</td>
<td>saturation of wetting fluid in the porous media</td>
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<td>2.2, 2.3</td>
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<tr>
<td>( s_{wo} )</td>
<td>irreducible saturation of wetting phase in the porous media</td>
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<td>2.2</td>
</tr>
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<td>( s_{nw} )</td>
<td>saturation of non-wetting fluid in the porous media</td>
<td>dimensionless</td>
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<tr>
<td>( s_{nw,0} )</td>
<td>irreducible saturation of non-wetting phase in the porous media</td>
<td>dimensionless</td>
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<tr>
<td>thickness</td>
<td></td>
<td>( m )</td>
<td>6.3</td>
</tr>
<tr>
<td>( t )</td>
<td>time</td>
<td>( s )</td>
<td>2.2, 2.3, 8.3</td>
</tr>
<tr>
<td>( T )</td>
<td>temperature</td>
<td>( K )</td>
<td></td>
</tr>
<tr>
<td>( T_{h} )</td>
<td>temperature of hot side</td>
<td>( K )</td>
<td>7.3, 8.3</td>
</tr>
<tr>
<td>( T_{C} )</td>
<td>temperature of cold side</td>
<td>( K )</td>
<td>7.3, 8.3</td>
</tr>
<tr>
<td>( V )</td>
<td>voltage</td>
<td>( V )</td>
<td>6.2</td>
</tr>
<tr>
<td>( V )</td>
<td>characteristic velocity scale</td>
<td>( m / s )</td>
<td>7.2</td>
</tr>
<tr>
<td>( v_j )</td>
<td>velocity of fluid ( j )</td>
<td>( m / s )</td>
<td>2.3</td>
</tr>
<tr>
<td>( W_{jk} )</td>
<td>work to separate two phases, ( i ) and ( j )</td>
<td>( J )</td>
<td>2.2</td>
</tr>
<tr>
<td>( W )</td>
<td>delamination width</td>
<td>( m )</td>
<td>6.3</td>
</tr>
<tr>
<td>( x )</td>
<td>through-plane direction</td>
<td>( m )</td>
<td>6.2, 6.3, 7.2, 8.2</td>
</tr>
<tr>
<td>( y )</td>
<td>in-plane direction</td>
<td>( m )</td>
<td>6.2, 6.3, 7.2, 8.2</td>
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### Greek Symbols

<table>
<thead>
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<th>Meaning</th>
<th>Unit</th>
<th>Section References</th>
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<tr>
<td>$\alpha$</td>
<td>transfer coefficient</td>
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<tr>
<td>$\delta$</td>
<td>membrane thickness</td>
<td>m</td>
<td>6.3</td>
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<tr>
<td>$\varepsilon$</td>
<td>porosity</td>
<td>dimensionless</td>
<td>2.2, 2.3</td>
</tr>
<tr>
<td>$\varepsilon_i$</td>
<td>porosity of component i</td>
<td>dimensionless</td>
<td>2.2, 2.3</td>
</tr>
<tr>
<td>$\kappa_i$</td>
<td>thermal conductivity of component i</td>
<td>$W / m \cdot K$</td>
<td>2.2, 2.3, 7.2, 8.3</td>
</tr>
<tr>
<td>$\kappa_{x,i}$</td>
<td>through-plane thermal conductivity of component i</td>
<td>$W / m \cdot K$</td>
<td>7.2, 8.3</td>
</tr>
<tr>
<td>$\kappa_{y,i}$</td>
<td>in-plane thermal conductivity of component i</td>
<td>$W / m \cdot K$</td>
<td>7.2, 8.3</td>
</tr>
<tr>
<td>$\eta$</td>
<td>overpotential</td>
<td>V</td>
<td>1.2</td>
</tr>
<tr>
<td>$\eta_{act}$</td>
<td>charge transfer (activation) overpotential</td>
<td>V</td>
<td>1.2</td>
</tr>
<tr>
<td>$\eta_{mt}$</td>
<td>mass-transfer overpotential</td>
<td>V</td>
<td>1.2</td>
</tr>
<tr>
<td>$\eta_{ohm}$</td>
<td>ohmic voltage loss</td>
<td>V</td>
<td>1.2</td>
</tr>
<tr>
<td>$\lambda$</td>
<td>number of water molecules hydrated to sulphonic acid site</td>
<td></td>
<td>1.3, 1.4, 2.1, 7.2, 7.3, 8.3</td>
</tr>
<tr>
<td>$\rho$</td>
<td>density</td>
<td>$kg / m^3$</td>
<td>2.2, 7.3, 8.3</td>
</tr>
<tr>
<td>$\rho_i$</td>
<td>density of component i</td>
<td>$W / m \cdot K$</td>
<td>2.2, 2.3, 7.3, 8.3</td>
</tr>
<tr>
<td>$\sigma_j$</td>
<td>surface tension between substance j and its own vapor phase</td>
<td>$N/m$</td>
<td>2.2</td>
</tr>
<tr>
<td>$\sigma$</td>
<td>(a) conductivity</td>
<td>$S/m$</td>
<td>6.2, 6.3</td>
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<tr>
<td>$\sigma$</td>
<td>(b) surface tension</td>
<td>$N/m$</td>
<td>2.2</td>
</tr>
<tr>
<td>$\sigma_{jk}$</td>
<td>interfacial energy of interface between j and k phases</td>
<td>$N/m$</td>
<td>2.2</td>
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<tr>
<td>$\theta$</td>
<td>contact angle</td>
<td>degree</td>
<td>2.2</td>
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<td>$\mu$</td>
<td>viscosity</td>
<td>$Pa-s$</td>
<td>2.2, 2.3</td>
</tr>
<tr>
<td>$\mu_j$</td>
<td>viscosity of fluid j</td>
<td>$Pa-s$</td>
<td>2.2, 2.3</td>
</tr>
<tr>
<td>$\tau$</td>
<td>tortuosity of porous media</td>
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### Standard Abbreviations

<table>
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<th>Abbreviation</th>
<th>Meaning</th>
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<tr>
<td>ABP</td>
<td>anode bipolar plate</td>
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</tr>
<tr>
<td>ACL</td>
<td>anode catalyst layer</td>
<td>6</td>
</tr>
<tr>
<td>AFP</td>
<td>anode flow-field plate</td>
<td>6</td>
</tr>
<tr>
<td>ADM</td>
<td>anode diffusion media</td>
<td>6</td>
</tr>
<tr>
<td>BP</td>
<td>bipolar plate (graphite plate)</td>
<td>6</td>
</tr>
<tr>
<td>CBP</td>
<td>cathode bipolar plate</td>
<td>6</td>
</tr>
<tr>
<td>CCL</td>
<td>cathode catalyst layer</td>
<td>6</td>
</tr>
<tr>
<td>CDM</td>
<td>cathode diffusion media</td>
<td>6</td>
</tr>
<tr>
<td>CFP</td>
<td>cathode flow-field plate</td>
<td>6</td>
</tr>
<tr>
<td>CL</td>
<td>catalyst layer</td>
<td>6</td>
</tr>
<tr>
<td>DM</td>
<td>diffusion media</td>
<td>6</td>
</tr>
<tr>
<td>DSM</td>
<td>dimensionally stable membrane</td>
<td>1</td>
</tr>
<tr>
<td>EMF</td>
<td>electromotive force</td>
<td>1</td>
</tr>
<tr>
<td>F/T</td>
<td>freeze/thaw</td>
<td>1</td>
</tr>
<tr>
<td>GDE</td>
<td>gas diffusion electrode</td>
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</tr>
<tr>
<td>HFR</td>
<td>high frequency resistance</td>
<td>1</td>
</tr>
<tr>
<td>MEA</td>
<td>membrane electrode assembly</td>
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<tr>
<td>MPL</td>
<td>micro-porous layer</td>
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</tr>
<tr>
<td>NR-MEA</td>
<td>MEA without membrane reinforcement</td>
<td>8</td>
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<tr>
<td>OCV</td>
<td>open circuit voltage</td>
<td>8</td>
</tr>
<tr>
<td>PEFC</td>
<td>polymer electrolyte fuel cell</td>
<td>8</td>
</tr>
<tr>
<td>PEM</td>
<td>polymer electrolyte membrane</td>
<td>8</td>
</tr>
<tr>
<td>PFSA</td>
<td>perfluorinated sulphonic acid</td>
<td>8</td>
</tr>
<tr>
<td>R-MEA</td>
<td>Gore-Primea® 5710 series MEA</td>
<td>8</td>
</tr>
<tr>
<td>R-PEM</td>
<td>Gore-Select® reinforced membrane (thickness =18µm)</td>
<td>7, 8</td>
</tr>
<tr>
<td>SEM</td>
<td>scanning electron microscopy</td>
<td>7, 8</td>
</tr>
<tr>
<td>TBA</td>
<td>Tetrabutylammonium</td>
<td>7, 8</td>
</tr>
<tr>
<td>TO</td>
<td>thermo-osmosis</td>
<td>7, 8</td>
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</table>
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Chapter 1

Introduction

1.1 Background

Fuel cells have the potential to provide the next generation of clean energy in many applications. Among several types of fuel cells, the hydrogen polymer electrolyte fuel cell (PEFC) is the most promising power source for automotive applications, and significant investments in the related technologies are under way to achieve cost effective and competitive fuel cells to replace internal combustion engine vehicles. The Department of Energy (DOE) has been driving fuel cell technology development. The DOE proposed technical targets for future fuel cells are shown in Table 1-1 [1].

The first fuel cell was invented by Sir William Grove in 1839 using reverse electrolysis of water [2]. However, the current generated was too low for a practical application because of high electrolyte resistance and low catalytic area. Hence the early interest in Grove’s invention was not long. The research and development of fuel cells did not get much attention until the late 1950s, during the “space race” between the Soviet Union and the United States. Fuel cells uniquely met the requirement of space applications for a highly efficient compact power plant, and the fuel and oxidant required was already carried on board.

Interestingly, the first fuel cell for US space program was a PEFC. Willard Thomas Grubb [3], a chemist at General Electric, invented the PEFC in 1955 utilizing a hydrocarbon based polymer, polystyrene-divinylbenzene sulfonic acid cross-linked with an inert fluorocarbon film. The PEFC had limited lifetime due to oxidative degradation of the C-H bonds in the
membrane, and required high platinum loadings to provide the required power densities. Despite these limitations, the PEFC was successfully deployed in the US Gemini space program in 1962.

Limited life time and higher cost of early PEFC technologies gave way to alkaline fuel cells (AFC) for space applications in the 1970s. However, owing to breakthroughs of the development of stable and durable polymer membrane material, Nafion® by DuPont, and a dramatic reduction of catalyst loading required using carbon-supported catalyst technology developed by a Los Alamos National Laboratory group [4, 5], the research of PEFCs became active again and is now in an extended renaissance.

Currently, there is a great interest in the PEFCs to replace power generation technologies in transportation, portable and residential power generation devices, which now employ either internal combustion engines or batteries. PEFCs have the following advantages over batteries and internal combustion engines [2, 6, 7]:

1. Fuel cells have higher potential energy conversion efficiency. Realistically, 40–60% is achievable. There will be a 50 percent reduction in fuel consumption for fuel cell vehicles.

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Units</th>
<th>2004 status</th>
<th>2010</th>
<th>2015</th>
</tr>
</thead>
<tbody>
<tr>
<td>Energy efficiency @ 25% rated power</td>
<td>%</td>
<td>59</td>
<td>60</td>
<td>60</td>
</tr>
<tr>
<td>Energy efficiency @ rated power</td>
<td>%</td>
<td>50</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>Power density</td>
<td>W / l</td>
<td>450</td>
<td>650</td>
<td>650</td>
</tr>
<tr>
<td>Specific power</td>
<td>W / kg</td>
<td>420</td>
<td>650</td>
<td>650</td>
</tr>
<tr>
<td>Cost</td>
<td>$ / kWe</td>
<td>120</td>
<td>45</td>
<td>30</td>
</tr>
<tr>
<td>Transient response time (10% → 90% rated power)</td>
<td>s</td>
<td>&lt;1.5</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Durability</td>
<td>hours</td>
<td>1000</td>
<td>5000</td>
<td>5000</td>
</tr>
<tr>
<td>Cold start-up to 90% rated power</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>@ - 20 °C ambient temperature</td>
<td>s</td>
<td>120</td>
<td>30</td>
<td>30</td>
</tr>
<tr>
<td>@ + 20 °C ambient temperature</td>
<td>s</td>
<td>60</td>
<td>15</td>
<td>15</td>
</tr>
<tr>
<td>Survivability</td>
<td>°C</td>
<td>-20</td>
<td>-40</td>
<td>-40</td>
</tr>
</tbody>
</table>

1) Cost is based on 500,000 units /year
when compared to a conventional vehicle with a gasoline internal combustion engine (ICE), on a well-to-wheels basis.

2. Unlike batteries, fuel cells can produce power as long as fuel and oxidizer are supplied. There is no charging of fuel cells.

3. Fuel cells operate quietly, excluding pumps and blowers, and are relatively compact.

4. Fuel cells can provide modular power, which means the applications could range from a few milliwatts to more than a megawatt.

5. Wide application of fuel cells can lead to a great reduction in greenhouse gas emissions, with harmful emissions resulting only from hydrogen generation.

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 1-2. Among the fuel cell types, the PEFC has a wide range of application area including the automotive industry, portable applications such as laptop power units, and stationary power generation systems. The basic operation of a PEFC is described in the next section.

Table 1-2: Different fuel cell types [8].

<table>
<thead>
<tr>
<th>Fuel cell type</th>
<th>Mobile ion</th>
<th>Operating temperature( °C )</th>
<th>Applications</th>
</tr>
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<tbody>
<tr>
<td>Alkaline fuel cell (AFC)</td>
<td>OH⁻</td>
<td>50~200</td>
<td>Space and military</td>
</tr>
<tr>
<td>PEFC</td>
<td>H⁺</td>
<td>30~100</td>
<td>Vehicle, portable and low combined heat and power (CHP) system</td>
</tr>
<tr>
<td>Direct methanol fuel cell (DMFC)</td>
<td>H⁺</td>
<td>20~90</td>
<td>Portable electronics</td>
</tr>
<tr>
<td>Phosphoric acid fuel cell (PAFC)</td>
<td>H⁺</td>
<td>~220</td>
<td>CHP (200kW)</td>
</tr>
<tr>
<td>Molten carbonate fuel cell (MCFC)</td>
<td>CO₃²⁻</td>
<td>~650</td>
<td>CHP (200 ~1000 kW)</td>
</tr>
</tbody>
</table>
1.2 Polymer Electrolyte Membrane Fuel Cell (PEFC)

Basic operation of the polymer electrolyte fuel cell is very simple: a reverse reaction of water electrolysis. Figure 1-1 shows the schematic operation of PEFC. Fuel (hydrogen) reacts with oxidant gases (oxygen) to produce water as shown in Eq. 1.1. Contrary to combustion reaction to release heat energy, electrical current is generated via separate half cell electrochemical reactions. Hydrogen gas is oxidized on the catalyst surfaces of an anode electrode into protons (H\(^+\)) and electrons (e\(^-\)), as shown in Eq. 1.2. At the cathode electrode, oxygen gas reacts with protons from the electrolyte, and electrons from the anode, to form water, as shown in Eq. 1.3.

![Figure 1-1: Schematic of PEFC operation.](image)

Overall cell reaction:

\[
\frac{1}{2} \text{O}_2 + \text{H}_2 \rightarrow \text{H}_2\text{O} \quad [1.1]
\]

Anode reaction:

\[
\text{H}_2 \rightarrow 2\text{H}^+ + 2\text{e}^- \quad [1.2]
\]
Cathode reaction:

\[
\frac{1}{2} \text{O}_2 + 2 \text{H}^+ + 2 \text{e}^- \rightarrow \text{H}_2\text{O}
\]  

[1.3]

In order to facilitate electrochemical cell reactions, carbon-supported nano-sized platinum catalyst particles are generally utilized in both anode and cathode electrodes.

1.2.1 PEFC Operation

The performance of PEFC is typically represented by a polarization curve, which is a graphical representation of fuel cell voltage versus current. A typical polarization curve is shown in Fig. 1-2. Actual fuel cell voltage is lower than theoretical voltage because of several irreversibilities, which manifest as a reduction in voltage: 1) activation loss, 2) ohmic loss, 3) concentration polarization, and 4) fuel crossover loss.

Figure 1-2: Typical polarization curve of a PEFC [10].

The maximum thermal electromotive force (EMF) can be described as:
where \( n \), \( \Delta H \), and \( F \) denote the number of electrons participating in one mole of water production shown in Eq. 1.3 (\( n = 2 \) for a \( \text{H}_2 \) PEFC), enthalpy change (kJ/mol) of the overall reaction, Eq. 1.1, Faraday constant (96485 C/mol), respectively. If all the energy from the hydrogen fuel, its enthalpy of formation, were transformed into electrical energy, the thermal EMF would be given by Eq. 1.1. However, the electrically available EMF can be calculated by by Gibbs free energy change of the overall fuel cell reaction:

\[
E^{\text{rev}} = -\frac{\Delta G}{nF} = -\frac{\Delta H + T \Delta S}{nF} \quad [1.5]
\]

Here, \( \Delta G \), \( \Delta H \), and \( \Delta S \) are the Gibbs free energy (kJ/mol), enthalpy (kJ/mol), and entropy (kJ/mol-K) released from the overall reaction Eq. 1.1. The maximum fuel cell voltage is 1.18 V in typical operating conditions (80°C and 1 atm).

Compared to the maximum voltage, actual fuel cell voltage, \( E(V) \), can be expressed by Eq. 1.6:

\[
E = E^{\text{rev}} - \eta_{\text{act}, a} - \eta_{\text{act}, c} - \eta_{\text{ohm}} - \eta_{\text{mass}, a} - \eta_{\text{mass}, c} \quad [1.6]
\]

where \( \eta_{\text{act}, a} \) and \( \eta_{\text{act}, c} \) are activation polarization loss (V) of anode and cathode each, \( \eta_{\text{ohm}} \) is ohmic loss (V), and \( \eta_{\text{mass}, a} \) and \( \eta_{\text{mass}, c} \) are concentration polarization loss (V) of anode and cathode, respectively.

The activation polarization dominates the low current density region, which is controlled by sluggish electrode kinetics. For a hydrogen polymer electrolyte fuel cell, the anodic activation loss is negligible and most of the activation loss is attributed to the oxygen reduction reaction. From thermodynamic derivation using electrochemical potential, the relation between activation
losses and current for a half cell reaction, which is limited by a charge transfer process, (the case for a typical PEFC), follows the Butler-Volmer equation [11, 12].

\[
i = i_0 \left( e^{\frac{\alpha_a n F}{RT} \eta_{act}} - e^{\frac{\alpha_c n F}{RT} \eta_{act}} \right) \tag{1.7}
\]

where \( i \) represents the current density (A/m\(^2\)), \( F \) is Faraday constant (96,485 C/mole), \( i_0 \) is the exchange current density (A/m\(^2\)), \( \eta_{act} \) is the activation over-potential (V) of that electrode, \( n \) is the number of electrons transferred in the elementary electrode reaction charge transfer sites, and, \( \alpha_a \) and \( \alpha_c \) are the anodic and cathodic transfer coefficients of each half cell reaction. The exchange current density is a crucial factor in reducing activation polarization loss, and increases with higher temperature and pressure, higher concentration of reactant species, more effective catalysts, and higher electrochemical active area [8, 9]. Degradation due to damage from freezing can decrease the catalyst active area and the exchange current density, leading to higher polarization loss in the low current density region.

Ohmic polarization loss is mainly a result of the limited ionic conductivity of the membrane. Additionally, the electrical resistances of the porous media and the flow-field plates as well as interfacial contacts contribute. The ohmic losses are more pronounced at moderate and high current density operation, and are strongly affected by the hydration level of the membrane. The ohmic loss can be expressed by Ohm's law:

\[
\eta_{ohm} = IR_{ohm} \tag{1.8}
\]

where \( R_{ohm} \) is the total resistance (\( \Omega \)) of a fuel cell including the contact resistance and the ionic resistance, and \( I \) is the current (A). Total resistance can be measured by AC impedance (typically, 1 kHz), called high frequency resistance (HFR).

Concentration polarization is caused by the decrease of concentration of reactant gases on the catalytic sites compared to bulk concentration. This mass transport limitation is predominant
in the higher current density region. During the cell operation, the produced water can condense and block available pores for gas transport in the diffusion media (DM) or catalyst layer (CL), which leads to reduced reactant gas fluxes into active reaction sites. The diffusive limitation in DM results in a concentration difference between the catalyst surface and DM, and subsequently causes a reduced electrode potential. According to the Nernst equation, the concentration over-potential can be written from the thermodynamic activity as \[8, 11, 12\]:

\[
\eta_{\text{over}} = \frac{RT}{nF} \left( 1 - \frac{i}{i_l} \right) \tag{1.9}
\]

where \(i_l\) is the limiting current density \((A/m^2)\), indicating the maximum rate at which a reactant can be supplied to an electrode. \(T\) is absolute temperature \((K)\). Note that this is only a thermodynamical effect in Eq. 1.9, and there is also a related kinetic effect to mass limitation.

Finally, another type of loss occurring in the fuel cell is fuel cross-over loss. In a PEFC, hydrogen gases diffuse through the polymer electrolyte membrane into the cathode electrode. The cross-over hydrogen reacts electrochemically with oxygen at the catalytic sites without producing external electrons, which results in decrease of open circuit voltage and fuel efficiency.

### 1.2.2 Fuel Cell Components

The maximum operating voltage of a single fuel cell is less than 1 V. For automotive applications \((80 \sim 100 \text{ kW}_{\text{net}} \text{ power}, 200 \sim 500 \text{ V})\), the single fuel cell unit is repeated several hundred times in series using bipolar cooling plates for compactness and simplicity. It is called a fuel cell stack, and its components are shown in Fig. 1-3. A fuel cell stack consists of a repeated single cell unit, current collector plate (not shown), compression end plate, and compression rods. A PEFC stack is usually connected in series. Therefore, the stack should be designed for every cell to have similar behavior and boundary conditions (flow and thermal conditions). In practice,
however, the end cell can often reduce cold start performance, resulting in irreversible damage because of additional heat loss to end plates with larger thermal mass.

In Fig. 1-3, the repeated single cell unit consists of bipolar cooling flow field plate, membrane electrode assembly, diffusion media, and gaskets (not shown). The core element of a PEFC is membrane electrode assembly (MEA), which consists of the proton conductive polymer electrolyte membrane and catalyst layers on both sides of the membrane. The electrolyte most commonly used by PEFCs today is a polyperfluorosulfonic acid membrane. DuPont produces the
industry's most widely used membrane, called Nafion®, although other similar products exist including Gore-Select® membranes with expanded PTFE based reinforcement. 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.

The catalyst layers coated on both sides of membrane typically consist of platinum powder roughly 2-4 nm in size and supported by larger (~40 nm) 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 typically the order of 5 - 30 μm. Outside the membrane electrode assembly structure, there are backing layers or gas diffusion media. The main purpose of DM is for the transport of reactant gases from the flow channels to the catalyst layer. In addition, due to the carbon fiber structure of the DM, it allows the necessary electron conduction from the catalyst layer to the external load and back. Other important features of this component are to remove heat and product liquid and gas-phase water from the catalyst layer into the flow channel. The bipolar flow field plates with coolant channels are made of an electrically conductive material such as graphite or metal. They distribute reactants to overall electrode area, and remove generated heat as well as product water. They also provide electron paths between the electrodes, and necessary robustness and stiffness to support the whole fuel cell structure.

1.3 Literature Review of Freeze-damage of PEFCs

The hydrogen proton electrolyte fuel cell is a promising power source for future clean transportation and zero emission vehicles. However, issues related to subfreezing operation, including rapid start-up, energy consumption, survivability, and durability have recently become
the subjects of investigation. For fuel cell vehicles to be competitive, they should deliver 90% of rated power in 30 seconds from a cold start at -20°C, with less than 62.5 J/We parasitic energy input [1]. Moreover, fuel cells should survive without damage after repeated soaking at -40°C. Cold start and survivability issues are attributed to the existence of residual liquid water after shutdown, or water generation during the cold start-up.

The main PEFC freeze and rapid cold start issues are to prevent fuel cell system damage caused by freezing, and to manage the energy/power production without damage for rapid startup in a subfreezing environment. There are numerous disclosed ideas to approach solutions. Pesaran et al. [14] reviewed numerous patents and categorized the proposed solutions into two strategies according to whether the system uses energy during the vehicle parking or mostly at vehicle startup: “Keep-Warm” and “Thaw and Heat at Startup”. The two strategies are summarized in Fig. 1-4.

The “Keep-Warm” method does not allow fuel cell system to freeze, which costs energy to keep fuel cell system above threshold temperature. The energy/fuel consumption requirements are highly dependent on difficult-to-predict parking time and ambient temperature variables. This strategy is effective for short-term parking and/or for mild subfreezing vehicle storage temperatures.

The other strategy, “Thaw and Heat at Startup”, requires water drainage from the fuel cell system during the shutdown, and additional heating energy for thawing residual ice and preventing ice formation during the startup. Internal heat sources (waste heat from fuel cell reaction, combustion energy from hydrogen fuel, and wire heating in MEA) and external sources (coolant heating and hot air blowing) are proposed. This strategy is more realistic, but dryness of fuel cell during the shutdown, and rehumidification during the startup are required. The disclosed patents are oriented to solution methods, but fundamental understandings of the phenomena which occur from freezing and rapid cold startup are not covered.
Existing findings on damage by freezing are chronologically summarized in Table 1-3. One important result shows that fuel cells dried during the shutdown experience neither observable physical damage nor electrochemical losses by freezing [15, 16, 17, 18]. However, there are conflicting results in case of a cell with no significant purge. Some reported physical damage, performance loss, and electrochemical loss (electrochemical catalytic surface area (ECSA), interfacial and charge transfer resistance increase) [16, 19, 20, 21, 22]. Physical damage includes membrane failure (holes and cracks), catalyst cracks and delamination, pore distribution change, and gas diffusion media fracture, as shown in Fig. 1-5. Others observed no significant performance loss even without dry purge during the shutdown [23, 24, 25]. Meyers and co-researchers observed severe damage from freezing, but with stack design changes, damage was prevented [21, 26, 27].
Liu [28] investigated the effects of membrane reinforcement and diffusion media on freezing damage. Contrary to MEAs with non-reinforced membrane (Nafion®), the MEA with a dimensionally stable reinforced membrane had no observable damage in the ex-situ immersion freeze/thaw (F/T) thermal cycling test, which indicated a reinforced membrane is more tolerable to F/T damage. Interestingly, both MEAs with diffusion media had no observable damage. This indicates diffusion media can be an important factor to mitigate F/T damage.

Damage from cold start tests was also reported: performance and ECSA loss, hydrophobicity loss [29, 30], and end cell loss, especially anode end cell [26, 27]. Compared to
thermal freeze/thaw cycling, more severe damage during the cold start may be expected because of fast ice formation and rapid processes.

The F/T damage may be a coupled effect of MEA and DM materials because the residual water content in each can behave as a source of damaging water. Hydrophobic treatment in the DM and micro-porous layer (MPL) can serve as a barrier for direct water flow from water outside the MEA structure, and as mechanical support for the CL. Therefore, effects of DM and MEAs on damage need to be separated to understand the possible damage modes.

The F/T damage is affected by several factors outside of operating conditions including MEA manufacturing processes, micro-structures, and CL compositions. Decal processes using tetrabutylammonium (TBA) type of ionomers could make a much stronger bonding between CL and ionomers compared to an ink spraying method. Direct coating on membrane with TBA type catalyst ink can form a more intimate membrane/electrode interface compared to decal process [23]. The conflicting results about freeze damage may be partially ascribed to different manufacturing processes. Physical damage can also be aggravated in the case of weakly bonded CL to ionomers or membrane. Therefore, micro-structure, composition, and manufacturing process of MEAs are also important factors on F/T damage.

Freeze-damage can also be due to stress induced by volume expansion at phase transformation. However, fuel cell materials are highly porous (70 ~ 85 % for DM and 40 % for CL). Therefore, the 9 % of volume expansion from ice formation can be absorbed without damage by the porous structure unless nearly fully saturated, providing formation is slow. Simple stress effects induced by ice formation are not sufficient to explain interfacial delamination damage mode. He and Mench [31, 32] suggested the most possible damage location by ice lens formation are the interfaces between DM, CL, membrane, and flow field plate under the flow channel, as shown in Fig. 1-6. The detailed summary of their model is covered in Section 2.3.
Water management during shutdown is a key for mitigation of freeze-damage as well as for achieving rapid start without damage from the frozen conditions. Liquid water has detrimental effects on PEFC under normal operation as well as cold start conditions. Local anode side flooding [33] during normal operation can cause local fuel starvation, resulting in cathode carbon corrosion in the cathode electrode [34], decreasing life time. Local ice from the residual water in the anode side can also cause the same carbon corrosion during the cold start. Water flooding in the cathode side can decrease performance and longevity, and ice formation from the residual water in the cathode may cause physical damage of fuel cell materials. Khandelwal et al. [35] showed that the residual ice delayed cold start due to significant latent heat. In addition, residual ice can cause voltage reversal during the cold start operation, specifically in end cells, resulting in severe irreversible loss, attributing to carbon corrosion [36].

Freeze-damage is affected by coupled and complex factors: 1) operation procedure (shutdown and cold startup procedure), 2) material micro-structures and composition, 3) fuel cell component matching between diffusion media, MEA and flow field plates, 4) material manufacturing process, and 5) others, such as fuel cell stack structures. Fundamental understanding and more controlled experiments are required, which can elucidate degradation mechanism and the controlling parameters to achieve rapid cold start without freeze-damage.
Table 1-3: Summary of observed PEFC damage due to freezing.

<table>
<thead>
<tr>
<th>Referral</th>
<th>Test mode</th>
<th>PEM</th>
<th>CL</th>
<th>MEA</th>
<th>DM</th>
<th>Test conditions</th>
<th>Results</th>
<th>Publication</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wilson <em>et al.</em> [23]</td>
<td>In-situ F/T</td>
<td>Nafion 117</td>
<td>20 wt% Pt/C (0.16 mg/cm²)</td>
<td>Decal process</td>
<td>ELAT hydrophobic carbon cloth</td>
<td>-10/80</td>
<td>3</td>
<td>No purge (wet)</td>
</tr>
<tr>
<td>McDonald <em>et al.</em> [15]</td>
<td>Ex-situ F/T</td>
<td>Nafion 112</td>
<td>0.4mg Pt/C/cm²</td>
<td>N/A</td>
<td>None</td>
<td>-40/80</td>
<td>385</td>
<td>Dry state (λ &lt; 3)</td>
</tr>
<tr>
<td></td>
<td>In-situ F/T</td>
<td>Nafion 112</td>
<td>0.4mg Pt/C/cm²</td>
<td>N/A</td>
<td>Carbon paper</td>
<td>-40/80</td>
<td>385</td>
<td>Dry state (λ &lt; 3)</td>
</tr>
<tr>
<td>Liu [28]</td>
<td>Ex-situ F/T (immersion)</td>
<td>Nafion 112</td>
<td>N/A</td>
<td>N/A</td>
<td>None</td>
<td>-40/50</td>
<td>10</td>
<td>Immersed in water</td>
</tr>
<tr>
<td></td>
<td>DSM</td>
<td>N/A</td>
<td>N/A</td>
<td>None</td>
<td>-40/50</td>
<td>10</td>
<td>Immersed in water</td>
<td>No observable loss</td>
</tr>
<tr>
<td></td>
<td>In-situ F/T</td>
<td>Nafion 112</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>-40/25</td>
<td>63</td>
<td>N/A</td>
</tr>
<tr>
<td></td>
<td>DSM</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>-15</td>
<td>N/A</td>
<td>N/A</td>
<td>End cell loss</td>
</tr>
<tr>
<td>Patterson <em>et al.</em> [26, 27]</td>
<td>In-situ F/T</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>-40/80</td>
<td>100</td>
<td>No purge (wet)</td>
</tr>
<tr>
<td></td>
<td>Cold startup</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>-80/80</td>
<td>10</td>
<td>No purge (wet)</td>
</tr>
<tr>
<td>Mukundan <em>et al.</em> [24, 25]</td>
<td>In-situ F/T</td>
<td>Nafion 1135</td>
<td>20 wt% Pt/C (0.2 mg/cm²)</td>
<td>Decal process</td>
<td>Wet proofed carbon cloth</td>
<td>SGL 30DC</td>
<td>-40/80</td>
<td>45</td>
</tr>
<tr>
<td></td>
<td>Nafion 1135</td>
<td>20 wt% Pt/C (0.2 mg/cm²)</td>
<td>Wet proofed carbon cloth</td>
<td>-80/80</td>
<td>10</td>
<td>No purge (wet)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

a) Decal printing (TBA+ form catalyst) and then hot pressing at 200 C
b) 20% PTFE treatment with MPL

Abbreviation: F/T: Freeze/thaw thermal cycling  DSM: Dimensionally stable membrane  GDE: Gas diffusion electrode  PEM: Polymer electrolyte membrane
<table>
<thead>
<tr>
<th>Referral</th>
<th>Test mode</th>
<th>PEM</th>
<th>CL</th>
<th>MEA</th>
<th>DM</th>
<th>Test conditions</th>
<th>Results</th>
<th>Publication</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cho et al.</td>
<td>In-situ F/T</td>
<td>Nafion 115</td>
<td>20 wt% Pt/C (0.4 mg/cm²)</td>
<td>GDE³</td>
<td>Wet proofed carbon paper</td>
<td>-10/80 4</td>
<td>No purge (wet) Performance loss, ohmic and charge transfer resistance increase ECSA loss</td>
<td>2003</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>4</td>
<td>Dry purge (λ &lt;2) No performance loss No ECSA loss</td>
<td></td>
</tr>
<tr>
<td>Gaylord</td>
<td>Field test (stationary)</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>Carbon paper</td>
<td>Exposed to freezing N/A N/A</td>
<td>DM fracture Membrane failure Severe CL delamination</td>
<td>2005</td>
</tr>
<tr>
<td>Meyers</td>
<td>In-situ F/T</td>
<td>Commercial MEAs (reinforced membrane)</td>
<td>N/A</td>
<td>N/A</td>
<td></td>
<td>-20/° 20 N/A</td>
<td>Membrane cracks CL delamination</td>
<td>2005</td>
</tr>
<tr>
<td>Oszcipok et al.</td>
<td>Cold startup</td>
<td>Catalyst coated membrane</td>
<td>N/A</td>
<td>N/A</td>
<td></td>
<td>-10 10 N/A</td>
<td>Dry purge Performance loss ECSA loss Hydrophobicity loss (MPL, DM)</td>
<td>2005</td>
</tr>
<tr>
<td>Yan et al.</td>
<td>Cold startup</td>
<td>Nafion 112,115,117</td>
<td>20 wt% Pt/C</td>
<td>GDE³</td>
<td>Carbon paper/cloth</td>
<td>-15 NA 2006</td>
<td>Interfacial delamination Membrane hole</td>
<td></td>
</tr>
<tr>
<td>Guo et al.</td>
<td>Ex-situ F/T</td>
<td>Commercial MEA with 30 μm membrane and 1.0mg Pt/cm²</td>
<td>None</td>
<td></td>
<td>Carbon paper</td>
<td>-30/20 6</td>
<td>No purge (wet) Dry purge (λ &lt;4) Negligible damage</td>
<td>2006</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>20 No purge (wet) No physical damage Severe damage Severe CL cracks</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hou et al.</td>
<td>In-situ F/T</td>
<td>Nafion 212</td>
<td>20 wt% Pt/C (0.8 mgPt/cm²)</td>
<td>GDE³</td>
<td>Carbon paper</td>
<td>-20/60 2006 20</td>
<td>No performance loss No ECSA loss No physical damage</td>
<td>2006</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2006</td>
<td>Easy flooding Severe CL cracks ECSA loss Negligible performance loss</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Dry purge (λ &lt;4) No physical damage</td>
<td></td>
</tr>
</tbody>
</table>

c) Catalyst ink sprayed on DM and then hot pressing at 140°C  
d) Sprayed on DM and then hot pressed
1.4 Freeze-damage Mitigation Methods

Several methods have been utilized in PEFCs to reduce residual water during shutdown before the fuel cell is frozen: 1) convective purge, 2) vacuum purge, 3) capillary drainage, 4) thermo-osmotic drainage, and 5) combination. Purge duration as well as energy consumption is important for automotive applications. Energy consumption including cold startup is required to be less than 62.5 J/We [1], and purge duration should be much less than one minute.

Water content in the MEA is a critical factor for purge duration. Water content ($\lambda$) in the electrolyte is defined as the number of moles of water per one mole of sulfonic acid group in the electrolyte. As mentioned in Section 1.2.1, ohmic losses are strongly affected by water content of the membrane. Thus the membrane should be well hydrated, but over-hydration may cause freeze-damage. From other studies, a dried MEA, of which the water weight percent is less than 6% (water content, $\lambda < 4$), did not suffer from freeze-damage [15, 16, 17, 19]. However, its ionic conductivity was too low to generate current from the frozen state [25, 37]. Mukundan et al. [25] observed that the optimal conductivity under sub-freezing conditions is obtained when $7 < \lambda < 12$ in Nafion®, and Tajiri et al. [37] also observed that ohmic loss is not significant for $6.2 < \lambda < 14$ in Gore Primea® MEA. These studies indicate that MEA equilibrated with relative humidity 80~95 %, but without liquid contact is preferable for rapid cold start. Excess water in the MEA due to liquid contact can cause freeze-damage because liquid contact caused water content of membrane to jump to $\lambda = 22$, a phenomenon known as Schroeder’s paradox [38, 39].

For a criterion of purge duration, St-Pierre et al. [40] suggested that the optimal purge strategy is to stop the purge operation at a point when water in the channels and diffusion media is removed but water in the membrane is still largely present. For a specific MK 9 series 10-cell
stack, the optimal purge duration is 88 seconds using dry 89 ℓ/min air / 25 ℓ/min H₂ at 70°C and 1.6 bar.

A convective dry gas purging method is typically used to reduce residual water within a stack at shutdown. A convective flow is effective to remove water inside the channel, but is not efficient due to low velocity inside the DM and CL, where water removal is dominated by capillary flow or evaporation. Typically, a convective purge with hot dry gases is used because of high evaporation rate. However, this purging method causes non-uniform water distribution along the channel. Reactant gas flow pattern as well as coolant flow pattern in the cooling bipolar plates also affects water removal and uniformity. For serpentine flow pattern shown in Fig. 1-7 (a) and (b), water content increases along the channel, and the membrane is dried-out near upper inlet flow regions, resulting in physical degradation due to mechanical stress [41]. However, for parallel counter-flow design shown in Fig. 1-7 (c) and (d), the non-uniformity can be mitigated. It should also be noted that in a convective cold purging of a serpentine channel design, liquid water also tended to accumulate along or under the channel walls at 180° turns [42], resulting in physical damage in the frozen state.

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Figure 1-7: Serpentine flow ((a) and (b)) and parallel flow ((c) and (d)) pattern.
The purge temperature is also important. A MK 513 series single cell of Ballard Power Systems Inc. [40, 43] showed that dry hot purging performed immediately after operation (one minute dry nitrogen purging at 85 °C for both sides) resulted in freeze-damage, but cold purging performed after cool down to ambient temperature for one minute with dry nitrogen did not result in freeze-damage. The reason is not disclosed, but may be attributed to flow pattern. MK 513 series fuel cell has serpentine parallel flow patterns similar to Fig. 1-7 (a) and (b), and each flow channel is significantly long. Hot purging may cause dry-out of MEA near inlet and wetted MEA near outlet, resulting in physical damage due to freezing or also due to localized dryout. However, for cold purging, liquid water drained from MEA into channel during cool down can be removed by a forced flow. Membrane dry-out and non-uniformity can also be mitigated because evaporation is negligible. However, the water drainage mechanism during cool-down is not elucidated.

To effectively remove water inside the DM and MEA, vacuum purging was proposed [44]. Vacuum should be sufficient to evaporate and remove enough water from the fuel cell as to prevent damage due to freezing. Water evaporation is proportional to difference between saturation pressure and vapor pressure, so pump pressure should be maintained to be lower than saturation pressure. Based on saturation curve, higher fuel cell temperature (at least about 50°C) is preferable because of small vacuum pump already installed in the electric vehicle.

Perry et al. [45, 46] observed in their proprietary fuel cell stack that residual liquid water in the MEAs was drained into porous bipolar cooling plates by capillary force at shutdown, and the freeze-damage was localized in the anode end cell. Resnick and Resiser [47] claimed that water accumulation in the end cells was due to evaporation and condensation due to temperature difference between center cell and end cell. To mitigate this water accumulation, the temperature difference between center cell and end cell should be less than 3°C, preferably 1°C. They
proposed several ideas: 1) thermal insulating materials for end plates, and 2) small heaters on end plates.

Recently, Perry et al. [45, 46] also observed water movement due to temperature gradient. A schematic of the water saturation level change of anode and cathode end cells during shutdown is shown in Fig. 1-8. From the schematic diagram, water flowed from hot to cold side, and water accumulated at the catalyst layers in front of membrane in the heat flow direction: 1) cathode catalyst layers for an anode end cell, and 2) anode catalyst layers for cathode end cell. Higher water content in the cathode catalyst layers caused delayed startup as well as damage due to lower oxygen reduction rate and higher mass transfer resistance. However, the cathode end cell was less damaged due to fast hydrogen oxidation rate and faster diffusion rate of hydrogen compared to oxygen. Perry et al. [45, 46] observed that diffusion media with lower permeability in the end cells is effective to reduce water accumulation in the catalyst layers, improving cold startup without damage.

Bradean et al. [48] also observed water flow under temperature gradient in their fuel cell stack. Natural water drainage utilizing temperature gradients in the through-plane direction was also proposed based on an experimental relation. Contrary to Resnick and Reiser’s [47] proprietary approach (uniform temperature), by increasing temperature gradient across the stack, the typical residual water amount (6~7mg/cm²-MEA) was significantly reduced to an optimal water amount (2.5 mg/cm²-MEA) for rapid startup without damage, by natural cooling process. During natural cooling, excess liquid water is drained from MEA and DM into flow channels. This method is effective because parasitic energy is not required and local dry-out does not occur compared to convective dry gas purging. They claimed that convective purge at room temperature is beneficial to remove water inside the channel, drained from MEA and DM during the natural cool down.
There are two water transport modes driven by temperature gradient in fuel cell: 1) thermo-osmosis in the membrane, and 2) phase-change induced flow in the porous media. Water flux is observed when membrane separates water with different temperatures, and this phenomenon is termed thermo-osmosis. For a hydrophilic membrane, thermo-osmotic water flux is from the cold to the hot side, although water flows from the hot to the cold side for a hydrophobic membrane. When water is divided by hydrophobic porous media and is under

Figure 1-8: Schematic water saturation level change of anode and cathode end cells induced by thermo-osmosis during the shutdown [45].
temperature gradient, water evaporates at the interface between water in the hot side and porous media, diffuses through porous media, and then condenses at the interface between water in the cold side and porous media. This water transport mode is termed phase-change induced flow (also known as heat pipe effect, although this is technically not a heat pipe).

Temperature gradient water flow in fuel cell materials has been investigated, but there are conflicts about water flux direction and rate in the literature. Zaffou et al. [49, 50] observed water flow from the hot to cold side only in a PTFE reinforced membrane. However, in Nafion® membrane and MEA, thermo-osmosis did not occur. However, Villaluenga et al. [51] and Tasaka et al. [52] observed that water moved from cold to hot side in the Nafion® membrane, which is contradictory to results observed in a PEFC. These conflicts may come from the fact that there exist phase-change induced flow and thermo-osmosis in fuel cell materials, resulting from different hydrophobicity. Thus separate understanding between thermo-osmosis and phase-change induced flow should be required.

As a diagnostic tool for purge duration, high frequency resistance (HFR) and relative humidity at the outlet can be measured while fuel cell is purged. HFR measurement is simple and is preferred. HFR change while purging is attributed to ionic resistance change of ionomers, and HFR increase is attributed to membrane dryness. St. Pierre et al. [40] utilized HFR for purge duration as shown in Fig. 1-9. This figure shows that slight resistance increase during the initial purging is due to the evaporation unevenness between the cell inlet and outlet, and MK9 series has counter-flow parallel flow pattern, as shown in Fig. 1-7 (c) and (d). This work notes that HFR is the averaged value of all active area and may change with water redistribution due to water equilibration. After purge ceased, HFR of fuel cell was observed to decrease with time and eventually reach asymptotic values. This is attributed to water redistribution in the electrolyte and ionomers because of the initial unevenness of water distribution in fuel cell.
1.5 Motivation and Objectives

Component level as well as system level approaches are required to mitigate freeze-damage in H₂ PEFC system. Note that this work is limited to PEFC, not balance of plant components.

Summarizing previous literature work mentioned in Sections 1.3 and 1.4:

- Dried membrane and MEA (water content ($\lambda$) < 4) is not damaged from freezing.
- For a wetted fuel cell, some did not observe significant freeze-damage, but others observed irreversible damage.
- A computational freeze-damage model in PEFC [31, 32] suggested interfacial delaminations, but it is not yet fully validated experimentally.
- To elucidate damage modes, more controlled experimentation should be performed because coupled and complex factors are involved.

Figure 1-9: HFR change with purging time [40].
To mitigate freeze-damage and enable rapid-cold start without damage, liquid water should be removed from fuel cell before fuel cell is frozen. Typically, convective purge is used, but it requires significant energy and may cause physical damage resulting from non-uniformity of water distribution along the flow channels.

Temperature gradient driven water flow has been attractive because of a potential for water removal from MEA without parasitic energy during shutdown. However, there are conflicts in fuel cell, and temperature gradient driven flow is not well understood. Separate understanding between thermo-osmosis and phase-change induced flow is required.

The motivation of this work is to resolve discrepancies in literature to elucidate freeze-damage mechanism, provide model validation data, and provide material and operational guidelines for prevention of freeze-damage.

This work consists of two main topics: 1) identification of freeze-damage mode, and 2) study of temperature-gradient driven water transport phenomena as a potential to mitigate freeze-damage.

General description of freeze-related issues in fuel cell and water transport phenomena are introduced in Chapter 1 and 2. Extensive ex-situ and in-cell F/T material testing are covered in Chapter 3, 4 and 5 to identify freeze-damage modes. As a diagnostic tool, a two-dimensional anisotropic current disruption model is discussed in Chapter 6. Chapter 7 and 8 present thermo-osmosis water transport and phase-change induced water flow. Finally, conclusion and future work are summarized in Chapter 9.
Chapter 2

Water Transport in PEFC Components

Water management is very important for PEFC performance and longevity. The current polymer electrolyte membrane requires hydration to provide acceptable proton conductivity. The membrane can be maintained in a hydrated state by pre-humidified reactant gases and produced water at cathode sites, but the condensed liquid water inside the catalyst layers and diffusion media can cause performance loss due to blockage of the reactants to the catalysts, which is called flooding. Water transport in a PEFC becomes complex because of two-phase flow through porous DM and CL as well as the special water transport mechanisms in the polymer electrolyte.

This chapter describes the necessary details to understand the multi-phase flow in the fuel cell components, especially membrane and porous media such as the CL and DM. In the first section, a brief review of structure, state of water, and water transport modes in Nafion® membrane are explained. In the subsequent sections, multi-phase flow fundamentals in the porous media, and available freezing models are discussed.

2.1 Water Transport in Nafion® Polymer Electrolyte Membrane

DuPont developed a perfluorosulfonic acid (PFSA) polymer membrane, Nafion® in 1962, which is the most commonly used electrolyte in PEFCs. The polymer consists of a PTFE backbone and perfluorovinyl ether pendant side chains with sulfonic groups on the ends. The chemical formula of Nafion® is shown in Fig. 2-1. Morphology and properties of Nafion® and alternative membranes are reviewed in detail [54, 55].
The nature of water, ionic conductivity, water transport modes, and freezing behavior in Nafion® are briefly reviewed here. Structural and transport properties of Nafion® membrane are strongly affected by water content. The water content of membrane ($\lambda$) is defined as the number of moles of water associated with a mole of sulfonic acid groups in the membrane. The membrane is hydrated when it is in contact with water vapor or liquid water, although the total uptake strongly depends on the state of water in contact with the membrane. The ionic conductivity of Nafion® membrane is affected by temperature and relative humidity, as shown in Fig. 2-2 using the relationship proposed by Springer [57]. In 1903, Schroeder [38] found that polymeric materials absorb less water from the saturated vapor phase than from the liquid phase, which is known as Schroeder’s paradox. Zawodzinski et al. [39] first measured the water uptake of a Nafion membrane as a function of water activity. As shown in Fig. 2-3, $\lambda$ is 14 H$_2$O/SO$_3^-$ for
saturated water vapor, and 22 H₂O/SO₃⁻ for liquid water saturation at 30°C, which shows Schroeder’s paradox. Water uptake from vapor phase is affected by the temperature and relative humidity, but water uptake from liquid water is not changed [58, 59].

Weber and Newman [58, 59] proposed a physical explanation of Schroeder’s paradox. They described the four steps during water uptake, as shown in Fig. 2-4. In the first step, the dry membrane absorbs water in order to solvate the acid groups, forming inverted micelles in the polymer matrix. With more water uptake, these clusters grow and form interconnections with each other. The third step corresponds to a state when the membrane is in contact with saturated water vapor, where a complete cluster network has formed. This allows for the liquid water to infiltrate and expand the collapsed channels in the fourth step. As a result a pore-like structure forms. They claimed that because the channels are filled with liquid, the uptake of the membrane has increased without a change in the chemical potential of the water, which is Schroeder’s paradox. The pore-like structure formed makes the Nafion® more like porous media. Liquid water

Figure 2-2: Ionic conductivity of Nafion® as a function of temperature and relative humidity, using the relationship proposed by Springer [57].
then flows into the membrane driven by capillary pressure, instead of the activity gradient. They claimed that Schroeder’s paradox actually represents a structure and transport mechanism transition.

Figure 2-3: Water uptake for Nafion® 117 at 30°C [39].

Figure 2-4: Evolution of the membrane structure as a function of water content (∆). The pictures are cross-sectional representations of the membrane where the gray area is the fluorocarbon matrix, the black is the polymer side chain, the light gray is the liquid water, and the dotted line is a collapsed channel [58, 59].

Low temperature transport properties of water and proton in the perfluorinated membrane are important for startup of fuel cells, especially from the subzero conditions. Proton conductance and its mechanism have been investigated for perfluorinated membranes as well as other
polymers [60, 61, 62, 63]. Arrhenius-type analysis of the conductance showed two different activation regimes having transition temperatures between 225K and 260K, which depends on the water content.

In general, transport mechanisms are strongly affected by water state in the membrane. In terms of sub-zero behavior, water inside the Nafion® membrane can be classified into freezable water and non-freezable water according to interaction with sulphonic group [54, 55, 61]. Freezable water can be further divided into free water and loosely bounded water. Non-freezable water is defined as water that is strongly bound to the ionic groups that is associated with the polymer. Water molecules that are highly polarized by the virtue of being in close proximity to an ion exist in hydration shells and are unable to crystallize. However, freezable water exhibits similar behavior as normal bulk water. Free water freezes at 0°C like bulk water, but loosely bounded water shows broad freezing points with water content. A simplified schematic of different types of water is shown in the Fig. 2-5. Non-freezable water is situated along the pore walls, whereas freezable water is located near the pore center, as suggested by modeling and X-ray studies [54,64, 65].

Figure 2-5: Schematic illustrating the different types of water in a polymeric membrane. Reducing the humidity reduces the amount of freezable water present in the pore and alters its size [61].
Differential scanning calorimetry (DSC) analysis is one of the methods to measure the unfrozen water content in the polymer membrane. Non-freezable water in the polymer yields no characteristic of thermal transition on the DSC analysis. Unfrozen water content in Nafion® can vary from 2.2 to 13.1 (total water content: 17 ~ 20.8), as reported by various researchers [24, 60, 61, 66]. The detailed comparison of DSC data and analysis to estimate the unfrozen water content is summarized by He [67], and He and Mench [31]. They estimated that unfrozen water content for membrane equilibrated with water vapor to be 2.5, and 12 for a membrane equilibrated with liquid water.

2.1.1 Modes of Water Transport

Membrane properties, especially density, proton conductivity, gas permeability and diffusion coefficient are strongly affected by membrane hydration. In PEFC operations, water is generally carried into the fuel cell by pre-humidified reactant gas streams. Some water passes through the DM, and reaches the membrane in the form of vapor, which in turn, increases the hydration level of the membrane. In addition to the input streams, the water vapor is also generated in the cathode catalyst layer by the electrode reaction. Water transport across the membrane originates from the imbalance in 1) water concentration, 2) static pressure, 3) electric potential, and 4) temperature, across the membrane. Therefore, the water transport mechanism across the membrane is a controlling factor that determines the level of membrane hydration. The water is transported through the membrane by: 1) diffusion, 2) hydraulic permeation, 3) electro-osmotic drag, and 4) thermo-osmosis. In the subsequent sections, the first three transport mechanisms for Nafion® and thermo-osmosis for polymer membranes will be discussed.

**Diffusion**
The diffusion of water between the electrodes is caused by a water concentration gradient across the membrane. In this model, the membrane is assumed to be a homogenous single phase media, and the water transport is governed by the activity gradient. This model was first proposed for PEFC application by Springer et al. [57], and Fuller and Newman [70], and later modified for chemical potential gradient by Janssen [71]. The water diffusive flux \( j_{w, \text{diff}} \) can be represented by Fick's Law given as [8, 72]:

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

where \( D_w \) is the diffusion coefficient (m\(^2\)/s, function of local water content of the membrane, \( \lambda \)), and \( C_w \) is the water concentration in the membrane (mol/l). It is important to note that using the activity gradient as driving force; diffusion model cannot describe the water transport in fully hydrated conditions. However, a modified form of the above equation can be used and is discussed by Ge et al. [73] in detail.

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

*Hydraulic Permeation*
Water may also be transported through the membrane by hydraulic permeation, which is driven by the differences in the pressures of the gas reactants across the membrane. In this model, the membrane is treated as a two phase porous medium and Darcy’s law is used to explain the water transport. This model was initially applied for PEFC by Bernardi and Vebrugge \[74\] and later modified to include effects of saturation, pore size distribution and hydrophobicity by Eikerling et al. \[75\]. The water flux transported by hydraulic permeation \((j_{w,\text{hyd}})\) is directly related to the pressure gradient across the membrane, and can be described as:

\[
j_{w,\text{hyd}} = -\rho_w \frac{k_{\text{hyd}}(\lambda)}{\mu} \frac{dp_w}{dx}
\]

where \(k_{\text{hyd}}\), \(\mu\), \(p_w\), and \(\rho_w\) denote the hydraulic permeability coefficient \((m^2)\) of the electrolyte membrane (function of membrane water content, \(\lambda\)), viscosity of water \((Pa\cdot s)\), water pressure\((Pa)\), and water density\((kg/m^3)\), respectively.

For operating conditions when both reactant gas pressures (anode and cathode) are relatively equal, as is a common practice in PEFCs, the hydraulic permeation rate approaches zero, thus can be neglected.

It is important to mention that both types of models (diffusion and hydraulic permeation) can be made to agree with the experimental data, but neither describes the full range of data nor all observed effects, like Schroeder’s Paradox. Weber and Newman’s \[58, 76\] hybrid model is a combination of both diffusion and hydraulic models. They used the diffusion mode between the unconnected clusters, and for the water pathways between the clusters, a capillary pressure gradient was used.

**Electro-osmotic Drag**

When \(H^+\) ions migrate from the anode to the cathode, they tend to attract and drag water molecules along with them across the electrolyte. This phenomenon is referred to as electro-
osmotic drag. The number of water molecules transported per proton (H\(^+\)) is called the drag coefficient \((n_d)\). The drag coefficient commonly ranges from 1 to 2.5 for Nafion\(^\circledast\) membranes, as reported by Janssen and Overvelde [68]. Ren and Gottesfeld [69] have reported the drag coefficients as high as 5 H\(_2\)O/H\(^+\) for fully hydrated Nafion\(^\circledast\) 117 membranes, and they observed that the drag coefficient is a linearly increasing function of temperature within the range of 20 to 120\(^\circ\)C. The water flux driven by electro-osmotic drag \((j_{w,EO})\) is proportional to the proton flux under a given condition (hydration level, temperature, etc.), and is described as:

\[
j_{w,EO} = n_d(\lambda) \frac{i}{F}
\]

[2.3]

where \(i\) is the local current density \((A/m^2)\), \(F\) is Faraday’s constant \((96,485 \text{ C/mol})\), and \(\lambda\) is the water content of membrane. \(n_d\) is a proportional constant named as "electro-osmotic drag coefficient", which physically indicates the number of water molecules dragged by each proton.

The drag coefficient strongly depends on the water content of the membrane \(\lambda\) since membrane exhibits the structural changes in various states of hydration. The rate of electro-osmotic drag from the anode to the cathode is directly proportional to the operating current density. At high current, the electro-osmotic drag increases, causing the cell to dry the anode side, while flooding the cathode side.

**Thermo-osmosis**

Water transport occurs across a membrane when the aqueous solution with different temperature is separated by a membrane. This phenomenon is known as thermo-osmosis. Thermo-osmosis has been known since the beginning of the twenty century, but it has received comparatively less interest because it does not have practical applications due to small transport flux compared to that of other processes. Thermo-osmosis is affected by membrane properties,
mean solution temperature, temperature difference across the membrane, solution composition, and hydrodynamic conditions of electrolyte solutions.

Thermo-osmotic flux can be written as:

$$j_{w,\text{TO}} = -D_{\text{TO}} \nabla T$$  \[2.4\]

where $D_{\text{TO}}$ is the thermo-osmotic diffusion coefficient of the electrolyte membrane $(kg/m \cdot K \cdot s)$, and $\nabla T$ is temperature difference across the membrane $(K/m)$. The thermo-osmotic diffusion coefficient ($D_{\text{TO}}$) can be negative or positive depending on membrane property although mass diffusivity is always positive. It increases with increasing mean membrane temperature, and shows Arrhenius behavior on mean temperature, which has activation energy for thermo-osmosis [51, 77].

For most hydrophilic cation exchange membranes, the direction of thermo-osmosis is from cold to hot side [52, 77, 78, 79, 80], where thermo-osmotic diffusion coefficient has a negative value. However, the direction can depend on the kind of positive ions in the electrolytes. For $H^+$ ion, like PEFC, its direction is from cold to hot, but its direction is the opposite for $Li^+$ ion solution [52].

For hydrophobic membranes like PTFE membrane, water moves from hot to cold side in the same direction as heat flow [78, 81] and has a positive thermo-osmotic diffusion coefficient. In hydrophobic diffusion media of fuel cell materials, the net water is expected to move from the hot to cold side. It should be noted that unlike a purely PTFE hydrophobic membrane, hydrophobic DM has mixed wettability, which can affect water transport, and the net thermo-osmosis direction.

Villaluenga et al. [51] first investigated thermo-osmosis in Nafion® 117 membrane (EW ~ 1100, thickness: 0.175 mm, non-reinforced type), which is used for PEFC, in pure liquid water as well as water-methanol mixture solution. They measured thermo-osmotic water flux at ambient
temperature. The magnitude is $7.5 \times 10^{-6}$ kg/m$^2$-s for 10°C of bulk temperature difference, with a flux direction from cold to hot side for a pure water solution. The water flux was found to increase in water-methanol mixture solution. Tasaka et al.\cite{52} also measured thermo-osmotic water flux from cold to hot side for Nafion® 417 (EW ~ 1600, thickness: 0.43 mm, reinforced type) and the magnitude is $3.6 \times 10^{-6}$ kg/m$^2$-s for 10°C temperature difference at 35°C. It should be noted that for water flow from cold to hot side, thermo-osmotic diffusivity is negative. On the contrary, fuel cell researchers\cite{46, 48, 49, 50} reported that net flux of water moved from hot to cold side in fuel cell stacks as mentioned in Section 1.4.

### 2.2 Transport Phenomena in the Porous Media

Besides transport in the membrane, the multi-phase flow in the fuel cell porous materials, CL and DM should be understood to optimize PEFC performance and prevent damage, both at normal and sub-zero operating conditions. Fluid flow through porous media (PM) has been researched in several engineering areas for several decades. This section will introduce the basics of multi phase flow and immiscible flow theory in the porous medium. For more details, please refer to a reference book\cite{82}.

#### 2.2.1 Fundamentals

This section will describe the basic definition and concepts for multi phase flow in porous media.

**Porosity**

Porous media (PM) are composed of a solid matrix material and void pores. Porosity ($\varepsilon$) is defined as the ratio of interconnected void space to the bulk volume of porous media. Isolated
pore volume does not contribute to fluid flow in PM, so it is not considered. Bulk porosity is defined as:

$$\varepsilon = \frac{\text{interconnected void volume}}{\text{Total volume of porous media}}$$  \[2.5\]

**Saturation**

The fluid in the PM can be gas, liquid or multi-phase mixture. In multi-phase mixture in the porous media, the volume fraction of total pore volume occupied by a phase is called saturation. Phase saturation, $s_j$ is expressed as:

$$s_j = \frac{\text{volume occupied by fluid j}}{\text{total interconnected pore volume}}$$  \[2.6\]

It is evident from the definition of saturation that it can vary from 0 to 1 for a particular phase and sum of all phases should add up to unity.

**Contact Angle and Surface Tension**

Contact angle is an important parameter in two phase flow and defined as the angle between the gas-liquid interface and solid surface. It is measured at the triple point, where all three phases intersect. The liquid droplet contact angle on any solid surface is defined by the mechanical equilibrium of the droplet under the action of three interfacial tensions. It indicates the measure of wetting of a surface by a liquid. Contact angle depends on material properties and morphology (roughness) of the surface. The interfacial energy $\sigma_{jk}$ is defined as the amount of work that must be performed in order to separate a unit area of fluid $j$ from $k$. $\sigma_j$ is the surface tension between substance $j$ and its own vapor phase. The work to separate two phases, $W_{jk}$ is expressed as:

$$W_{jk} = \sigma_j + \sigma_k - \sigma_{jk}$$  \[2.7\]
Figure 2-6 shows a droplet of liquid (l) on top of solid (s), equilibrated with gas (g). By a simple force balance on the droplet contact surfaces, one can derive the Young's Eq.:

$$\cos \theta = \frac{\sigma_{sg} - \sigma_{sl}}{\sigma_{gl}}$$  \hspace{1cm} [2.8] $$

where $\sigma_{sg}$, $\sigma_{sl}$, and $\sigma_{gl}$ represent the solid-gas, solid-liquid and gas-liquid interfacial tensions, respectively, $\theta$ is the contact angle.

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%

**Figure 2-6:** Illustration of contact angle.

$\sigma_{gl} \cos \theta$ is called the adhesion tension. A surface can be considered as hydrophilic when contact angle ($\theta$) is smaller than 90° (liquid will be wetting fluid), whereas a surface is defined as hydrophobic for contact angles greater than 90° (liquid will be non-wetting fluid). On a hydrophilic surface, liquid water droplets tend to spread over the surface, whereas on a hydrophobic surface, the droplets tend to be more of a sphere-like shape, covering less surface area.

**Capillary Pressure**

The curvature of the interface of two fluids is formed by balancing interfacial tension with the pressure difference between the two fluids. The pressure difference is called as the
capillary pressure $p_c$, which is defined as the pressure difference between the non-wetting and wetting fluids, known as the Laplace Equation:

$$p_c = p_{nw} - p_w = \sigma_{12} \left( \frac{1}{r'} + \frac{1}{r''} \right) \approx \frac{2\sigma_{12}}{r} \quad [2.9]$$

Here, $r'$ and $r''$ are the two principal radii of the interface, as shown in Fig. 2-7. $r$ is the mean radius, which is of the order of magnitude of the pore size. For a capillary tube model, in which the PM is composed of capillary tubes of different radii, when the mean radius of the capillary tubes is $r^*$, the capillary force can be written as:

$$p_i = \frac{2\sigma \cos \theta}{r^*} \quad [2.10]$$

Figure 2-7: Equilibrium at a curved interface and interfacial tension between two immiscible fluids [82].

Interfacial tension and wettability also depend on whether a fluid-fluid interface is advancing or receding on a solid surface. The phenomenon is called hysteresis. Figure 2-8 shows two hysteresis effects. The ink-bottle effect takes place in pores with non-uniform width, as we expect in DM and CL. Wetting an initially dry or drying an initially wet capillary give two different stable configurations. The raindrop effect shows the different advancing and receding
contact angles for a droplet on a declining surface. The process for wetting fluid replacing non-wetting fluid in a PM is called imbibition. The opposite process is called drainage. Figure 2-9 shows a typical capillary pressure and wetting fluid saturation relationship, $p_c = p(s_w)$, during imbibition and drainage for a porous soil medium. $s_{iw}$ is called the irreducible saturation of the wetting fluid, which represents the quantity of wetting fluid remaining in the PM even at high capillary pressure. Similarly, $s_{nwo}$ is called the residual saturation of the non-wetting fluid. Point A shows the bubbling pressure, $p_b$, which is the minimum pressure needed to initiate displacement of wetting fluid by non-wetting fluid.

![Figure 2-8: Illustration of hysteresis effects \[82\].](image)

Leverett [81] proposed a semi-empirical Eq. to relate the curves, ignoring hysteresis,

$$J = J(s_w) = \frac{p_c}{\sigma} \sqrt{\frac{k}{\varepsilon}} \tag{2.11}$$
Here, $\sqrt[3]{\frac{k}{\epsilon}}$ is the empirical mean pore diameter for a PM. The J-Leverett function is not unique because of hysteresis. From Leverett’s experimental data [83], Udell [84] proposed the functional form of J-Leverett function as:

$$J(s_w) = 1.417s_w - 2.120s_w^2 + 1.263s_w^3$$  \[2.12\]

Some fuel cell models pick another type of Leverett function [84, 85, 86] which is based on the capillary tube model and thus includes the contact angle effect.

$$J = J(s_w) = \frac{P_i}{\sigma \cos \theta} \sqrt[3]{\frac{k}{\epsilon}}$$  \[2.13\]

![Figure 2-9: Typical wetting/drying curves illustrating hysteresis [82].](image)

(a) hydrophilic porous media  
(b) hydrophobic porous media

Kumbur et al. [87] found the Leverett function could be applied at low saturation for the fuel cell diffusion media, but could cause large errors especially at high saturation values.
Appropriate equivalent Leverett function for commercial fuel cell DM was determined by Kumbur and presented as part of his PhD work [88].

Permeability

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

\[ k = Cd^2 \]  \hspace{1cm} [2.14]

where \( k \) and \( d \) are intrinsic permeability (\( m^2 \)) and average pore diameter (\( m \)). \( C \) represents the dimensionless constant describing the configuration of the flow path.

When a measured value of absolute permeability is unavailable, Carman-Kozeny [89, 90] equation shown below can be used to estimate the absolute permeability of the porous medium.

\[ k = \frac{r^2 \varepsilon^3}{18 \tau (1 - \varepsilon)} \]  \hspace{1cm} [2.15]

Here, \( r \), \( \varepsilon \), and \( \tau \) are the mean radius (\( m \)) of the pores, porosity and tortuosity of the medium, respectively.

In a multi phase flow in porous media, the available pore space is shared by all the phases e.g. liquid and gas. Thus, the effective cross sectional area available for each fluid is less than the total available pore space. This effect is taken into account by the relative permeability parameter \( (k_r) \), which is defined as the ratio of the intrinsic permeability for a phase \( (k_j) \) to the total intrinsic permeability \( (k) \) of the porous media:

\[ k_{r,j} = \frac{k_j}{k} \]  \hspace{1cm} [2.16]
Figure 2-10 shows a typical relation of the relative permeability versus liquid saturation for unconsolidated sands. For PEFC application, there exists no direct experimental data of the relative permeability as function of saturation, although estimation from soil science like \( k_{r,w} \propto s_w^3 \) has been used [84].

2.2.2 Immiscible Flow Theory

The multiphase flow through PM is usually treated as immiscible fluids with the following assumptions [91]:

1) All continuous phases flow simultaneously and do not mix.
2) Every single phase follows its own tortuous path in the pore space.

Figure 2-10: Typical relative permeability as function of saturation pressure [82].
For phase $j$, if gravity effects are neglected, the flow rate can be derived through Darcy’s law,

$$v_j = -k_{r,j} \frac{k}{\mu_j} \nabla p_j$$ \hspace{1cm} [2.17]

For mass balance,

$$\frac{\partial (\rho_j s_j)}{\partial t} = -\nabla \cdot (\rho_j v_j) + S_{m,j}$$ \hspace{1cm} [2.18]

Here, $\rho_j$ is the density and $S_{m,j}$ is the mass source term for phase $j$. The mass source term could be from phase change. Plugging in Darcy’s law and assuming constant density, porosity, and isotropic PM, one can derive:

$$\varepsilon \frac{\partial (s_j)}{\partial t} = \nabla \cdot (k_{r,j} \frac{k}{\mu_j} \nabla p_j) + \frac{S_{m,j}}{\rho_j}$$ \hspace{1cm} [2.19]

For each phase involved, we can write down such a flow equation to describe the phase flow.

The porous media can be treated as a mixture of the backbone material and the flowing fluids within the voids. The energy balance is typically written as:

$$\frac{D(\rho C_p T)}{Dt} = \nabla \cdot (\kappa \nabla T) + S_h$$ \hspace{1cm} [2.20]

Here, $\bar{\rho C_p}$ and $\bar{\kappa}$ are averaged thermal parameters; $S_h$ is the heat source term. One approach to obtain the thermal parameters for $\bar{\rho C_p}$ and $\bar{\kappa}$ is to use volume averaging as $\sum_i (\varepsilon_i \rho_i C_{p,i})$ and $\sum_i (\varepsilon_i \kappa_i)$, respectively. $C_{p,i}$ the heat capacity and $\kappa_i$ the thermal conductivity of component $i$.

Thus, Eq. 2.20 can be written as:

$$\frac{D[\sum_i (\varepsilon_i \rho_i C_{p,i}) T]}{Dt} = \nabla \cdot [\sum_i (\varepsilon_i \kappa_i) \nabla T] + S_h$$ \hspace{1cm} [2.21]
With additional capillary force and thermodynamic relationships and assumptions, a closed equation system can be formed.

The water-air two-phase flow is a simple case. The gas phase pressure can be assumed constant throughout the PM [92]. Then $\nabla p_\text{g} = 0$ and there’s only one phase flow equation. For hydrophobic DM, $\nabla p_w$ is simply given by:

$$\nabla p_w = \nabla p_c = \frac{dp}{ds_w} \nabla s_w \tag{2.22}$$

For hydrophobic DM, the water phase flow Eq. 2.19 becomes the Richards equation:

$$\epsilon \frac{\partial s_w}{\partial t} = \nabla \cdot (k_{r,w} \frac{dp}{\mu_w ds_w} \nabla s_w) + \frac{S_{m,w}}{\rho_w} \tag{2.23}$$

### 2.3 Freeze-induced Damage in Porous Media

Several damage modes are observed when PEFC experienced freezing, including catalyst cracks, membrane cracks, interfacial delamination, and diffusion media punch. Frost heave damage in the porous media will be introduced to understand freeze-induced damage in fuel cell components. In the last section, a unified frost heave model applied to fuel cell freezing is summarized.

#### 2.3.1 Frost Heave in Soil Science

It is known that road surface experienced frost heave damage under freezing situations, for example, cracks and heave damage on the pavement in the central city of Sweden as shown in Fig. 2-11 [93]. It is well known that water in small pores does not freeze at 0°C and has broad freezing points which vary with pore size. When saturated porous media consisting of fine pores,
like soil or pavement, is exposed to freezing environments, the water in the large pore freezes into ice crystals along the freezing temperature plane. Ice crystals attract water from adjacent pores due to the resulting capillary pressure difference, which freezes on contact and forms larger ice crystals. Crystals continue to grow and join, and forming ice lens, of which the vertical upward pressure heaves surfaces, resulting in cracks and damage, as shown in Fig. 2-11. This is called frost heave and its schematic mechanism is shown in Fig. 2-12.

![Frost heave on a city street in central Sweden](image)

Figure 2-11: Frost heave on a city street in central Sweden [93].

This frost heave has caused much damage to roads, buildings, pipe lines in cold places and liquid-natural gas storage tanks, so soil science researchers have investigated the phenomenon of frost heave during the last century. There are three requirements for frost heave damage: 1) porous media (PM) with fine pores, 2) subfreezing temperatures, and 3) water availability. By removing any of the three conditions above, frost heave will be eliminated. The degree of frost susceptibility is strongly affected by the properties of porous media: 1) thermal properties related to rate of heat transfer rate (heat removal and temperature gradient), 2) water permeability, 3) PM structures (density, texture, structure, etc.).

This section will introduce frost heave models and characteristic curves. Two frost heave models: 1) Miller's Rigid ice model [94, 95, 96] and Harlan's hydraulic model [97], will be
covered in this section. Detailed reviews on physical phenomena and frost heave models are well described in the literature [98, 99].

Rigid Ice Model in Soil

Miller and co-researchers [94, 95, 96] proposed the rigid ice model to approximate the secondary frost heave in saturated soil. Frost heave is divided to primary heave and secondary heave, depending on whether there is a frozen fringe, a two-phase zone where ice content increases from 0% at the freezing front to 100% at the location of the latest lens, as shown in Fig. 2-13.

Figure 2-12: Formation of Ice Lenses in a Pavement Structure [93].
Primary heave refers to the frost heave with no frozen fringe. With an adequate water supply, no ice will penetrate into the unfrozen area, and the rate of heat loss controls the rate of frost heave. Secondary heave refers to the frost heave with a frozen fringe. The ice lens grows and penetrates into the frozen fringe. Unfrozen water flow takes place at least in the frozen fringe. New ice lenses will grow within the fringe, while ice lens growth is determined by both hydraulic permeability and heat loss.

Figure 2-13: Comparison of (a) primary and (b) secondary frost heave [97].

Figure 2-14 gives a more detailed view of secondary frost heave. During the frost heave, the interaction of heat and mass transfer is very strong. The saturation change due to phase change creates a capillary pressure gradient within the frozen fringe. O’Neill and Miller [95] described that “the extremely thin adsorbed layers, tightly bound to the mineral particles, pulling nearby water into it while simultaneously pushing away the ice and forming an ice lens”. High overburden pressures and low temperature gradients will tend to increase the fringe thickness.
The speed of growth is much faster for newer ice lens, since the permeability of liquid water around it is much larger [100].

The saturated freezing in PM can be treated as a two-phase problem. The PM is gas free, so convective flow of vapor phase and ice phase are neglected. The main process is assumed to be the unfrozen water flow driven by the capillary pressure. There are seven unknowns: $s_i, s_w, p_i, p_u, v_i, v_w$, and $T$.

For a saturated condition,

$$s_i + s_w = 1$$  \[2.24\]
For ice and liquid water added together, the mass conservation Eq. is:

$$\frac{\partial (\sum_j \rho_j \delta_j)}{\partial t} + \nabla \cdot (\sum_j \rho_j v_j) = 0 \quad [2.25]$$

The energy conservation equation is:

$$\frac{D(\rho C_v T)}{Dt} = \nabla \cdot (k \nabla T) + \rho \frac{h_f}{\partial t} \frac{\partial s}{\partial t} \quad [2.26]$$

The unfrozen water flow is driven by water phase pressure, written as:

$$v_w = -k_{rw} \frac{k}{\mu_w} \nabla p_w \quad [2.27]$$

A major assumption of the rigid ice model is that the ice in the pores is rigidly connected to the growing ice. It moves upwards like one rigid body, with a velocity equal to the heaving rate.

$$v_i = v_{fi} \delta s_i \quad [2.28]$$

Here, $v_{fi}$ is the frost heave rate. The boundary condition at the ice lens surface next to the frozen fringe is:

$$\rho_f v_{fi} = \rho_i v_i + \rho_w v_w \quad [2.29]$$

Eq. 2.22 - 2.27 combined with empirical unfrozen water versus temperature curve, and the generalized Clapeyron equation (GCE) (will be discussed in the section, 2.3.1. characteristic curves for model closure), forms a closed equation system. With appropriate boundary conditions and numerical methods, the frost heave process can be solved.

For initiation of ice-lens, Miller assumed that there exists a critical point when the combined pressure of liquid phase and ice phase reaches the overburden pressure,

$$P_{ovbd} = \chi P_w + (1 - \chi) P_i \quad [2.30]$$
Here, $\chi$ is a weighting factor, determined by experimental data, and $P_{ovbd}$ is the overburden pressure, defined as:

$$P_{ovbd} = P_0 + g \int_0^z \rho(z) dz$$  \[2.31\]

**Hydraulic Model in Soil**

Harlan proposed his hydraulic model \[97\] by presenting an analogy between mechanism of water transport in partially frozen soils and unsaturated soils. Harlan used a single suction force to account for all capillary effects. This implies an assumption that the existence of ice below 0°C influences the water flow only by hydraulic conductivity. The transient flow equation is defined as:

$$\frac{\partial(\varepsilon \rho_s s_w)}{\partial t} + \frac{\partial(\varepsilon \rho_s s_i)}{\partial t} = \nabla \cdot (\rho_s k_e \nabla p_c)$$  \[2.32\]

Here, $k_e$ is the effective permeability. To account for the reduced flow observed in the frozen zone, Jame and Norum \[101\] introduced an arbitrary impedance factor:

$$k_e = k \times 10^{-E e_s}$$  \[2.33\]

Here, $E$ is the impedance factor. Gosnik et al. \[102\] report the typical values for $E$ are 8 for fine sands and 20-30 for coarse gravel soils. For DM in PEFCs, this could be around 10 based on averaged pore size. Newman and Wilson \[103\] claimed, by using the relationship for permeability versus suction proposed by Fredlund et al. \[104, 105\], they could exclude the impedance factor. They also gave a compact form of the hydraulic model, derived as below.

By using the unfrozen water versus temperature characteristic curve ($s_w \sim T$) and assuming constant properties, Eq. 2.32 can be written as:

$$\varepsilon \frac{\partial s_w}{\partial T} \frac{\partial T}{\partial t} = \nabla \cdot (k_e \nabla p_c) - \varepsilon \frac{\rho_s}{\rho_w} \frac{\partial s_i}{\partial t}$$  \[2.34\]
By putting this equation into the energy equation, Eq. 2.26

\[
\frac{\rho C_p}{\rho C_p} \frac{\partial T}{\partial t} = \nabla \cdot (\kappa \nabla T) + h_{sf} \rho_w \left[ \nabla \cdot (k_e \nabla p_e) - \varepsilon \frac{\partial s_w}{\partial \varepsilon} \frac{\partial T}{\partial t} \right]
\]

[2.35]

By using the capillary force versus saturation characteristic curve, \( p_e \sim s_w \),

\[
\frac{\partial p_e}{\partial T} = \frac{\partial p_e}{\partial s_w} \frac{\partial s_w}{\partial T}
\]

[2.36]

The energy equation can be converted to

\[
(\rho C_p + h_{sf} \rho_w \varepsilon \frac{\partial s_w}{\partial T}) \frac{\partial T}{\partial t} = \nabla \cdot (\kappa \nabla T) + h_{sf} \rho_w \nabla \cdot (k_e \frac{\partial p_e}{\partial s_w} \frac{\partial s_w}{\partial T} \nabla T)
\]

[2.37]

This is a simple equation of the temperature, if the above two characteristic curves are known. Since the hydraulic model uses a single suction force to account for all the capillary effects, there is no inclusion of phase pressure. Thus it cannot directly use the overburden criteria for frost heave, as proposed by the rigid ice model.

**Characteristic Curves for Model Closure**

Several characteristic curves are needed to form closed solutions by PM theories. These include unfrozen water versus temperature characteristic curve, capillary pressure versus saturation characteristic curve, and the thermodynamic relation, GCE.

For freezing in PM, there is also a freezing-point depression [106] and super-cooling could take place at the same time. From soil science, it is well established that all water in a fine-grained soil does not freeze at a unique temperature, but rather, unfrozen water content in soils decreases continuously with temperature. The finer grained a soil is, the greater the freezing point depression from bulk value. The freezing temperature depression will be the same through a uniform PM if this effect is solely dependent on the mean pore size \( r \). The unfrozen water content as a function of temperature can be measured by several techniques including differential scanning calorimetry (DSC).
Besides the unfrozen water versus temperature curve, another characteristic curve is needed to form a closed equation system. In the hydraulic model, the measured capillary force versus saturation curve is used (see Fig. 2-9). In the rigid ice model, this curve is replaced by the GCE. The GCE was derived from Gibbs-Duhem equation and the chemical potentials equilibrium between water phase and ice phase [107, 108].

\[
\frac{P_i - P_w}{P_i - P_w} = -h_{sf}(\frac{T - T_f}{T_f}) = -h_{sf}(\frac{\Delta T}{T_f}) \tag{2.38}
\]

Here, \(\Delta T\) is the freezing temperature depression; \(h_{sf}\) is the heat of fusion for water; \(T_f\) is the freezing temperature for bulk water. This equation relates ice phase pressure, water phase pressure, and temperature depression together. From this equation, if \(p_i\) is constant, when there is temperature distribution in the PM, there will be a gradient of \(p_w\), which is the driving force of the water flow.

2.3.2 Unified Frost Heave Model for Freezing in Fuel Cell

He and Mench [31, 32, 109] developed a 1-D unified transient frost heave model for the frost heave process in a PEFC based on theories of porous media flow and soil frost heave to understand freeze-damage modes. The model was a combination and improvement of Harlan’s hydraulic model and Miller’s rigid ice model, applied to both saturated and unsaturated zones in a PEFC. The GCE, capillary force versus saturation, and the unfrozen water versus temperature characteristic curves were integrated into the model. Model results will be briefly introduced here, and refer to reference for details [67].

- Ice lens induced damage could occur at the interfaces located under the channel: 1) membrane/catalyst layer interface, 2) catalyst layers/diffusion media interface, and 3)
DM/channel/land interface, as shown in Fig. 2-15.

- Ice lens formation under the land could be negligible because ice lens pressure is less than overburden pressure by stack assembly compression force.
- Two modes of physical damage have been proposed: 1) diffusion media punch through caused by ice lens formation under the channel at the interface of diffusion media and catalyst layers; 2) catalyst layer delamination caused by sub-zero unfrozen water diffusion from the electrolyte membrane to the interface of catalyst layers.
- As the thickness of membrane increases, the ice lens thickness increases because the thicker membrane has more available unfrozen water due to the larger freezing temperature depression of Nafion®. The ice lens thickness prediction with membrane thickness is shown in Fig. 2-16.
- The ice lens thickness is negligible for one cycle, so that over many freeze/thaw cycles, interfacial delamination or DM punch would occur.
- Due to the 3-D structure in catalyst layer, water accumulation due to unfrozen water flow towards the catalyst layer could exist in ice lens form on the surface of Nafion®.
components inside the catalyst layers, or freeze inside Nafion® and cause expansion. This mode could cause detachment of carbon particles and platinum particles. The situation can be even worse when the pores of catalyst layer are all filled up with ice locally. When the catalyst layer pores are not filled up locally, the ice lens at CL|Nafion® membrane interface could be considered as reversible. A drier initial membrane condition, lower irreducible water content, and higher hydrophobicity of the catalyst layer would help to reduce this ratio.

- Two main sources of ice lens water were found 1) residual water in the catalyst layer and diffusion media and 2) excess water in the electrolyte. During freezing, the driving force of unfrozen water flow is proportional to the temperature gradient between the ice and the liquid water, with unfrozen flow toward the cold location. Several factors were found to exacerbate ice lens initialization and growth under the channel location including a rapid heat transfer process, slower liquid drainage into the channel, cooling toward the catalyst layer, and a high irreducible liquid saturation. Also, increasing material thermal conductivity reduces the temperature gradients, decreasing ice lens growth.

- The role of the micro-porous layer (MPL) is mixed. While the MPL can block unfrozen water flow from the DM towards CL, it also prevents drainage of liquid water from the catalyst layer. The effects of multiple freeze thaw cycles can be cumulative if the gap space between the catalyst layer and diffusion media plastically deforms and grows. This interfacial gap will act as a pooling location for future cycles, accumulating further damage.
Figure 2-16: Maximum thickness of ice lens that could be formed by water expelled from Nafion® during freezing, as a function of the initial water content and membrane type, if the boundary condition is saturated with water vapor and $\lambda = 14 \frac{H_2O}{SO_3^-}$ [31].
Chapter 3
Ex-situ Freeze/Thaw Cycling Test: MEA Micro-structure

3.1 Introduction

Membrane electrode assemblies and diffusion media are the key components in a PEFC. Freeze-damage depends strongly on the operational procedure, material micro-structure and composition, fuel cell components matching, material manufacturing process, and cell/stack structure. Due to the strong inter-relation of the above factors, conflicting results have been reported on the freeze-damage in the published literature [16, 18, 20, 21, 23, 24, 25, 26, 27]. Physical damage modes like membrane crack [21], catalyst delamination [16, 21], and diffusion media punch [20] were observed during freeze/thaw cycle. The factors affecting the damage mechanisms have not yet been fully explained. A combined modeling and controlled experimentation (both operational procedure and material) is required to physically understand the damage mechanism in the PEFC during the freezing. He and Mench [31, 32] developed a frost heave model to predict the various physical damage modes during the freezing in the PEFC. In order to validate the proposed physical damage mode (esp. interfacial delamination due to ice lens formation), experimentation is needed.

This work investigates the effect of the MEA micro-structures and diffusion media on freeze-damage. Liquid water submerged freeze/thaw cycling conditions were used to simulate the worst case scenario and accelerate the freeze-damage. The results from the study will be used to validate the damage modes predicted from the computational model [31, 32], and to develop the material design criteria for freeze-tolerable MEA.
3.2 Method of Approach

Material Testing

Figure 3-1 shows a schematic of the ex-situ test setup consisting of four test vessels, an environmental chamber (Thermal Product Solutions, Model: T10S-1.5), and a National Instruments Labview™ based data acquisition system. The test vessels were thermally cycled and controlled by an integrated programmable temperature controller with an operating temperature range from -40°C to 200°C. A test cell consisted of two graphite flow field plates with seven channels (2 mm width and depth) and two stainless steel compression plates. Test samples were sandwiched by graphite plates and stainless steel compression plates, and compressed by bolts and spring lock washers by the same pressure forces as a normal fuel cell, which was verified by pressure paper. The test cells were assembled with additional stainless steel end plates in order to have similar temperature boundary conditions. Two identical micro-structured MEAs were tested in the same vessel, where the upper test cell was assembled with a MEA without DM/MPL and the second lower cell with a MEA with DM/MPL. Two additional DM/MPL materials were inserted between the upper test cell and end plate to maintain uniform compression and similar temperature boundary conditions.

The thermal profile of the environmental chamber was calibrated, and Figure 2 shows the measured thermal profile of the test bath and chamber. The thermal profile used for cycling was set to the following by the internal programmable unit:

I) Soaking at 70°C for 4 hours 30 minutes
II) Cooling from 70°C to 5°C for 30 minutes
III) Cooling from 5°C to -10°C for one hour
IV) Cooling from -10°C to -40°C for 30 minutes
V) Soaking at -40°C for 5 hours 15 minutes
VI) Heating from -40°C to 70°C for 15 minutes.

As shown in Fig. 3-2, temperature profiles of the upper cell and the lower cell are almost the same, so that comparison between two test cells is valid. To identify damage induced by only freeze/thaw cycling, additional thermal cycling without freezing between 5°C and 70°C was also
performed. To make the heat transfer rates of the two cases (without freezing / with freezing) similar, the chamber temperature profile was calibrated. From Fig. 3-3, it is clear that temperature profile during the heat up and cooling down of both cases are almost the same, so legitimate comparison is possible, and the potential heat transfer rate effect on liquid transport is not a factor in these tests.

![Figure 3-2: Thermal freeze-thaw cycling profile of the environmental chamber and the water of the upper cell (TC 1) and the lower cell (TC 2) inside the test vessel.](image)

Four MEA types, supplied by W.L. Gore and Associates, were tested to investigate effects of membrane thickness, reinforcement of membrane, and virgin CL crack density. The four MEA types consisted of 1) virgin non-cracked CL with 18 μm reinforced membrane, 2) virgin cracked CL with 18 μm reinforced membrane, 3) virgin non-cracked CL with 18 μm non-reinforced membrane, and 4) virgin non-cracked CL with 35 μm reinforced membrane. The composition and manufacturing processes of the CL of all four MEAs were identical, and the Pt loading in the anode and cathode CL, respectively, was 0.4 mg/cm². Micro-structures and
compositions of anode and cathode were also identical, which enabled us to eliminate compositional and manufacturing effects on F/T damage. All four types of MEAs experienced 30 thermal cycles with freezing (-40 to 70°C) and without freezing (5 to 70°C). To investigate effects of DM/MPL on F/T damage, a paper DM/MPL, SGL 10BB (SGL Carbon Group, USA) was used.

Figure 3-3: Temperature and pressure profile of water inside the vessel between 70°C / 5°C cycling and 70°C / -40°C cycling.

The MEAs without DM were directly in contact with liquid water, the worst possible case. However, in case of the MEAs with DM/MPL, SGL 10BB blocks direct contact of liquid water with MEA if external pressure is not applied to overcome capillary pressure. Pressurizing the test vessels is required to ensure the MEA humidified. In this ex-situ test, water vapor pressure increase as a result of temperature change during the F/T cycling was utilized, as shown in Fig. 3-11. The pressure of the sealed test vessel increases with temperature increase, because of water saturation vapor and ideal gas effects. The pressure was measured by a pressure
transducer (Omega Engineering, Inc., Model: PX209-30V15GL, gauge pressure range: -100 kPag ~ 100 kPag). The gauge pressure reaches 37.92 kPag at the maximum temperature and as cooling proceeds, the pressure decreases to – 8.96 kPag. Even when pressure profile is repeated, water saturation inside the porous media should not change with time, because the negligible hydrostatic pressure difference across the porous material fully immersed in the water can not transport water out of the porous media. Based on experimental capillary pressure versus saturation level of SGL10BB, the liquid water saturation level is estimated to be about 50% in these conditions [109]. Therefore, water level in the thermally cycled MEA with DM/MPL (SGL10BB) is above fully vapor saturated. This test condition is less severe than MEA without DM/MPL (with 100% liquid contact), but is anticipated to be more severe than actual fuel cell situations, allowing us to observe the key factors in physical damage under F/T conditions.

The thickness and surface crack density of tested MEAs are summarized in Table 3-1. The surface crack area density of virgin cracked MEA was measured by using ImageJ [111] software. It should be noted that cracks did not include internal voids observed occasionally in the membrane/catalyst layer interfaces, and were a result of the manufacturing process. Five scanning electron microscopy (SEM) images (magnification 50) were used for crack density measurement.

<table>
<thead>
<tr>
<th>MEA</th>
<th>Thickness (μm)</th>
<th>Virgin crack density ( % by area )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Membrane</td>
<td>CL</td>
</tr>
<tr>
<td></td>
<td>Reinforced part</td>
<td>Non-reinforced part</td>
</tr>
<tr>
<td>Non-cracked CL with 18 μm reinforced membrane</td>
<td>5~6</td>
<td>10~12</td>
</tr>
<tr>
<td>Cracked CL with 18 μm reinforced membrane</td>
<td>5~6</td>
<td>10~12</td>
</tr>
<tr>
<td>Non-cracked CL with 35 μm reinforced membrane</td>
<td>8~10</td>
<td>20~25</td>
</tr>
<tr>
<td>Non-cracked CL with 18 μm non-reinforced membrane</td>
<td>0</td>
<td>15~19</td>
</tr>
</tbody>
</table>
Sample Preparation for SEM Image

Tested samples were stored in a sealed Ziploc® bag to maintain the same humidity level. To observe morphologies by SEM, tested samples were exposed to ambient atmosphere to dry out for at least 8 hours. Surface morphologies of thermally cycled MEAs without DM/MPL were observed using a template. The template had the same size as test samples, and consisted of three windows across the channel to observe uniformity of damage. To observe the cross sectional image of cycled MEAs without DM/MPL, sectioning of samples was prepared by applying a new razor blade vertically on the cycled sample across the channel. The sectioned MEA was assembled between aluminum templates having the same channel and land geometry.

To observe surface and cross sectional images of cycled MEAs with DM/MPL, the DM/MPL should be removed without damage. The cycled DM/MPL-attached MEA was cut across the channel with 2~3 mm width. Then the DM/MPL sample was cut from the surface side intended for observation, enabling the DM/MPL to be removed with negligible damage. By cutting with a new razor blade on the removed sliced MEA surface, sectional samples were prepared. The same template used for MEA samples without DM/MPL was used for cross sectional image. The cutting direction is important, because the sectioning itself may cause delamination. The membrane/electrode interface under the membrane (bottom part) may be delaminated, but delamination of interface of the top part from the sectioning should be negligible. Figures in this work are shown as cut from top to bottom. A typical sectioned image is shown in Fig. 3-4. Surface images of cycled MEA with DM/MPL were observed by rotating and tilting the same cross sectional sample. A close-up image of DM/MPL-removed surface (denoted as a dotted rectangle) is shown in the bottom of Fig. 3-4. The wedge gap between MEA and DM/MPL was ascribed to uneven compression of sample holder, not to F/T damage. Surface morphologies and cross sectional images of virgin, F/T cycled, and thermally cycled but not frozen materials were observed.
Figure 3-4: Typical cross sectional and magnified images of CL surface of cycled MEA with DM/MPL.
3.3 Results

Figure 3-5 shows surface SEM images of virgin MEAs with cracked (6.0~6.8% by area) and non-cracked catalyst layers. It also shows sectional SEM images of virgin MEAs with reinforced membrane [113] and non-reinforced membrane. It should also be noted that membrane was exposed inside the cracks, which can serve as water pooling sites.

(a) non-cracked catalyst layers  (b) cracked catalyst layers

(c) MEA with reinforced membrane  (d) MEA with non-reinforced membrane

Figure 3-5: SEM surface and sectional images of virgin MEA samples used in testing.

Thermal cycling effects of MEAs without DM

Figure 3-6 shows images of the non-cracked CL with 18 µm reinforced membrane. On the top row of images, no damage was observed in the condition subjected to thermal cycling.
without freeze between 5°C and 70°C. However, separation of catalyst layers was observed under the channel when thermally cycling with freezing from -40°C to 70°C. No such damage was observed under the land, due to the high compression force applied, which restricts ice lens growth and expansion damage. A cross sectional view of the damage for this configuration is given in Fig. 3-7, showing the catalyst layer separation exclusively under the channel location for the frozen condition.

Figure 3-6: SEM surface images of thermally cycled non-cracked CL with 18 µm reinforced membrane without DM.
Figures 3-8 and 3-9 show surface and cross sectional SEM images of a thermally cycled initially cracked CL with 18 µm reinforced membrane without DM/MPL. Similar to the non-cracked MEA, the damage was observed under the channels. On account of the initial cracking, however, it appears the resultant damage after freeze/thaw cycling was more severe. It was also observed that simple thermal cycling without freeze did not induce morphological damage. The membrane in the initially cracked MEA, of which the membrane between the cracks was exposed to water, was not apparently damaged by F/T cycling.

Figure 3-7: Cross sectional images of thermally cycled non-cracked CL with 18 µm reinforced membrane without DM.

(a) - 40°C /70°C, land, x 500  (b) - 40°C /70°C, channel, x 200  (c) 5°C /70°C, channel, x 500

Figure 3-8: SEM surface images of F/T cycled cracked CL with 18 µm reinforced membrane without DM located under the channel.
Figures 3-10 and 3-11 show surface and cross sectional SEM images of a thermally cycled initially non-cracked CL with 35 µm reinforced membrane without DM/MPL. Interestingly, the damage for this MEA was much more severe than for the similar non-cracked 18 µm reinforced case, indicating the thickness of the MEA does play a role in the damage process, as predicted by the modeling results [31]. Nearly complete delamination of the catalyst layer under the channels was seen. Again, the non-frozen samples do not show any obvious morphological damage, although a thin crack along the channel/land interface was seen. We determined from other results that this was prevented with use of the diffusion media.

Figures 3-12 and 3-13 show surface and cross sectional SEM images of a thermally cycled initially non-cracked CL with 18 µm non-reinforced membrane without DM/MPL. The damage for this non-reinforced membrane case was much more severe than for the similar case with a reinforced membrane. The extent of damage is similar to the non-cracked 35 µm reinforced case. Nearly complete delamination of CL under the channels was observed. Similar to
non-cracked CL with 35 µm reinforced membrane without DM/MPL, a slight line crack along the channel/land interface was observed in the non-frozen MEA that is eliminated with a DM.

Figure 3-10: SEM surface images of 30 cycled non-cracked CL with 35 µm reinforced membrane under the channel locations without DM.

Figure 3-11: Cross sectional images of F/T cycled cracked CL with 35 µm reinforced membrane without DM located under the channel.
Thermal Cycling Effects with DM/MPL

Figure 3-14 shows cross sectional SEM images of a thermally cycled initially non-cracked CL with 18 µm reinforced membrane with DM/MPL. The results from cycle testing indicate that this configuration (thin, reinforced, with DM/MPL, without virgin cracks) is the most tolerant to freeze-damage. Unlike the case of the same MEA without DM (shown in Fig. 3-6...
and 3-7), the surface morphology of CL under the channel was not changed in this case. Some minor cracking under the channels was observed in the frozen case, but it is unclear if this is a result of sectioning, manufacturing, or freeze/thaw. Some isolated locations of CL bubbling can be seen, but they are sporadic and the MEA remained largely intact. The common trend of negligible under-the-land physically observable damage was detected. Thermal cycling without freeze did not cause any damage, and negligible damage under frozen conditions indicates that the DM/MPL can generally withstand F/T cycling.

Figure 3-14: Cross sectional images of F/T cycled non-cracked CL with 18 µm reinforced membrane under the channel locations with DM/MPL.
Figures 3-15 and 3-16 show surface and cross sectional SEM images of a thermally cycled initially cracked CL with 18 µm reinforced membrane with DM/MPL. In this case, it is obvious that the initial cracks in CL promote severe damage. Compared to the non-cracked 18 µm case, the DM/MPL reduced the extent of F/T damage observed in Fig. 3-8 and 3-9, but CL delamination and frost heave were observed under the channels. Under the lands, there does appear to be some morphological change in the cracks, but no delamination was observed.

(a) - 40°C/70°C, land, x 100  (b) - 40°C/70°C, channel, x 100  (c) 5°C/70°C, land, x 200

Figure 3-15: SEM surface images of thermally cycled cracked CL with 18 µm reinforced membrane with DM/MPL.

(a)  (b) magnified image of the dotted box of (a)

Figure 3-16: SEM cross sectional images of F/T cycled cracked CL with 18 µm reinforced membrane under the channel location with DM/MPL.
Figures 3-17 and 3-18 show surface and cross sectional SEM images of a thermally cycled initially non-cracked CL with 18 µm non-reinforced membrane with DM/MPL. As in the non-DM testing, with these samples, there was much more severe damage of the under-the-channel location of the frozen samples compared to the reinforced membrane results of the same thickness. The DM/MPL reduced significant surface damage because the DM/MPL can block liquid water contact in MEA as well as absorb stress due to ice expansion. However, it should be noted that DM/MPL can not completely prevent interfacial delamination. A more dimensionally stable reinforced membrane [113] can help to limit the damage. Again, the non-frozen samples do not show any obvious morphological damage. Interestingly, there was no thin crack along the channel/land interface observed, as there had been for the case without DM.

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Figure 3-17: SEM surface image of F/T cycled non-cracked CL with 18 µm non-reinforced membrane under the channel location with DM/MPL.
Figures 3-19 and 3-20 show surface and cross sectional SEM images of a thermally cycled initially non-cracked CL with 35 µm reinforced membrane with DM/MPL. Figure 3-21 shows additional SEM images of frost heave damage from under the channel locations of the same MEA type having undergone freeze cycling. The membrane in this case is reinforced, and protected by DM/MPL, and the virgin CL is non-cracked. However, the extensive frost heave damage and CL separation were observed compared to the similar 18 µm reinforced membrane case. This demonstrates conclusively that the membrane itself can be a source of water for damage in CL. As in all cases, the non-frozen thermally cycled samples do not show any obvious morphological damage, and severe delamination or surface heave of frozen cells is limited to under-the-channel locations.
Figure 3-19: SEM surface image of F/T cycled non-cracked CL with 35 µm reinforced membrane under the channel location with DM/MPL.

(a) (b) magnified image of the dotted box in (a)

Figure 3-20: Cross sectional images of F/T cycled non-cracked CL with 35 µm reinforced membrane under the channel location with DM/MPL.
3.4 Discussion

In summary, thermal cycling without freeze did not cause significant damage for all cases in the water immersion test conditions. However, line cracks along channel/land interfaces were observed for 35 µm reinforced membrane and 18 µm non-reinforced membrane cases, of which the damage was prevented using a rigid diffusion media (SGL10BB). Damage to the catalyst layers under lands was not observable for both freezing and non-freezing cases. Damage of
catalysts layers under channels was strongly dependent upon micro-structures of MEAs and existence of a rigid gas diffusion layer with MPL. Rigid diffusion media reduce the surface damage of catalyst layers significantly, but could not prevent all interfacial delamination between membrane and catalyst layers observed. Interfacial delamination of CL from membrane and frost heave were observed for thicker (35 µm) membrane, cracked catalyst layers and non-reinforced membrane. However, non-cracked catalyst layers with thinner (18 µm) reinforced membrane showed negligible damage. It should also be noted that the membrane cracks or holes seen by other studies [20, 21, 22] were not observed for any cases. The test results are summarized in Table 3-2.

Table 3-2: Summary of ex-situ F/T cycling test of four different micro-structured MEAs under channels

<table>
<thead>
<tr>
<th>Thermal Cycles</th>
<th>MEA Type</th>
<th>Non-cracked CL with 18 µm reinforced membrane</th>
<th>Cracked CL with 18 µm reinforced membrane</th>
<th>Non-cracked CL with 35 µm reinforced membrane</th>
<th>Non-cracked CL with 18 µm non-reinforced membrane</th>
</tr>
</thead>
<tbody>
<tr>
<td>70°C / 5°C No DM/MPL</td>
<td>Non-cracked CL with 18 µm reinforced membrane</td>
<td>Negligible damage</td>
<td>Negligible damage</td>
<td>Negligible but line cracks along channel/land interface</td>
<td>Negligible but line cracks along channel/land interface</td>
</tr>
<tr>
<td>70°C / -40°C No DM/MPL</td>
<td>Non-cracked CL with 18 µm reinforced membrane</td>
<td>Severe CL delamination</td>
<td>Severe CL damage &amp; delamination</td>
<td>Severe CL damage &amp; delamination</td>
<td>Severe CL damage &amp; delamination</td>
</tr>
<tr>
<td>70°C / 5°C with DM/MPL</td>
<td>Non-cracked CL with 18 µm reinforced membrane</td>
<td>Negligible damage</td>
<td>Negligible damage</td>
<td>Negligible damage</td>
<td>Negligible damage</td>
</tr>
<tr>
<td>70°C / -40°C with DM/MPL</td>
<td>Non-cracked CL with 18 µm reinforced membrane</td>
<td>Slight surface damage, but severe interfacial separation &amp; heave</td>
<td>Slight surface damage, but severe interfacial separation &amp; heave</td>
<td>Slight surface damage, but severe interfacial separation &amp; heave</td>
<td>Slight surface damage, but severe interfacial separation &amp; heave</td>
</tr>
</tbody>
</table>

Note a): CL damage under lands was negligible for all cases
From SEM images of three different micro-structured MEAs with and without DM/MPL, the extent of damage was different, but interfacial delamination (membrane / catalyst layers) and frost heaves were common. F/T damage behaviors can be classified into two basic modes: 1) interfacial delamination by frost heave and 2) ice expansion damage. Damage of the catalyst layer of MEAs with DM/MPL was similar to frost heave damage in the road surfaces exposed under freezing conditions, as shown in Fig. 3-22 (a) and (b). The schematic of frost heave damage mode proposed for PEFC [31, 32] is depicted in Fig. 3-22 (c). Liquid water transport rate, heat transfer, residual liquid water, and water phase in the fuel cell materials during the freezing are important factors for this damage mode. From comparison of SEM images of non-cracked MEAs with DM/MPL with 18 µm reinforced / non-reinforced and 35 µm reinforced membranes (Figures 3-14, 3-18, and 3-20), the damage is ascribed to the membrane itself because the only difference was the membrane thickness and reinforcement. The damage mode can be explained by considering factors of frost heave damage in the following ways.

As mentioned in the Method of Approach section, heat transfer rate may be a factor in F/T damage, but it is not a factor in this study. In this study, the water content in the ionomers inside CL and membrane was expected to have liquid equilibrated water content (λ>14), as the MEAs were in direct contact with liquid water in these test conditions. Even if DM/MPL was used, the pressurized condition induced during the soaking step at 70°C enabled liquid water to penetrate into the catalyst layers, because the pressure is higher than the measured breakthrough pressure of about 7 kPag for virgin SGL10BB DM. Thus liquid water saturation in DM was expected to be more 50%.

There are two water sources for ice lens growth. One is inside the MEA, and the other is outside the MEA: diffusion media and channels. The freezing point depression of diffusion media is negligible, and that of pores in the CL is less than 2°C [53, 112], but water freezing inside the membrane occurs from 0°C to below – 20°C [60, 61, 66]. From the fact that non-cracked CL with
18 µm reinforced membrane experienced negligible F/T damage while the non-cracked CL with 35 µm reinforced membrane experienced severe damage, the water inside the membrane was shown to be a source of water for frost heave interfacial delamination. The water outside the MEA (DM and channels) did not contribute to frost heave damage.

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(a) heave and crack of F/T cycled MEA  
(b) frost heave on a city street in central Sweden [93]  
(c) schematic damage mode of the non-cracked MEA

Figure 3-22: Schematic of direct evidence of frost heave damage in PEFCs.

The water amount inside the membrane is determined by the ionomers and liquid contact. As freezing proceeds, the temperature of the membrane is the highest in the test cell. During the freezing, free water may be frozen inside the membrane or transported to the interface of
membrane and CL, where liquid water is changed into ice. Loosely bounded water transports into the interface over a longer time scale compared to free water. The total water amount in thicker (35 µm) membrane is higher than that of thinner (18 µm) membrane. The water amount of non-reinforced membrane is also slightly higher than that of reinforced membrane due to the reinforcement structure. Therefore some liquid water contact with the ionomer on shutdown is a critical factor for damage to occur. Note that water content is different with direct liquid water contact or vapor equilibrated condition. Separate tests were performed with vapor-equilibrated sample, which did not show any observable damage. Due to the full submersion, more damage is expected in these test conditions. However, these conditions simulate localized sites of flow field of real fuel cells, when the liquid water is not fully purged during the shutdown.

Catalyst layers under the lands were not damaged in all test cases, but CLs under the channels were severely damaged. As predicted in the modeling work [31, 32], CL/membrane interface delamination was not observed because ice lens under the land can not grow owing to lower ice lens pressure compared to the cell assembly pressure. These results imply that narrower channel width and stiffer diffusion media may be preferable to mitigate F/T damage. Ongoing work is clarifying the role of stiffness and compressive stress transmission on frost heave suppression and will be reported in a separate publication.

In addition to frost heave interfacial damage mode, ice expansion can cause F/T damage. From comparison of F/T damage of non-cracked and cracked catalyst layers with 18 µm reinforced membrane (Figures 14 and 16), the F/T damage mechanism of the cracked catalyst layers may be different from that of the non-cracked MEAs, as depicted in Fig. 3-23. The crack gap (10 ~ 18 µm) is large enough to have negligible depression in the freezing point, so that liquid water in the crack gap is likely to behave like water inside the channel during the freezing. This liquid water is difficult to drain on shutdown in a fuel cell due to the MPL. For the case of a DM/MPL, the cracks in CL will be a location of relatively low capillary pressure. Therefore,
MPL will offer no real protection in this submerged scenario, since any saturation in the MPL will drain into CL and be trapped until freezing occurs. Essentially, cracks in CL, when a highly hydrophobic media are involved, trap liquid water. If using a cracked electrode, it may be likely that a non-MPL coated DM would be preferred, since some water could drain from these locations upon shutdown. To remove this trapped water, evaporation would be needed since capillary motion is unfavorable. The interface between membrane and CL inside the crack can act as a crack initiation site and ice formation can exacerbate its growth because of shear stress induced by ice expansion inside the crack, especially in the inverted V-shaped cracks as shown in Fig. 3-23 (a). However, the upward V-shaped crack may not affect crack growth because stress induced by ice expansion would not contribute to crack initiation along the interface, as shown in Fig. 3-23 (b). As shown in the cross sectional view of the virgin cracked 18 µm MEA of Fig. 3-23 (c), the bottom gap of the crack was slightly larger than the surface gap. Therefore, we can conclude that the damage of the cracked MEAs during the F/T cycling was greater than the non-cracked MEA because of local water pooling and ice expansion stress.

Catalyst layers without DM/MPL were much more severely damaged compared to those with DM/MPL cases. For the non-cracked CL with 18 µm reinforced membrane (Figures 3-7 and Fig. 3-14), interfacial delamination was observed without a DM/MPL, but was negligible with a DM/MPL. All MEAs showed significantly reduced damage using a DM/MPL, but interfacial delamination and heave damage could not be completely prevented. There may be another potential pore level damage in the catalyst layer by ice expansion. This pore level damage can not be observed by SEM, but can be studied by investigating pore size distribution using mercury intrusion or other methods.

Ice expansion in the confined channels can cause stress if the expanded volume can not be absorbed by porous media. Ice formation may have occurred first in the lower and top of the vertical channels, blocking water flow through the channel, and causing stress on CL, resulting in
bending or fracture of CL, as shown in Fig. 3-23 (d). As shown in Fig. 3-23 (e), the DM/MPL can serve as mechanical buffer layers to absorb stress, and can restrict direct contact of liquid water, mitigating this damage.

As shown in the thermal cycling without freezing, line cracks along the channel/land interfaces observed in thicker membrane and non-reinforced membrane were attributed to greater swelling. Increased swelling exacerbates interfacial delamination between membrane and catalyst layers and can accelerate both F/T damage modes (frost heave and ice expansion). The mechanisms for this occurrence can be ionomer expansion of frozen water inside the membrane, or ice lens formation, but nevertheless the membrane is a source of damage. The thinner the membrane, the less the water, and therefore the less damage is expected.

It is difficult to quantify the relative level of importance with the testing done here, but clearly the diffusion media (either through the stiffness or highly hydrophobic MPL), the thickness, the reinforcement, and the initial surface cracks all play an important role in frost heave damage. It should be noted that the damage from the membrane itself can likely be eliminated with a purge of the system on shutdown to remove residual liquid water in contact with the electrolyte. Reduction of the liquid contact with the membrane on shutdown by natural drainage processes (non-parasitic effects) is a focus of continued study.
Figure 3-23: Schematic of possible ice expansion damage modes.

(a) inverted V-shaped cracked MEA

(b) V-shaped cracked MEA

(c) evidences of inverted V-shaped crack shapes in the cracked MEA

(d) non-cracked MEA without DM/MPL

(e) non-cracked MEA with DM/MPL
3.5 Conclusions

This extensive investigation of ex-situ MEAs and DM/MPL testing has suggested guidelines for freeze-tolerable PEFC material selection and helped to conceptually validate the previous computational model performed of Mench and coworkers [31, 32]. Specifically, the membrane was found to be a source of water that can damage the MEA upon thermal cycling to -40°C. Damage was found to occur almost exclusively under the channel, except for an along the land interface line crack that develops for non-DM equipped samples immersed in liquid. From the fact that there was no damage under the land in the worst scenario (liquid water contact and non-DM), the channel/land ratio and geometry could also be important factors. Although the larger land can be better for F/T, at a certain point it would cause dead zones in the center of land and worsen flooding in high relative humidity conditions. The preferred material to reduce F/T damage is a crack free catalyst layer with low water content and dimensionally stable membrane, with a stiff diffusion media. The role of the DM is investigated in Chapter 4. It helps to provide a stiff boundary to prevent expansion, eliminating interfacial gaps which can serve as a pooling location, and a hydrophobic barrier to limit water intrusion. However, it can also detrimentally trap residual liquid water in the catalyst layer on shutdown. In order to prevent F/T damage, it is necessary that the liquid contact with the membrane is reduced or eliminated, which can be accomplished through a variety of parasitic and non-parasitic approaches beyond the scope of this work.
Chapter 4

Ex-situ Freeze/Thaw Cycling Test: DM Micro-structure

4.1 Introduction

One of the remaining technical challenges for polymer electrolyte fuel cell (PEFC) commercialization is to achieve shutdown to a frozen state and rapid start from frozen conditions without damage. PEFCs generate water as reaction product, so when PEFCs are subjected to sub-freezing environments without removal of residual water, they can experience irreversible damage. There exist conflicts in the literature regarding freeze-damage [15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25]. One important result shows that fuel cells dried to remove all liquid water during the shutdown experience neither observable physical damage nor electrochemical losses by freezing [15, 16, 17, 18]. However, there are conflicting results in case of a cell with no significant purge. Some reported physical damage, performance loss, and electrochemical loss (electrochemical surface area, interfacial and charge transfer resistance increase) [16, 19, 20, 21, 22]. Physical damage includes membrane failure (holes and cracks), catalyst cracks and delamination, pore distribution change, and gas diffusion media fracture. Others observed no significant performance loss even without dry purge during the shutdown [23, 24, 25]. Freeze-damage can result from coupled factors including fuel cell design (flow field plate and stack structure), operation (water redistribution on shutdown) and materials (membrane electrode assembly and diffusion media). Thus, fundamental understanding of several factors on freeze-damage is required.

Kim and Mench [114] performed extensive ex-situ study on micro-structure effects of MEA on freeze-damage described in Chapter 3. This investigation of MEAs and diffusion media
subjected to a submerged freezing environment has revealed very strong direction for the material choices in the PEFC and helped to conceptually validate the previous computational model performed of Mench and coworkers [31, 32]. Specifically, the membrane was found to be a source of water that can damage the MEA upon thermal cycling to - 40°C. Damage was found to occur almost exclusively under the channel, and not under the land, due to the high overburden pressure of the land. From the fact that there was no damage under the land in the worst case scenario of [114] (direct liquid water contact with no diffusion media protection), the channel/land ratio and the channel width are also important factors. Although the larger land can be better for freeze/thaw (F/T), at a certain point it would cause dead zones in the center of the land and worsen flooding in high relative humidity conditions. The most robust material found to reduce F/T damage was determined to be a crack free virgin catalyst layer and a dimensionally stable membrane (e.g. reinforced) with low water content (e.g. thinner membrane), with diffusion media protection.

Discussed in Chapter 3, the role of the diffusion media (DM) was not yet fully explored. That is, while it was obvious that the diffusion media play a critical role in damage mitigation, the influence of DM stiffness, thickness, and the presence of a micro-porous layer was not explored. Thus, effects of these DM properties on freeze-damage of MEA were studied and are reported here.

4.2 Method of Approach

Test cells were 30 times thermally cycled between - 40°C and 70°C in the water-submerged conditions. Figure 4-1 (a) shows a schematic of the ex-situ test setup consisting of four test vessels, an environmental chamber (Thermal Product Solutions, Model: T10S-1.5), and a National Instruments Labview™ based data acquisition system. As shown in Fig. 4-1 (b), one
freeze/thaw thermal cycle took 12 hours, and test cells were maintained more than 5 hours below the water freezing point (0°C): 1) 7.25 hours for cooling, and 2) 4.75 hours for heating. Thermal boundary conditions of two test cells in the same test vessel were identical, which enabled comparison.

(a) schematic of test setup and pictures of a test cell and a graphite flow field plate

(b) thermal profile of water in the test vessel per one freeze/thaw cycle

Figure 4-1: Schematic and thermal profiles of test setup used for the ex-situ freeze/thaw thermal cycling tests.
The MEA was sandwiched between diffusion media, and then compressed by graphite flow field plates and stainless end plates with the same compression pressure as a typical fuel cell (approximately 1.5MPa). Note that the MEAs in the test cells were fully hydrated even though hydrophobic diffusion media with a micro-porous layer was used. The detailed method for these ex-situ tests was described in a previous paper [114].

Four kinds of diffusion media were investigated: 1) one flexible cloth type (CARBEL-CL™, W.L. Gore and Associates, USA), and 2) three rigid non-woven types (SGL series, SGL Carbon Group, USA). The CARBEL-CL™ consists of a macro-gas diffusion layer and a micro-porous layer (MPL). The non-woven types of DM consist of carbon felt type (SGL 10BA and 10BB) and carbon paper type (SGL 25BC). SGL 10BA has no micro-porous layer, but micro-porous layer is coated on the one side of the 10BB and 25BC. Macro-gas diffusion layers of SGL 10BB and 25BC, and SGL 10BA DM have the same PTFE content (5 wt %). The micro-porous layer on the SGL 10BB and 25BC DM has 23 wt % of PTFE content. The thickness of SGL 25BC and 10BB DM is 235 µm and 415 µm, respectively. The material properties supplied by manufacturers are summarized in Table 4-1. In addition to liquid submerged F/T cycling tests (worst scenario), vapor exposed F/T cycling tests were also performed using the SGL 10BB material and virgin non-cracked catalyst layer (CL) with 35 µm reinforced membrane. Additionally, submerged tests with non-freezing conditions (5 to 70°C) were also performed to assure the observed damage was a direct result of the freeze/thaw process.

<table>
<thead>
<tr>
<th>DM type</th>
<th>Thickness (µm)</th>
<th>PTFE content (wt %)</th>
<th>Existence of MPL</th>
</tr>
</thead>
<tbody>
<tr>
<td>CARBEL-CL™</td>
<td>400</td>
<td>N/A</td>
<td>MPL</td>
</tr>
<tr>
<td>SGL10BB</td>
<td>415</td>
<td>5</td>
<td>MPL</td>
</tr>
<tr>
<td>SGL25BC</td>
<td>235</td>
<td>5</td>
<td>MPL</td>
</tr>
<tr>
<td>SGL10BA</td>
<td>390</td>
<td>5</td>
<td>None</td>
</tr>
</tbody>
</table>
The most tolerable MEA (a virgin non-cracked CL with 18 µm reinforced membrane) determined from the previous study [114] was used for a majority of testing. In some tests to determine the effect of DM thickness, a virgin non-cracked CL with 35 µm reinforced membrane was used. Note that composition and micro-structures of the catalyst layer and the membrane are identical for all MEAs used.

F/T cycled samples were observed by scanning electron microscope (SEM) to investigate physical damage. To observe surface and cross sectional images of cycled MEAs with DM, the DM should be removed without damage. The cycled DM-attached MEA was cut across the channel dimension with 2~3 mm width. Then, the DM sample was cut from the surface side intended for observation, enabling the DM to be removed with negligible damage to the surface. A new razor blade was used to slice MEA surface, providing sectional samples. The cutting direction of the blade can be important, because the sectioning itself may cause delamination. During sectioning, the membrane/electrode interface under the membrane (bottom part in the direction of cutting) may be delaminated in this manner, but delamination of any interface of the top part as a result of sectioning should be negligible. Figures in this work are shown as cut from top to bottom, so that observed delamination on the top surfaces is relevant. A more detailed description of the sample preparation for SEM was described in the previous study [114].

To investigate the effect of F/T cycle number, tests with 30 and 100 F/T cycles were conducted with both SGL10BB and SGL25BC DM. In addition to SEM observation, high frequency resistance (HFR) of the tested samples was also measured at 1 kHz by an Agilent 4338B milliohmmeter to correlate physical damage to interfacial resistance change. The F/T cycled samples, as well as non-cycled virgin samples were evaluated for comparison in the fully hydrated state at the ambient temperature and under identical compression.
4.3 Results and Discussion

*Effect of DM Stiffness*

As shown in Fig. 4-2, after 30 F/T cycles from -40°C to 70°C, the catalyst layer under the channel experienced severe surface cracks when a flexible cloth DM with MPL was used, but surface cracks were prevented using stiff carbon paper type DM with MPL (SGL 10BB). Note that the virgin surface crack density of the tested MEAs was negligible, and catalyst layers under the land were not damaged in all cases. From the previous study [114], the catalyst layers under the land were not damaged regardless of MEA micro-structures. Additionally, no damage was observed for cycling from 5°C to 70°C, indicating all damage observed is a unique result of freezing. This result agrees with computational model result [31, 32, 109] that the higher compression pressure under the land than the pressure of ice lens can suppress the ice lens growth at the interfaces (CL/membrane, CL/DM).

![Figure 4-2](image-url)

(a) CARBEL-CL™ (cloth type) DM  
(b) SGL 10BB (non-woven felt type) DM

Figure 4-2: Surface images of MEAs cycled 30 times between -40 and 70°C with negligible virgin cracks in the catalyst layer and 18 µm reinforced membrane. Images shown correspond to locations under the channel.
Interfacial delamination can occur when a shear force induced by ice expansion or ice lens formation overcomes compressive forces from the material and overburden pressure (assembly compressive force). In a fuel cell with multi-layered structures, stiffness of diffusion media, assembly compression, and channel width and channel/land ratio are therefore key parameters in suppressing damaging delamination force. Stiffness is a material property that is a measure of resistance to deformation from an applied force, and is defined as ratio of applied force to deformation [116]. In the interfacial delamination due to F/T cycles, shear stiffness is an important parameter, and is defined as ratio of applied shear force to shear deformation [116]. Additionally, the material stiffness is a key parameter to transmit compressive forces under the lands to the diffusion media under the channels: The higher stiffness enables the more uniform compressive force under the channels. An infinitely stiff DM would have no variation in compression load across the CL, which is not the case for a fuel cell. The channel width and channel/land ratio are also important factors to determine the compressive force distribution on the catalyst layers under the channels: The smaller channel width or the smaller channel/land ratio, the more uniform compressive force distribution under the channels.

The thickness of the flexible cloth and stiff non-woven (felt or paper type) DM used in the tests was almost the same and the MEAs were identical, and the channel width and channel/land ratio were identical. Therefore, the resisting force for the interfacial delamination was determined by material stiffness alone. The stiffness of the non-woven type DM (SGL10BB) is significantly higher than that of the cloth type DM, which can be supported by observations that the cloth type DM has around twice the compressibility, and higher intrusion into the flow field channel than non-woven type DM [117]. Thus we can conclude that the flexible cloth type DM has lower compressive force under the channels, and lower deformation resistance due to lower stiffness for the same ice lens pressure, compared to the non-woven type stiff DM (SGL 10BB). This is a factor in the excessive damage observed in Fig. 4-2 (a).
When the flexible diffusion media (cloth type) is used, the lower resisting forces can’t suppress the ice lens formation between catalyst layers and diffusion media with repeated F/T cycles, resulting in sag and the observed damage. During normal operation, liquid water can accumulate in this interfacial gap because of reduced capillary pressure in the large local pore, causing bending stress on the catalyst layers due to ice expansion, resulting in the surface cracks.

The channel width is an important parameter, so the smaller channel width can mitigate this damage. The channel width used in testing here was 2 mm, which is larger than typically used in fuel cell design, but selected to show the damage that can occur from cycling in an accelerated manner.

**Effect of DM Thickness**

From Fig. 4-3, physical damage (surface cracks and interfacial delamination (CL/membrane)) was not observed in both thin (SGL 25BC, 235 µm) and thick (SGL 10BB, 415 µm) diffusion media when a non-cracked CL with 18 µm reinforced membrane was used. On the contrary, when a non-cracked CL with 35 µm reinforced membrane was used, severe interfacial delamination was observed in both diffusion media. The MEA with a 35 µm membrane was used especially because it is known that a thicker membrane is much more susceptible to delamination damage under freezing [114]. We can conclude that stiff diffusion media having thickness between 235 µm and 415 µm does not significantly affect freeze-damage on catalyst layers. Note that a gap between diffusion media and catalyst layers was not observed for the observed number of cycles in both cases.

Uniform compression force under the channels and lands is a key factor to prevent interfacial delamination. Compression force distribution under the channel is dependent on DM material properties, the land width, and assembly pressure. For the fixed land width and channel/land ratio with typical fuel cell assembly pressure, material property (stiffness) affects
compressive force distribution under the channel; the higher stiffness, the more uniform compression force.

Stiffness is determined by micro-structure and thickness. Non-woven felt type DM (SGL 10 series) has higher stiffness than that of non-woven paper type DM (SGL 30 series and 20 series) because the felt type DM has more three dimensional structure compared to two dimensional structure of non-woven paper type DM (SGL 25BC). The higher stiffness of SGL
10BB DM is also attributed to higher thickness than SGL 30 and 20 series DM. The transverse and longitudinal (machine direction) bending stiffness of SGL 10AA (0.4mm thick) are 10 N mm and 2.5 N mm, respectively and those of SGL 20AA (0.2 mm thick) are 2.5 N mm and 1.0 N mm respectively \[118\]. SGL 25BC DM has significantly lower stiffness than SGL 10BB DM, which may imply less uniform compression forces under the channel compared to SGL 10BB DM. However, for the SGL non-woven type DM ranging thickness from 235 µm to 415 µm, no significant difference in freeze-damage on the MEA was observed in 30 cycles. In the cycling effect section discussed later, both DM showed significant permanent damage, but higher deformation and more carbon fiber fracture were observed in the thinner DM (SGL 25BC), which may be attributed to a lower uniformity in compression forces. However, the damage extent was very similar, so we can conclude that the thickness of stiff non-woven diffusion media is not a major factor for freeze-damage.

**Effect of Micro-Porous Layer**

In the case of SGL 10BA (without MPL) DM, interfacial delamination (CL/membrane) was not observed, similar to that of SGL 10BB with MPL (cross sectional images not shown here for brevity). From Fig. 4-4, small surface cracks in the catalyst layers were observed in case of SGL 10BA. The surface cracks were also observed under the land locations. Surface cracks were not attributed to F/T cycling, but intrusion of the carbon fibers from the DM, which can be prevented by MPL. These cracks can cause electrical short problems or localized water pooling, which can cause more flooding and voltage instability in operation. From these results, the MPL was not a major factor for freeze-damage in this ex-situ testing, where liquid water exists in contact with the catalyst layers due to the submerged condition. However, in an operating fuel cell, the MPL does play a role in maintaining water balance and reduce flooding in the catalyst layer, which itself can mitigate freeze-damage since the ultimate cause of damage is residual
liquid water in contact with the catalyst layer. Stiff diffusion media with micro-porous media is more preferable to prevent electrical shorts, diffusion media sag, and delamination.

**Effects of Thermal Cycles**

In the tests with only 30 F/T cycles, interfacial delamination between diffusion media and catalyst layers was not observed in both thin (SGL 25BC) and thick (SGL 10BB) diffusion media. As shown in Fig. 4-5, after 100 F/T cycles, a different damage mode, interfacial delamination between catalyst layers and diffusion media was observed in both thick and thin DM. This was attributed to permanent deformation of the stiff diffusion media. The gap in the thin DM (SGL 25BC) seems higher than that in the thick DM (SGL 10BB) as shown in Fig. 4-5. A permanent gap increases electrical resistance, resulting in higher polarization loss. Additionally, the gap created results in a higher heat transfer resistance that can accelerate membrane degradation, or serve as a location of water pooling that can increase flooding, reducing longevity and causing voltage stability at high current density.

Fracture of carbon fibers along the channel/land interface was also observed, as shown in Fig. 4-5 (a) and (b). The extent of damage in the SGL 25BC seems larger than that in the SGL
10BB, but this is difficult to quantify. On the contrary of diffusion media damage, from Fig. 4-5 (c) and (d), catalyst layer damage (interfacial delamination of CL from membrane and surface cracks) was not observed for either thick or thin diffusion media, when using the more freeze-tolerable MEA (non-cracked catalyst layers with 18 µm reinforced membrane) from the previous study [114].

Figure 4-5: Cross sectional images of MEAs with negligible virgin cracked catalyst layers with 18 µm reinforced membrane, F/T cycled 100 times.

Figure 4-6 shows the measured high frequency resistance of the test cell cycled 100 times with SGL 10BB DM. The HFR of the cycled cell was 2.5 times higher than that of non-cycled
test cell (using virgin MEA and SGL 10BB DM) at ambient temperature, a fully hydrated state. High frequency resistance of the test cell cycled 100 times with SGL 25BC DM was measured to be 2.6 times higher than that of non-cycled test cell (using virgin MEA and SGL 25 BC DM). The slightly higher HFR increase in the SGL 25BC may be attributed to more damage compared to that of SGL 10BB because of its significantly lower stiffness. The significant increase in the HFR was attributed to the permanent gap observed between diffusion media and the catalyst layer, and pore level damage in the catalyst layer. It is also possible that the membrane suffered some ionic contamination from corrosion of stainless steel 316L test vessel. By assuming all interfacial delamination between CL and channel and neglecting distorted current passage through catalyst layers and membrane under the delaminated parts because of higher aspect ratio (channel width to MEA thickness), the maximum effects of interfacial delamination on HFR increase can be estimated. The maximum HFR increase was estimated to be 2.15 times compared to the virgin material, but the actual HFR increase due to interfacial delamination may be much lower. The difference between the measured HFR increase of around 2.5 times and the maximum area effect of 2.15 times may be attributed to pore-level damage or membrane contamination.

![Graph](image.png)

Figure 4-6: High frequency resistance at ambient temperature of non-cycled and cycled MEAs (100 times) with SGL10BB DM.
**Effect of Vapor Exposure**

As shown in Fig. 4-7 (a), even a much less freeze-tolerable MEA with 35 µm reinforced membrane did not experience any observable physical damage (interfacial delamination or surface cracks) when the MEA with SGL10BB was exposed to only fully humidified water vapor. On the contrary, the same MEA in contact with liquid water experienced severe interfacial delamination shown in Fig. 4-7 (b). It is obvious that liquid water contact with the catalyst layer is responsible for all observed damage, and should be removed from the catalyst layer at shutdown to mitigate freeze-damage.

![Figure 4-7: Cross sectional images of MEAs (negligible virgin cracks in catalyst layers and 35 µm reinforced membrane) with SGL 10BB DM, F/T cycled 30 times.](image)

**4.4 Conclusions**

Uniform compression pressure from the diffusion media to the catalyst layer surface is a key parameter for selection of diffusion media and design of the flow field to mitigate freeze-induced physical damage of the membrane electrode assembly. Stiffer diffusion media enabled more uniform compression pressure on the catalyst layers under flow field lands and channels,
mitigating damage. On the contrary, flexible diffusion media which transmit less compression to
the catalyst layer surface can not significantly suppress ice lens growth under the channel, and
experienced significant observable surface damage of catalyst layers. In case of stiff diffusion
media, the thickness and MPL was not a major factor for freeze-damage in the tests conducted,
although the MPL assisting in limiting residual water at shutdown is a key factor. To mitigate
freeze-damage, stiff diffusion media and more freeze-tolerable MEA are required.

As another damage mode, permanent interfacial delamination between diffusion media
and catalyst layers was observed after 100 freeze/thaw cycles, even with the best material
combination. As F/T cycles are repeated, water in the catalyst layers and/or diffusion media may
increase ice lens thickness between DM and CL, resulting in permanent deformation of DM, as
predicted by [109]. This permanent deformation of stiff diffusion media as well as fractures of
carbon fibers increased the measured electrical resistance significantly, and may increase water
floodling and mass transfer resistance, resulting in reduced longevity and operational stability. An
MEA with stiff diffusion media was not damaged in vapor exposed F/T cycling, but severely
damaged in liquid water submerged testing.

Freeze-tolerable MEA design (negligible virgin cracked catalyst layers with thinner
reinforced membrane) with stiff diffusion media can reduce the freeze-damage in the worst
scenario test condition, but irreversible damage (DM/CL interfacial delamination) can still occur
as the worst conditions are repeated. Therefore, in addition to use of the most robust materials
described here and in [114], liquid water should be removed from the catalyst layer at shutdown
to mitigate freeze-damage, and the channel/land design should be optimized to reduce cycle-to-
cycle damage accumulation.
Chapter 5

In-cell Freeze/Thaw Cycling Test

Ex-situ testing is helpful in providing the guidelines for material selection for freeze-tolerant MEA and DM. However, to identify the electrochemical damage mode such as electrochemical catalytic surface area (ECSA) loss and increase in resistance (charge transfer resistance, ohmic and mass transfer resistance), in-cell freeze-thaw cycling testing is required. This chapter presents the effect of F/T thermal cycling on the fuel cell damage. The most freeze-tolerant MEA with the stiff DM were used from the ex-situ test results. Electrochemical diagnostic tools, electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV), were utilized to identify the electrochemical losses. Postmortem of the MEA was also performed to identify the physical damage mode (e.g. interfacial delamination) in a fuel cell environment.

5.1 Method of Approach

Fuel cell freeze/thaw testing using the most tolerable MEA from ex-situ tests in Chapters 3 and 4 was performed with the same thermal profile test condition as the ex-situ testing. A Fuel Cell Technology 5 cm² active area single serpentine fixture was used. The channel width and depth is 0.8 and 1.0 mm, respectively. The land width is 0.8mm. The flow-field of anode and cathode is identical. Two cells were assembled in the same conditions: one cell (termed F/T cell) was used for freeze-thaw cycling test, and the other cell (termed control cell) was used to separate degradation effects of the test system and cell fixture from freeze/thaw cycling. The control cell was stored in the ambient conditions without thermal cycling. Every 25 cycles, the performance of two cells were characterized to identify degradation. After cell assembly and leakage rate
check, the cell was fully activated by repeating 10 minute 0.4V operation and 1 minute open
circuit operation for 6 hours at fully humidified test conditions. The cell temperature was
maintained at 65°C. Relative humidity (RH) of anode and cathode inlet was 90% and 85%,
respectively, with a flow rate of 139 sccm and 332 sccm, respectively, for all tests. Every 25 F/T
cycles, reversible loss was recovered by repeating 10 minute 0.4V operation and 1 minute OCV
operation in the fully humidified conditions for 6 hours. A conditioning step (30 minute 0.6V
operation) was used before each polarization characterization. Polarization was evaluated by
constant current operation, where each step is 5 minute, resulting in steady state. Three
consecutive polarization tests were used to get averaged polarization curve.

Full cell AC impedance experiments were performed using a Zahner™ IM6 frequency
response analyzer at a current density of 0.1 A/cm². AC impedance experiments were performed
at a steady flow rate of 139/332 sccm with 90/85 % inlet RH of H₂/air with cathode as the
working electrode and anode as both counter and reference. A voltage signal of ±10 mV was
applied to the fuel cell the AC signal frequency was between 10 kHz and 100 mHz. Before
collecting the impedance data, the fuel cell was operated at 0.6 V for 30 min and at 0.1 A/cm² for
5 min to ensure steady state. Under frozen condition, HFR (high frequency resistance) was also
compared between a control cell and the F/T cell. HFR was measured with an Agilent 4338B
Milliohmmeter (1 kHz).

Cyclic voltammograms were obtained between 50 mV and 500 mV at a scan rate of 20
mV/s and the area under the hydrogen desorption peak was used to estimate the electrochemical
active surface of the working electrode. For cyclic voltammetry (CV), the electrode under
investigation is used as the working electrode and the other served both as counter and reference.
A flow rate of 200 cm³/min of N₂ and 50 cm³/min of H₂ were used on the working and the
counter electrodes, respectively.
5.2 Results and Discussion

In-cell testing was conducted using the MEA (18 µm reinforced membranes with no initial CL cracks) and SGL 10BB DM, as described in the method of approach. No purge was conducted at all in the freeze/thaw cell, to emulate a worst-case scenario. As shown in Fig. 5-1 and 5-2, no damage was seen on the control cell, while significant damage in the test cell was observed, both in the kinetic and mass transfer regions of the polarization curve. In mass transfer controlled regimes, voltage instability was also observed to increase with F/T cycles. Figure 5-3 shows an interesting result that the performance was nearly completely recovered if the anode and cathode were switched. This result indicates that the cathode sustained a majority of the damage on freeze (since the anode reaction is facile, even on a damaged electrode), and the liquid water in the cell is not evenly redistributed in the fuel cell on shutdown.

![Figure 5-1: Polarization behavior of control cell (non-F/T cycling) with equivalent storage periods to freeze/thaw cycles](image-url)
Figures 5-4 and 5-5 shows Nyquist plots of non-F/T cycled cell (control cell) and F/T cycled cell. As expected in polarization curve (Fig. 5-1), non-F/T cell do not show any variation in the overall fuel cell impedance even after being stored for 50 days (which is shown as an
equivalent of 100 F/T cycles). For F/T cycled cell, the overall fuel cell impedance increased continually during cycling.

Figure 5-4: Nyquist plots of F/T cycled cell.

Figure 5-5: Nyquist plots of non-F/T cycled cell (control cell).
The Nyquist data were fitted with an equivalent electrical circuit shown in Fig. 5-6. The circuit consists of an ohmic resistance ($R_{ohm}$) and a parallel circuit of polarization resistance ($R_p$) and double layer constant phase element ($CPE_{dl}$). The $R_{ohm}$ corresponds to the high frequency resistance (HFR) of a fuel cell which includes the ionic resistance of the membrane, electronic resistance of all other components and interfacial resistance. The $R_p$ corresponds to the overall polarization resistance of the fuel cell at 0.1 A/cm$^2$ and $CPE_{dl}$ refers to a modified capacitance of the double layer expressed as a constant phase element in order to account for the non-ideality in the capacitive behavior of the porous electrodes. It was not attempted to delineate the overall polarization resistance into charge transfer and mass transfer resistance, because charge transfer is dominant at low current density (0.1A/cm$^2$). The ohmic and polarization resistances as a function of cycle number are shown in Fig. 5-7 for both the control and freeze/thaw cycled cells. For the control cell, there is not a statistically significant change in the $R_{ohm}$ and $R_p$ values. However for the fuel cell that underwent freeze/thaw thermal cycling, electrochemical polarization resistances have increased significantly with cycles. The rate of degradation was higher in initial F/T cycles (within 25 F/T cycles) and was slower after 25 F/T cycles.

Increase in high frequency resistance of F/T cycled cell was negligible at normal operating temperature, although significant HFR increase and interfacial delamination was observed in the ex-situ testing (see Chapter 3 and 4). This is attributed to different flow-field geometry and water amount in the cell. It should be noted that for ex-situ testing (worst scenario case), channel width and depth are 2 mm, respectively, and channel is filled with liquid water, although for this testing, channel width and depth is less than half of the ex-situ cases.

Impedance was also measured for the switched anode and cathode of the F/T cycled cell (not shown here). The change in charge transfer and ohmic resistance was observed to be negligible compared to baseline case.
From CV testing, electrochemical catalytic surface area of control and F/T cycled cells was measured and summarized in Table 5-1. There was no significant variation of ECSA for the control cell. However, for F/T cycled cell, significant ECSA loss was observed in both anode and cathode electrodes. Based on results of switched anode/cathode testing (Fig.5-3) and cyclic resistance. 

Figure 5-6: Equivalent circuit used to fit the impedance data.

Figure 5-7: Comparison of resistance between control and F/T cycled cells
voltammograms (Table 5-1), it may be not conclusive that ECSA loss can result in performance loss. As shown in Fig. 5-8, interestingly, HFR of 100 F/T cycled cell under freezing temperatures significantly increased compared to that of non-cycled cell, although HFR change between F/T cycled cell and non-cycled cell was negligible at normal operating temperature. This indicates the presence of a very thin delaminating ice lens under frozen conditions.

Table 5-1: Comparison of electrochemical catalytic surface area

<table>
<thead>
<tr>
<th></th>
<th><strong>Anode</strong></th>
<th></th>
<th><strong>Cathode</strong></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td><strong>Control cell</strong></td>
<td><strong>100 F/T cycled cell</strong></td>
<td><strong>Control cell</strong></td>
<td><strong>100 F/T cycled cell</strong></td>
</tr>
<tr>
<td>Baseline</td>
<td>49 m²/g</td>
<td>47.5 m²/g</td>
<td>42.5 m²/g</td>
<td>40.5 m²/g</td>
</tr>
<tr>
<td>100 F/T cycles or equivalent storage</td>
<td>42.6 m²/g (13% ↓)</td>
<td>29.1 m²/g (39% ↓)</td>
<td>45 m²/g (6% ↑)</td>
<td>25.7 m²/g (37% ↓)</td>
</tr>
</tbody>
</table>

Figure 5-8: Comparison of HFR between control cell and F/T cycled cell
5.3 Conclusions

The in situ study affirmed that significant damage can occur for a single cell with no purge, indicating that water removal from the cell, especially from the catalyst layer pores, during shutdown is critical for robust PEFC operation in frozen conditions.

From in-cell freeze/thaw testing, results can be summarized:

1. For cathode, charge transfer resistance of oxygen reduction reaction (ORR) was significantly increased (about 20%) by freeze/thaw cycles, but for anode, the increase in charge transfer resistance of ORR was negligible.

2. Charge transfer resistance of hydrogen oxidation reaction (HOR) for both anode and cathode was sufficiently fast although freeze/thaw cycles were conducted. Effect of freeze-damage on HOR may be insensitive to that of ORR.

3. Electrochemical catalytic surface area of anode and cathode electrodes was reduced by 30~40% by F/T cycles.

4. Mass transfer resistance of the cathode was increased significantly, but change in mass transfer resistance of the anode was negligible.

5. At normal operating temperature, change in high frequency resistance by freeze/thaw cycles was negligible, but at freezing temperature, freeze/thaw cycles caused significant high frequency resistance. It may be attributed to very thin reversible ice lens between interfaces.

6. When water at the cathode electrode is not removed during shutdown, the cathode electrode suffers damage.

7. Diagnostic tool under freezing condition should be developed because damage which is not detected at normal operating condition can be detected under freezing condition.
(see Fig. 5-8). Fundamental study on electrochemical reaction mechanism, ice formation and distribution, and proton transport should be explored.
Chapter 6
Effect of Interfacial Delamination on Performance

6.1 Introduction

In the last decade, polymer electrolyte fuel cell (PEFC) powered vehicles have demonstrated competitive dynamic performance compared to conventional internal combustion engine vehicles. Fuel cell engines provide unique advantages including high energy efficiency, low vibration, and noise reduction. However, a number of technical challenges, especially fuel cell durability, must be surmounted for successful PEFC commercialization. Comprehensive and focused research has made significant advances by improving the durability of key materials, including membranes and catalysts. Du Pont de Nemours & Co. has developed membranes with almost a 5,000 hour life under typical vehicle operating conditions \[119\]. However, from vehicle demonstration programs, the state-of-the-art fuel cell stack was projected to operate only up to 1,700 hours with 10% cumulative degradation \[119\]. This degradation was accelerated by severe operating conditions, including rapid voltage cycling, frequent start/stop, startup from a frozen state, and low humidity and high temperature operation. Details on the durability of PEFCs are well reviewed in existing literature \[120\].

Among the severe automotive operating conditions, freezing has been shown to cause physical damage of materials as well as electrochemical performance loss \[16, 19, 20, 21, 22, 114, 115, 121\]. The Fuel Cell Dynamics & Diagnostics Laboratory (FCDDL) at The Pennsylvania State University has explored these freeze-induced damage mechanisms using modeling as well as experimental approaches \[31, 32, 109, 115, 114, 121\]. He and Mench \[31, 32, 109\] predicted interfacial delamination damage modes at the polymer electrolyte membrane
(PEM) | catalyst layer (CL) and CL | diffusion media (DM). Kim and Mench [114, 115, 121] validated these interfacial delamination modes via extensive experimental work. Figure 6-1 (a) and (b) shows PEM | CL and CL | DM interfacial delamination caused by repeated freeze/thaw cycling without proper water management at shutdown [114, 115, 121]. As shown in Fig. 6-1 (c), Kim et al. [114] also observed that the permanent gap between the CL and DM caused by freeze/thaw cycles caused a significant increase in high frequency resistance (HFR), and is consistent with existing literature [133]. They also observed that in a frozen state, cell subjected to 100 freeze/thaw cycles had almost twice the ohmic resistance compared to a non-freeze/thaw cycled cell. However, the HFR gap was recovered at elevated temperature (65°C), as shown in Fig. 6-1 (d) [121], indicating that some delamination might be reversible if caused by ice formation.

In addition to interfacial delamination resulting from freeze/thaw cycling, interfacial delamination between membrane and catalyst layers was observed in the MEA with non-perfluorinated sulphonic acid (PFSA) membrane, where Nafion® ionomer is used in the catalyst layers. This interfacial delamination comes from different swelling/contraction of different ionomers between membrane and catalyst layers [122, 123]. To compare the performance of non-PFSA membranes, generally well-established Nafion®-ionomer electrode has been used. Recently non-PFSA ionomer electrode has also been studied to overcome interfacial delamination issue, however it has not been explored in the existing literature [122]. To evaluate compatibility between electrode and non-PFSA membrane, measurement of interfacial resistance is very important. Piovar and Kim [122] determined interfacial resistance by subtracting electronic contributions from non-membrane HFR. Non-membrane HFR was determined by extrapolating HFR of MEA with different membrane thickness to zero thickness of membrane. This method can be a powerful tool to optimize non-PFSA ionomer electrode and interface. However, this
method may not be suitable in testing MEA durability, because this methodology required MEA with varying membrane thickness. And MEA durability is strongly affected by membrane thickness.

To improve the durability and performance of PEFCs, a robust interface should be developed, and diagnostic tools for investigating interfacial phenomena are required. Diagnostic tools such as HFR have been used to verify proper cell assembly, as well as to quantify the overall degradation of the fuel cell during durability testing. Interfacial delaminations of fuel cell components increase ohmic resistance and may also decrease the effective electrochemical catalytic surface sites. HFR can be used to conduct non-destructive in-situ measurements of overall ohmic resistance, including the bulk ohmic resistance of fuel cell components as well as any interfacial contact resistance. Even though HFR increase does not represent a direct increase in interfacial delamination, but along with an interfacial model, it can be used as a potential diagnostic to investigate the effect of interfacial delamination on fuel cell performance. Moreover, quantitative analysis of interfacial delamination on increase in HFR is also useful to understand underlying physics as well as to guide postmortem analysis of degraded test cells.

Increase in HFR due to interfacial delamination, which comes from freeze/thaw cycling [115, 121] or different swelling/contraction of different ionomers in the electrode and non-PFSA membrane [122, 123], was observed. However, the quantitative effects of delamination location, width, density, DM thickness and anisotropic properties on fuel cell HFR increase have not been explored. In the current work, a two-dimensional anisotropic model is developed to diagnose the effect of interfacial delamination and determine the key controlling parameters for the performance loss. The developed model was validated experimentally. A detailed parametric study is also presented to investigate the effect of delamination location, width, density, DM thickness and anisotropic properties on fuel cell performance. The developed model can also give
insights into how to improve materials and design fuel cell components with an enhanced lifetime and better performance.

6.2 Method of Approach

Modeling and experimental work were simultaneously explored to utilize HFR as a diagnostic tool to identify the interfacial delamination. A test cell was designed to simulate the

Figure 6-1: Interfacial delamination caused by freeze/thaw cycling (-40°C / 70°C).

(c) HFR at 20°C of ex-situ freeze/thaw cycled samples with SGL 10BB DM [115]
(d) HFR of in-cell freeze/thaw cycled cell with reversible frozen delamination [121]
interfacial delamination resulting from freeze/thaw cycling, and HFR measurements were performed to validate the diagnostic model.

**Computational Voltage Disruption Model Development**

The schematic of the test cell, components, and computational model domain is shown in Fig. 6-2 (a). A charge conservation law was applied to a differential control volume to estimate the voltage distribution in the computational domain. Equivalent electrical circuits are shown in Fig. 6-2 (b) and (c).

The key assumptions in the model formulation are:

1. The protonic or electronic transport in the fuel cell is considered two-dimensional and has reached a steady state.

2. All material properties are homogeneous, but can be anisotropic.

3. Electrical contact resistance is neglected except for within the simulated delamination region. In Fig. 6-2 (c), $R_{c, ij} = 0$ or $R_{it, ij} = 0$ where $i$ and $j$ are adjacent components, respectively; $R_{c,AFP ADM}$ indicates interfacial resistance between anode flow-field plate and anode diffusion media.

4. Delamination is modeled as an infinite contact resistance with zero thickness.

5. Physical deformation of fuel cell components due to interfacial delaminations is not considered.

6. Catalyst layer is approximated by transmission line model and protonic resistance is significantly larger than electronic resistance in the catalyst layers. HFR in the catalyst layers can be approximated by electronic resistance due to parallel circuit theory [124, 125].

7. Proton transfer from the catalyst surfaces is assumed. It is because interfacial area between catalyst layer and membrane is negligible compared to interfacial area between ionomers and catalyst in the catalyst layers. Thus charge transfer reaction occurs inside
the catalyst layers. All interfaces in the equivalent electrical circuit can be approximated by interface resistance.

From the equivalent circuit at high frequency (Fig. 6-2 (c)), HFR represents the proton resistance in membrane, electronic resistance in CL, DM and flow-field plate, as well as interfacial contact resistances, as expressed by:

\[
HFR = \sum R_{e,i} + \sum R_{e,i,j} + \sum R_{H^{+},i} + \sum R_{H^{+},i,j}
\]  \[6.1\]

where \( R_{e,i} \) and \( R_{H^{+},i} \) are bulk resistances of electronic conductor (flow-field plate, DM and CL) and protonic conductor (membrane), respectively.

The governing equation in each component derived from a charge conservation law can be written as Laplace equation [126]:

\[
\sigma_x \frac{\partial^2 V}{\partial x^2} + \sigma_y \frac{\partial^2 V}{\partial y^2} = 0
\]  \[6.2\]

where \( \sigma_x \) and \( \sigma_y \) are the ionic/electronic conductivity in the x and y-direction, respectively.

The model is developed to estimate the increase in cell resistance due to the delamination. So either a constant voltage boundary condition on both sides, or a constant voltage on one side and current specification on the other side can be used. In the following description, a constant voltage boundary condition is used:

\[
V_{|_{x=0}} = V_0 \quad \text{[6.3a]}
\]

\[
V_{|_{x=l}} = 0 \quad (\text{reference}) \quad \text{[6.3b]}
\]

where \( V_0 \) is the arbitrary constant voltage. For this study, 0.2V is chosen because typical ohmic voltage loss at the maximum current (1.5 ~ 2A/cm\(^2\)) is between 0.1V and 0.2V.

For the top and bottom boundary, a symmetrical boundary condition is used. At all interfaces, voltage and current continuity is imposed.
Electrical properties of the materials for the base case simulation are summarized in Table 6-1. It should be noted that these electrical properties reported in the literature have significant variation [127, 128, 129, 130]. These variations depend on the manufacturer, material composition, as well as the micro-structures of CL and DM. For example, the through-plane and in-plane conductivity of Toray Carbon Fiber Paper (TGP-H) are reported to be 1,250 S/m and 17,857 S/m, respectively [127]. However, for SGL 10 series carbon paper type diffusion media, the through-plane conductivity lies between 250 and 350 S/m [128] while in-plane conductivity is
not reported to the authors’ knowledge. As baseline properties, through-plane conductivity of the DM is chosen to be 300 S/m since the SGL 10 series diffusion media were used for the experimental validation. The in-plane conductivity is assumed to be 10 times higher than the through-plane conductivity, which is consistent with that reported in the manufacturer’s data sheet. The electronic conductivity of the catalyst layer depends on its composition, and is reported to be about 100 S/m for 30% ionomer volume fraction, and 300 S/m elsewhere. In this study, CL electronic conductivity of 200 S/m is used. Based upon average values of conductivity under the typical fuel cell operating conditions, a value of 10 S/m is used for the membrane ionic conductivity.

In case of interfacial delamination, the effective area for current flow reduces and effective current flow passage increases in the adjacent components, resulting in resistance increase (in Eq. 6.1, increase of $R_{\text{c,i/i}}$ and $R_{\text{H,i/i}}$). Calculation of localized resistance and effective contact resistance is complicated, but averaged total resistance can be easily calculated from Ohm’s law, where current is calculated from 2-D numerical computation of governing equation. Thus, the change in overall resistance resulting from interfacial delamination was compared to baseline resistance for this analysis.

Table 6-1: Material properties for base case simulation.

<table>
<thead>
<tr>
<th>Component</th>
<th>Compressed thickness (µm)</th>
<th>$\sigma_{\text{x,thru-plane}}$ (S/m)</th>
<th>$\sigma_{\text{y,in-plane}}$ (S/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Graphite plate</td>
<td>1000</td>
<td>20,000$^{20}$</td>
<td>20,000$^{20}$</td>
</tr>
<tr>
<td>Diffusion Media</td>
<td>291</td>
<td>300</td>
<td>3000</td>
</tr>
<tr>
<td>Catalyst layer</td>
<td>10</td>
<td>200</td>
<td>200</td>
</tr>
<tr>
<td>Membrane</td>
<td>18</td>
<td>10</td>
<td>10</td>
</tr>
</tbody>
</table>
**Experimental Setup**

A model test cell was developed to simulate a delamination scenario, and a schematic of the experimental setup is shown in Fig. 6-3. HFR measurements were used to validate the developed model. To simulate the permanent gap between the CL and DM observed in ex-situ freeze/thaw cycling tests, the DM was masked with a thin (20 µm) PTFE film. As shown in Fig. 6-3 (b), three PTFE films (5 mm × 35 mm) were inserted between the cathode catalyst layer and diffusion media to mimic a delamination between the cathode CL and DM. SGL 10BB (thickness 0.42 mm) with 35 mm width and 35 mm height were used for both the anode and cathode diffusion media. A Gore 5710-series three-layer membrane electrode assembly (MEA) was used. The MEAs were soaked in de-ionized water for over 12 hours at ambient temperature to ensure the MEA was fully saturated prior to measurement. The test sample was assembled using a 5 cm² fuel cell test fixture (Fuel Cell Technologies, Inc., USA) and two graphite plates (60 mm × 60 mm × 10 mm). Four PTFE-coated fiberglass gaskets (thickness of 0.152 mm each) were inserted along the outer edges between the graphite plates to prevent localized over-compression (edge bending), which enabled a uniform compression strain (25 ~ 30 %) on the DM, identical to a common fuel cell stack assembly. HFR was measured at ambient temperature with an Agilent 4338B Millohmometer (1 kHz). An additional test fuel cell with an active area of 22 cm² and SGL 10AA DM was assembled to investigate the effects of temperature and electrochemical activation on HFR.
Experimental Validation

The measured and predicted HFR of non-masked (base) and masked (simulated delamination) cases is shown in Fig. 6-4. HFR of non-masked and masked cases was measured to be 88 and 148 mΩ-cm², respectively. The results of the model are highly dependent on material electrical properties, especially so for the membrane. Even though the HFR values depend on the chosen properties, the resistance ratio of an interfacial delamination to non-interfacial delamination ($R/R_b$) does not depend on membrane properties. Therefore, the resistance ratio ($R/R_b$) is used as the primary measure for the effects of delamination.

It should be noted that HFR measurements were conducted at ambient temperature (~20°C) and test samples were not electrochemically activated, e.g. no current was ever drawn in the membrane. In this model, contact resistance besides the local delamination was also considered negligible. The electron conductivity of the CL and DM is relatively constant over
various temperature ranges and operating conditions, but the proton conductivity is highly dependent on temperature, relative humidity, and electrochemical activation. For example, the base conductivity of 10 S/m is appropriate for an activated membrane at 65°C, but not an inactivated membrane at 20 °C. It was observed that the HFR of the fuel cell increased significantly with decreasing temperature; HFR at 20°C was measured to be 80.4 mΩ·cm², 40% higher than at 65°C. It was also observed that electrochemical activation slightly decreased cell HFR by around 10%. The other important factor is contact resistance, which is a result of imperfectly matched material interfaces in the fuel cells, specifically DM | CL and DM | BP interfaces [117, 134]. The contact resistance is strongly dependent on cell assembly compression pressure and can be treated as constant for the same compression pressure and assembly. It should be noted that the model assumes perfect contact except for delamination.

Figure 6-4: Overall cell HFR comparison between experiment and modeling with varying membrane conductivity. $R_b$ = HFR of unmasked, non-delaminated base case. $R$ = HFR of masked, delaminated case.
In order to make comparisons more generally applicable despite variations in hydration or contact resistance, it is useful to develop dimensionless parameters. Selection of different property values will result in different absolute resistance; however increase in resistance due to delamination or resistance ratio \((R/R_b)\) was identical and is shown in Fig. 6-4. Therefore, this developed model is able to investigate the effect of interfacial delamination compared to non-interfacial delamination by quantifying the resistance ratio \((R/R_b)\).

### 6.3 Results and Discussion

The effect of delamination width, location, density, DM thickness, as well as anisotropic electrical properties of DM and membrane on HFR was investigated. Detailed test cases are summarized in Table 6-2. Three non-dimensional parameters: delamination width, \(W/\delta\) (\(W\) is the delamination width and \(\delta\) is the membrane thickness), delamination area, \(A/A_b\) (\(A\) is the delamination area and \(A_b\) is the total area), and resistance ratio, \(R/R_b\) (\(R\) is the overall ohmic resistance, \(R_b\) is the base resistance (non-delamination)) are used to present the detailed parametric study in the subsequent sections. The size and the number of interfacial delamination for a given dimension are major parameters to determine resistance increase ratio. The size parameter, \(W/\delta\), is defined because the membrane resistance is a key parameter for overall cell ohmic resistance and the increase in the resistance due to delamination. The density parameter, \(A/A_b\), is used to characterize effect of the number of interfacial delamination on the resistance increase. The resistance ratio, \(R/R_b\), is introduced since this accounts for a resistance increase which is independent of the specific conductivity of the membrane.
Effects of Delamination Width and Location

Ohmic resistance was calculated for a single local delamination of various widths ($W$) at different locations: 1) PEM | CL, 2) CL | DM, and 3) DM | BP. A 3 mm control volume height ($H \approx 167\delta$) is chosen to investigate the effect of delamination area fraction. The delamination is located at the center of the height with varying width. From Fig. 6-5, as the delamination width increases, the delamination area fraction increases linearly, but the resistance ratio, $R/R_{\beta}$, increases sharply in a non-linear fashion. A delamination at the PEM | CL and CL | DM interfaces caused a more significant resistance increase than one present at the DM | BP interface. The maximum limit of the resistance ratio can be predicted by neglecting any in-plane current flow that results from the delamination, which is equivalent to removing all conducting materials

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Test case variation</th>
<th>Comment</th>
</tr>
</thead>
</table>
| Delamination location | PEM | CL  
CL | DM  
DM | BP | $0.5 \leq W/\delta \leq 83$  
Single delamination ($n = 1$) |
| Delamination width | $0.5 \leq W/\delta \leq 83$ | $n = 1$ |
| Delamination density | $1 \leq n \leq 50$ | $W/\delta = 25, 50$ |
| DM thickness(mm) | 0.291, 0.21, 0.14 | |
| Material conductivity (S/m) variation | Membrane | 10, 1, 0.1, 0.01, 0.001 |
| DM | $\sigma_{x,\text{through-plane}}$ | $\sigma_{y,\text{in-plane}}$/ $\sigma_{x,\text{through-plane}}$ | $n = 20$  
$W/\delta = 50$ |
| | 300 | 1 |
| | 600 | 4 |
| | 1,200 | 8 |
| | 2,400 | 16 |

Table 6-2: Summary of test cases for the parametric study.
adjacent to the delamination. Thus maximum limit of $R/R_b$ can be calculated by $A_b/(A_b - A)$, denoted as the dotted line in Fig. 6-5.

Figure 6-5: Effect of delamination width and location on resistance ratio; $A =$ delaminated area, $A_b =$ total area (base area), $R =$ overall cell HFR, and $R_b =$ overall cell HFR without delamination.

The overall resistance increase is attributed to an electrical insulation barrier due to the local delamination, which causes voltage and current distortion. Voltage and current density distortion plots for a delamination at three different locations with $W/\delta = 50$ (here $W = 0.9$ mm, equivalent to a typical channel width) are shown in Fig. 6-6. It is apparent that a significant distortion of the voltage contour occurs near the delamination, resulting in significant in-plane current flow as well as the existence of a zone of little current flow (dead zone). For a delamination located at the PEM | CL and CL | DM interfaces, the voltage contour and current density vector plots seem almost identical, but the magnified view of current vector plots in Fig. 6-6 (c) shows that there is a larger dead zone for a delamination at PEM | CL interface than one at
the CL | DM interface. On the contrary, voltage contour and current density vectors across the MEA were not significantly affected by a delamination located at the DM | BP interface. The size of current dead zone by delamination at DM | BP is significantly lower than those of PEM | CL and CL | DM delamination cases. This is because the DM and BP have significantly lower in-plane resistance as well an in-plane-to-through-plane resistance ratio of near unity. The slight ohmic resistance increase due to a delamination at the DM | BP was attributed to an increased effective mean current flow path. The effect of an in-plane-to-through-plane resistance ratio is discussed in detail in a subsequent section of this paper.

Based on these simulation results, the key controlling parameters influencing voltage and current distribution near a local delamination are the in-plane resistance and in-plane-to-through-plane resistance ratio of the components adjacent to the delamination. In-plane, through-plane resistance, and the ratio of these two for each component are expressed as:

\[
R'_{y,i} = \frac{1}{\sigma_{y,i}} \frac{W}{t_i} \quad [6.4a]
\]

\[
R'_{x,i} = \frac{1}{\sigma_{x,i}} \frac{t_i}{W} \quad [6.4b]
\]

\[
\frac{R'_{y,i}}{R'_{x,i}} = \left( \frac{\sigma_{x,i} W}{\sigma_{y,i} t_i} \right)^2 \quad [6.4c]
\]

where \( W \) is delamination width, \( t_i \) is the cross-sectional thickness of component \( i \), \( R \) is the resistance per unit depth (shown in the \( Z \) direction of Fig. 6-2), and \( y \) and \( x \) are in-plane and through-plane direction, respectively. \( W/t_i \) is referred to as a geometry factor.

It is challenging to characterize the size, density, shape, and distribution of interfacial delamination in fuel cell because interfacial delamination shape may be 3-dimensional and non-uniform. The approximate maximum size can be estimated by considering compression force distribution in the MEA. The interfacial delamination can be determined by the balance of: 1) source force: mechanical stress (dry/wet cycles, mismatched ionomer in the electrode and
membrane, and freeze/thaw cycles) and thermal stress (startup and shutdown), 2) resisting force: compression force and material strength. In the resisting compression force, uniformity of compression force between under the land and under the channel is an important factor to mitigate interfacial damage. However, compression force under the channel is significantly lower than that under the land, depending on materials and flow-field design. Thus the possible maximum size of interfacial delamination can be channel width, which was verified in the ex-situ freeze/thaw cycling testing\(^1\). In this study, the worst scenario (interfacial delamination width ~ typical channel width) was considered.

In Table 6-3, the calculated in-plane, through-plane resistance, and resistance ratio for each fuel cell component are shown. The delamination width, 0.9 mm, was chosen because the width is comparable to typical channel width and the interfacial delamination due to ice lens formation typically occurs under the channel [121,115,114, 32, 109]. In the case of perfect contact where the through-plane resistance determines ohmic resistance, the membrane and diffusion media are the dominant factors determining the total ohmic resistance, as shown in the overall resistance fraction of Table 6-3, with negligible CL and BP resistances. However, in the case of a local delamination, in-plane resistance and the in-plane-to-through-plane resistance ratio become important and the voltage contour and current flow distributions are significantly altered.

In-plane current flow near a delamination is obviously affected by in-plane resistance. From Eq. 6.4a, in-plane resistance strongly depends on geometry, specifically the cross sectional area in the in-plane direction. The membrane has an order of magnitude higher in-plane resistance than the catalyst layer, and is 5,000 and 100,000 times greater than the diffusion media and bipolar plate, respectively, for a delamination of 0.9 mm width (Refer to Table 6-3). The in-plane-to-through-plane resistance ratio affects the shape of the current dead zone near the delamination. The in-plane-to-through-plane resistance ratio of the CL and membrane was three orders of magnitude higher than the DM and BP. From Eq. 6.4a and Eq. 6.4c, for constant
component thicknesses, as the delamination width \((W)\) increases, in-plane resistance increases linearly and the in-plane-to-through-plane resistance ratio increases by the geometry factor squared. Therefore, as the delamination width increases, the current dead zone increases, causing a sharp increase. The interfacial delamination width due to freezing was dependent on channel width, so smaller channel designs may prove beneficial to decrease delamination widths.

Figure 6-6: Comparison of, voltage contour and current vector plots for interfacial delamination location at PEM | CL, CL | DM, and DM | BP with \(W/\delta = 50\) and base properties.
Among the fuel cell components, the membrane is the critical component controlling an ohmic resistance increase caused by delamination. This is because the through-plane resistance of the membrane is 46% of the overall cell ohmic resistance and the membrane has the highest in-plane resistance as well as a large in-plane-to-through-plane resistance ratio. Ohmic resistance increases due to delamination was mainly determined by the extent of the dead zone generated in the membrane. Therefore, in the following parametric case studies, a delamination located at the PEM|CL interface with delamination width 50\( \delta \) (0.9 mm) and 25\( \delta \) (0.45 mm) is chosen. These two widths are based on the fact that interfacial delamination occurs under the channel (two different channel widths chosen) [31, 32, 109].

Effect of Delamination Density

To investigate the effect of the number of delaminations (delamination density) on ohmic resistance, a large cell height \( (H = 2000\delta) \) is chosen to include sufficient number of delamination sites. The delamination location was distributed symmetrically to simulate a parallel channel

<table>
<thead>
<tr>
<th>Component</th>
<th>( \sigma_x ) (S/m)</th>
<th>( \sigma_x/\sigma_y )</th>
<th>Thickness (m)</th>
<th>( R_y ) (( \Omega )-m)</th>
<th>( R_x )</th>
<th>( R_y/R_x )</th>
<th>Overall resistance fraction (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anode BP</td>
<td>20,000</td>
<td>1</td>
<td>0.001</td>
<td>4.50\times10^{-5}</td>
<td>5.56\times10^{-5}</td>
<td>0.81</td>
<td>1.3</td>
</tr>
<tr>
<td>Anode DM</td>
<td>300</td>
<td>10</td>
<td>2.91\times10^{-4}</td>
<td>1.03\times10^{-3}</td>
<td>1.08\times10^{-3}</td>
<td>0.96</td>
<td>24.6</td>
</tr>
<tr>
<td>Anode CL</td>
<td>200</td>
<td>1</td>
<td>1.00\times10^{-3}</td>
<td>0.45</td>
<td>5.56\times10^{-5}</td>
<td>8,100</td>
<td>1.3</td>
</tr>
<tr>
<td>PEM</td>
<td>10</td>
<td>1</td>
<td>1.80\times10^{-5}</td>
<td>5.00</td>
<td>2.00\times10^{-3}</td>
<td>2,500</td>
<td>45.7</td>
</tr>
<tr>
<td>Cathode CL</td>
<td>200</td>
<td>1</td>
<td>1.00\times10^{-5}</td>
<td>0.45</td>
<td>5.56\times10^{-5}</td>
<td>8,100</td>
<td>1.3</td>
</tr>
<tr>
<td>Cathode DM</td>
<td>300</td>
<td>10</td>
<td>2.91\times10^{-4}</td>
<td>1.03\times10^{-3}</td>
<td>1.08\times10^{-3}</td>
<td>0.96</td>
<td>24.6</td>
</tr>
</tbody>
</table>
Two delamination widths, $25\delta$ and $50\delta$, were chosen to investigate the coupled effects of density and width. As mentioned earlier, the delamination located at the PEM | CL interface is considered since it causes the most severe resistance increase. Figure 6-7 shows the effect of area fraction on the resistance ratio ($R/R_b$) for various delamination density and widths. As the delamination area fraction increases, resistance tends to increase sharply, similar to the single delamination case. Even if the delamination area fraction is identical, the larger delamination results in higher ohmic resistance due to a higher in-plane resistance and in-plane-to-through-plane resistance ratio resulting from the geometry factor. The single delamination with variable width is overlaid in Fig. 6-7, which shows the same trend: for the same area fraction (50%), a larger delamination ($83\delta$) has higher resistance increase. This further reinforces the fact that smaller channel widths result in lower resistance increases due to delaminations.

Figure 6-7: Effects of delamination width ($W/\delta = 25$ and 50) on the resistance ratio as a function of the number of delamination, $n$ and area fraction, $A/A_b$. Delamination is located at the PEM | CL interface (green triangle represents single delamination and variable width.).
Effect of Membrane Conductivity

From the previous section, the in-plane resistance of the membrane was observed to be a critical parameter for resistance increases caused by delamination at the PEM | CL interface. The in-plane resistance is inversely proportional to conductivity of membrane. The effect of membrane conductivity on ohmic resistance was investigated with delamination width \( W = 50\delta \) and varying number of delaminations at the PEM | CL interface, and the results are plotted in Fig. 6-8. Figure 6-8 (a) shows that the lower membrane conductivity results in much steeper resistance increase with increasing area fraction. Figure 6-8 (b) shows that the resistance ratio asymptotically approaches to a maximum limiting value when membrane conductivity is lower than 1.0 S/m. The asymptotic approach is attributed to the fact that the total ohmic resistance is overwhelmed by membrane resistance in the lower membrane conductivities (less than 1.0 S/m). As membrane conductivity decreases to 1.0 S/m, the membrane accounts for 90% of the overall cell ohmic resistance.

---

**Figure 6-8**: Effect of membrane conductivity on resistance ratio with multiple delaminations \( W/\delta = 50 \) at the PEM | CL interface.
Mukundan et al. [25] reported that the conductivity of Nafion® 117 membrane was sensitive to water content and temperature, and ranged between 0.02 and 1 S/m under subzero conditions. This indicates that a small interfacial delamination at PEM | CL under frozen condition can result in a greater ohmic resistance loss. Kim et al. [121] reported that the frozen state (-36°C) HFR of a fuel cell subjected to 100 freeze/thaw cycles was two times higher than a non-cycled cell. The channel-to-land ratio of the freeze/thaw cycled cell is 1:1, giving a 50% channel area fraction. Assuming all channels have a very thin delamination at the PEM | CL or CL | DM interface, the experimental increase ratio of 1.99 in HFR observed at a frozen state corresponds to that of 1.98 predicted by the model.

It should be also noted that membrane conductivity is assumed as homogeneous in this analysis. However, when HFR is measured under real operation, membrane water content near interfacial delamination may be lower because of concentrated localized current, resulting in lowering membrane conductivity and increasing HFR. Thus this model may underestimate resistance increase resulting from delamination.

Anisotropic Effect of Diffusion Media

Diffusion media generally have an anisotropic structure, leading to anisotropic thermal and electrical properties. Typically, the in-plane electrical conductivity is ten times higher than the through-plane electrical conductivity. Figure 9 shows the effect of property changes in the in-plane and through-plane conductivity on ohmic resistance. Here a delamination of width (50δ) and the number (n = 20, A /Ah = 50%) located at the PEM|CL interface is used for the parametric study. To investigate the effect of anisotropic properties on HFR, another non-dimensional parameter, overall resistance to isotropic resistance ratio (R/Riso) was introduced. Riso represents overall resistance when σx,through-plane is equal to σy,in-plane. From Fig. 6-9, an ohmic resistance increase due to delamination depends on both the through-plane and in-plane conductivity. As the
through-plane conductivity increases, the overall resistance tends to reduce asymptotically and
the anisotropic effect is negligible (within 5% of $R/R_{iso}$) when through-plane conductivity is
greater than 1,250 S/m. However, the anisotropic effect was significant when the through-plane
conductivity is less than 500 S/m.

Anisotropic effects are negligible at higher through-plane conductivities because the
contribution of the DM to the total ohmic resistance is reduced with increasing through-plane
conductivity. For example, each diffusion media in the anode and cathode accounts for 25% of
the overall ohmic resistance when $\sigma_{x,\text{through-plane}}$ is 300 S/m, but only 10% when $\sigma_{x,\text{through-plane}}$ is
1,250 S/m. Therefore, anisotropic effects should be considered for SGL DM, which has a typical
through-plane conductivity of 300 S/m. However, these effects can be neglected for Toray carbon
paper diffusion media, which has a typical through-plane conductivity of 1,250 S/m [127].

Figure 6-9: Anisotropic effect of diffusion media on resistance ratio with delamination width
$W/\delta = 50$ and number $n = 20$ ($A/A_b = 0.5$), located at PEM|CL interface; $R_{iso}$ is the overall
resistance with isotropic properties. The solid circle and square in the x-axis indicate typical
through-plane conductivity for SGL and Toray DM, respectively.
**Effect of Diffusion Media Thickness**

Typical thickness of diffusion media used for fuel cell applications ranges between 0.2 mm and 0.42 mm. The effects of diffusion media thickness on ohmic resistance were investigated with delamination of width \((50\delta)\) and number \((n = 20, \, A/A_b = 50\%)\), and are shown in Fig. 6-10. It should be noted that the compressed \((25\sim30\%)\) DM thickness was used for this modeling. From Fig. 6-10, the overall ohmic resistances of both the non-delamination and delamination cases increase with increasing thickness. However, the resistance ratio \((R/R_b)\) due to interfacial delamination decreases because of the reduced in-plane resistance.

![Figure 6-10: Effect of DM thickness on resistance ratio for delamination width \(W/\delta = 50\), number, \(n = 20\) \((A/A_b = 0.5)\) and base case properties. The delamination is located at the PEM | CL interface.](image)

If interfacial delamination can be prevented, thinner (for example, 0.2 mm) diffusion media have several benefits compared to thicker DM (0.42 mm). These benefits include: reduced ohmic loss by approximately 10 m\(\Omega\)-cm\(^2\), volume reduction by approximately 10% for an 80kW
stack, enhanced power density, and lower absolute water retention. However, thinner diffusion media may suffer from interfacial delamination due to ice lens formation in a fuel cell with a wide channel design since those DM give a lower compressive force under the channel compared to that of thicker diffusion media. For the wide channel design, thicker diffusion media have higher stiffness, theoretically leading to better transmission of compressive force from under-the-land to under-the-channel, thereby reducing the chances of ice lens formation and delamination [115]. For thinner diffusion media, a narrow channel width should be considered to prevent delamination and limit deleterious performance effects if delamination does occur.

**Design Recommendation to Minimize the Ohmic Loss Caused by Interfacial Delamination**

The in-plane resistance and the in-plane-to-through-plane resistance ratio of components adjacent to the interfacial delamination are found to be key controlling parameters for ohmic resistance increase. The membrane is also found to be a key component determining ohmic losses due to interfacial delamination. To investigate the effect of the in-plane-to-through-plane resistance ratio of adjacent components (membrane and cathode catalyst layer) at the PEM | CL interfacial delamination, theoretical case studies for a single delamination with widths of $25\delta$ and $50\delta$ were conducted. Extreme range of anisotropic properties of the membrane and CL were chosen for these simulations. It should be noted that such properties may be difficult to obtain using current state-of-art fuel cell technologies, but simulation of them greatly helps to elucidate the limiting effects of in-plane-to-through-plane resistance ratio on fuel cell performance. Figure 6-11 shows that the membrane in-plane-to-through-plane resistance ratio significantly affects the ohmic resistance ratio ($R/R_b$), but its effect is negligible below 0.1. The resistance ratio effect of the cathode catalyst layer (CCL) is less significant compared to the membrane’s resistance ratio effect. In Fig. 12, solid lines represent the overall cell resistance ratio, while the CCL’s in-plane-to-through-plane resistance ratio is that of the base case (8,100 for $50\delta$ and 2,025 for $25\delta$). The dotted lines show the overall cell resistance ratio variations when the CCL’s in-plane-to-through-
plane resistance ratio is reduced to one. It should be noted that the in-plane conductivity of membrane and CCL is 25,000 S/m and 1,620,000 S/m, respectively for 50\(\delta\) interfacial delamination, which can not be achieved with today’s materials.

Figure 6-11: Effects of in-plane-to-through-plane resistance ratio of membrane and cathode catalyst layer for PEM | CCL interfacial delamination with \(n = 1\) and \(W/\delta = 50\) and 25.

The effect of the membrane’s and CCL’s in-plane-to-through-plane resistance ratio on voltage contours is shown in Fig. 6-12. In Fig. 6-12 (b), for \(\frac{R_{x,\text{PEM}}}{R_{x,\text{CCL}}} = 2,500\) and \(\frac{R_{y,\text{PEM}}}{R_{y,\text{CCL}}} = 1\), the voltage distortion in the CCL almost disappears in comparison to Fig. 6-12 (a). Similarly, Fig. 6-12 (c) shows a voltage contour for \(\frac{R_{x,\text{PEM}}}{R_{x,\text{CCL}}} = 1\) and \(\frac{R_{y,\text{CCL}}}{R_{y,\text{PEM}}} = 8,100\), and the voltage distortion in the membrane is significantly reduced. From the voltage contour plots of Fig. 6-12 (a) - (d), as \(\frac{R_x}{R_y}\) of the components near the delamination reduces to less than unity, the voltage distortion in that
component almost disappears, reducing the current dead zone, and therefore reducing ohmic resistance increase. Again, the membrane plays a much more significant role in determining the overall cell resistance in comparison to the cathode catalyst layer. Even if the in-plane-to-through-plane resistance of the components adjacent to the interfacial delamination is reduced to less than one, the overall ohmic resistance is not as low as the non-interfacial delamination case. This is because an interfacial delamination causes an increase of the mean effective current flow path compared to a non-delamination case. Similarly, voltage contour plots for smaller interfacial delamination widths (25δ) are shown in Fig. 6-12 (d), (e), and (f). Voltage distortions are smaller than those of the 50δ cases, and the mean effective current flow path decreases, which results in a lower overall ohmic resistance increase.

The in-plane-to-through-plane resistance ratio is also found to be a key parameter to determine the current flow shape near the interfacial delamination. If the in-plane resistance is of the same order or lower than the through-plane resistance, current dead zones can be significantly reduced, thereby lowering the ohmic resistance due to delamination. However, an increased mean effective current flow path increases overall ohmic resistance. This mean effective path increases with increasing delamination width.

Based on the modeling results, the following recommendations are suggested to reduce the overall ohmic resistance increase due to interfacial delamination:

1) The in-plane-to-through-plane resistance ratio of components adjacent to the delamination should range from 1 to 0.1.

2) Stiff materials (diffusion media) and flow field designs with small channel widths and large channel-land ratios are required to minimize the delamination width.
It should be noted that the membrane is a key component and the first criterion, $\frac{R}{R} = 1 \sim 0.1$, cannot be achieved in reality because of the very thin geometry of the membrane.

<table>
<thead>
<tr>
<th>$W/\delta = 50$</th>
<th>$RR_{M}=2500$</th>
<th>$RR_{CCL}=8100$</th>
<th>$RR_{M}=2500$</th>
<th>$RR_{CCL}=1$</th>
<th>$RR_{M}=1$</th>
<th>$RR_{CCL}=8100$</th>
<th>$RR_{M}=1$</th>
<th>$RR_{CCL}=1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a)</td>
<td>(b)</td>
<td>(c)</td>
<td>(d)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>$W/\delta = 25$</th>
<th>$RR_{M}=625$</th>
<th>$RR_{CCL}=2025$</th>
<th>$RR_{M}=625$</th>
<th>$RR_{CCL}=1$</th>
<th>$RR_{M}=1$</th>
<th>$RR_{CCL}=2025$</th>
<th>$RR_{M}=1$</th>
<th>$RR_{CCL}=1$</th>
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</thead>
<tbody>
<tr>
<td>(e)</td>
<td>(f)</td>
<td>(g)</td>
<td>(h)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure 6-12: Effect of delamination widths, and ratio of in-plane and through-plane resistance of components (membrane and cathode catalyst layer) near interfacial delamination on voltage contour ($RR_{M}$ and $RR_{CCL}$ are in-plane and through-plane resistance ratio of membrane and cathode catalyst layer respectively).

Interface design in fuel cell materials as well as diagnostic tool for interface resistance is important to achieve durable fuel cell performance. HFR can be used as a potential diagnostic tool for fuel cell durability testing or extreme operating conditions. In this study, with the use of
an analytical model, HFR was used to investigate the effect interfacial delamination. However, HFR does not measure directly resistance resulting from interfacial delamination, but measures overall resistance. Therefore it must be complemented with other work like impedance spectroscopy, morphology analysis, or modeling to separate the interface contribution from overall HFR.

6.4 Conclusions

A two-dimensional anisotropic electrical model was developed to investigate the quantitative effects of interfacial delamination on fuel cell performance. The in-plane and in-plane-to-through-plane resistance ratio of components adjacent to the interfacial delamination were shown to be key parameters influencing the ohmic resistance increase. Among the components, the membrane is the critical component due to its relatively low conductivity and thickness. Interfacial delamination at the PEM | CL and CL | DM interfaces can significantly increase the ohmic resistance. As the interfacial delamination width and area increases, the ohmic resistance sharply increases. A delamination results in a greater ohmic resistance increase under frozen conditions due to deceased membrane conductivity.

The following are suggested to reduce the overall ohmic resistance increase due to interfacial delamination: 1) the in-plane-to-through-plane resistance ratio of components adjacent to the delamination should range from 1 to 0.1. 2) Stiff materials (diffusion media) and flow field designs with small channel widths and large channel-land ratios are required to minimize the delamination width and impact of delaminations when they do occur. It should be noted that the membrane is a key component and the first criterion, \( \frac{R}{R_i} = 1 \sim 0.1 \), can not be achieved in reality because of the very thin geometry of the membrane. To minimize ohmic losses due to interfacial
delamination, material selection and flow field design are important criteria to consider in order to obtain uniform compressive force under the channels and lands.
Chapter 7

Temperature-driven Water Transport: Thermo-osmosis in Membranes

7.1 Introduction

Water transport modes by electro-osmotic drag, diffusion and hydraulic permeation in the polymer electrolyte membranes have been well explored. Capillary and diffusion water transport modes in the porous media (diffusion media) have also been well studied \[135, 136, 137]\. However, temperature-driven water transport modes, \textit{thermo-osmosis in the membrane} and \textit{phase-change induced flow (termed heat pipe effect) in the porous media} are not yet well explored. Temperature-driven water flow is potentially attractive because of the possibility of tailoring material properties to avoid flooding, or for non-parasitic water drainage during shutdown using naturally occurring temperature gradients within the stack \[48, 138, 139]\.

Under fuel cell operation, a temperature difference can occur in the thru-plane direction depending on operating conditions, such as at high current \[126]\. At 1 A/cm\(^2\) current density, the interfacial temperature of the membrane in contact with cathode catalyst layers can be greater than 1 °C higher than that of the bulk membrane, and an even higher difference can occur across the diffusion media \[138, 139]\. Weber \textit{et al.} \[139]\ and Wang \textit{et al.} \[140]\ showed in their non-isothermal models that water transport mode by evaporation motion in the porous media (evaporation in the catalyst layers and condensation in the diffusion media or flow-field plates) plays an important role in high current and operating temperature regimes. Hickner \textit{et al.} \[141, 142, 143]\ observed the importance of water transport by evaporation in the higher current region.

As a first approximation, temperature-driven flow in the porous media (phase-change induced flow) can be treated as a gas-phase diffusion process induced by a thermodynamic
saturation pressure gradient. However, temperature-driven flow in the membrane (thermo-osmosis) is a fundamentally different transport mode. When a membrane separates liquid water with different temperatures, water flows from hot to cold direction or vice versa, a process known as thermo-osmosis. The direction of water flow depends on entropy difference between water in the membrane and external to the membrane; for example, water in a hydrophilic membrane can be considered to have a relatively ordered state compared to water existing outside the membrane. Therefore, unbound water transport from outside of the membrane cold side to the hot side leads to an increase of total entropy, and is thus thermodynamically favored [78]. For hydrophobic membranes, water typically flows from hot to cold direction based on a similar entropy-based argument [78, 52]. Despite this established conventional understanding, disagreement in the literature on the direction and magnitude of water flux for different fuel cell materials still exists, as summarized in Table 7-1.

Table 7-1: Summary of temperature-driven flow in PEFC.

<table>
<thead>
<tr>
<th>References</th>
<th>Materials</th>
<th>Observations</th>
</tr>
</thead>
</table>
| Villaluenga et al. [51] | Nafion® 117 (t=0.183mm, EW=1100) | $J=7.5 \times 10^{-6} \text{ kg/m}^2\text{s}$ @ $T_{\text{avg}}=26.5 \degree \text{C}$, $\Delta T_b=10 \degree \text{C}$ Water flows \textit{from cold to hot side}.
| Tasaka et al. [52] | Nafion® 417 (t=0.43mm, EW=1613) | $J=3.6 \times 10^{-5} \text{ kg/m}^2\text{s}$ @ $T_{\text{avg}}=35 \degree \text{C}$, $\Delta T=10 \degree \text{C}$ Water flows \textit{from cold to hot side}.
| Zaffou et al. [49, 50] | Nafion® 112 (t=0.051mm, EW=1100) | No water flow                                                                 |
|                  | PTFE-reinforced Nafion® 112      | $J=4.1 \times 10^{-4} \text{ kg/m}^2\text{s}$ @ $T_{\text{avg}}=65 \degree \text{C}$, $\Delta T=1 \degree \text{C}$ Water flows \textit{from hot to cold side}.
|                  | Catalyst-coated Nafion® 112      | No water flow                                                                 |
|                  | Catalyst-coated Gore-Select® membrane (5510 MEA) | $J=6.9 \times 10^{-4} \text{ kg/m}^2\text{s}$ @ $T_{\text{avg}}=65 \degree \text{C}$, $\Delta T=1 \degree \text{C}$ Water flows \textit{from hot to cold side}.
| Bradean et al. [48] | MEA (20 cell stack) | $J=3.0 \times 10^{-6} \text{ kg/m}^2\text{s}$ during cooling (66$\degree \text{C} \rightarrow \sim 33 \degree \text{C}$ (3 hours)) Water flows \textit{from hot to cold side}.
| Perry et al. [45, 46] | MEA (30 cell stack) | Water flows \textit{from hot to cold side}. Freeze-damage of anode end cell.
Villaluenga et al. [51] observed that water flows from the cold to hot side in the Nafion® membrane, which agrees with Tasaka’s [52] observation in Nafion®. Water flux was proportional to temperature difference and increases with average membrane temperature. The temperature dependency of water flux showed Arrhenius behavior for Villaluenga et al. [51]. However, Zaffou et al. [49, 50] observed that there was thermo-osmosis in the PTFE-reinforced membrane and flow direction from hot to cold side, but did not observe thermo-osmosis in the non-reinforced Nafion® membranes. Bradean et al. [48] and Perry et al. [45, 46] observed water flow from hot to cold side in the complete membrane electrode assemblies (MEAs) of a real fuel cell stack. It should be noted that Villaluega et al. [51] and Tasaka et al. [78, 52] used bare membrane in their circulated test cell, but Zaffou et al. [49, 50] used fuel cell fixtures where the membrane was sandwiched between highly porous diffusion media.

Temperature-driven flow during fuel cell operation, as well as at shutdown, can be important, but is still not completely understood. Water transport in the diffusion media driven by a phase change has been implemented in a non-isothermal thermodynamic model [139, 140], but thermo-osmotic water transport mode in the membrane is not yet accounted for, because empirical relations are not available. This work is motivated to elucidate a description of water transport driven by a temperature gradient in the fuel cell membranes, and to develop empirical relations describing this thermo-osmotic flow. Three different commercial perfluorinated membranes, typically used in PEFCs were investigated by measuring water flux using in-house fuel cell test fixtures. Membrane surface interfacial temperature was determined by two-dimensional thermal modeling, enabling the development of empirical relations for membrane thermo-osmotic diffusion flux as a function of actual membrane surface temperature gradient.
7.2 Method of Approach

A uniform in-plane membrane surface temperature in contact with hot and cold solutions is required to properly quantify the thermo-osmotic water flux. To reduce temperature difference between bulk solution and interface, and enhance surface temperature uniformity, a high flow rate circulation has been used in previous thermo-osmotic studies [52, 77, 78, 79, 80, 81]. The difference in the mean temperature between hot and cold solutions, instead of the surface temperature, was used, since measuring the surface temperature is challenging due to the convective thermal boundary layer [51, 79]. For this study, non-teflonized porous media were used on both sides of the membrane to enhance the uniformity of surface temperature and provide access to the full cross-sectional area for thermo-osmotic flux across the membrane. In this study, water flux was measured in the static condition with circulating, and separate coolant flow. The surface temperature of the membrane was obtained by using a two-dimensional thermal model in conjunction with directly measured flow-field plate temperature data, as described below.

Direct Thermo-osmotic Experimental Setup

The test cell utilized was designed for direct water flux measurement driven by temperature gradient as well as for fuel cell testing (Figure 7-1). The test setup consisted of two precisely temperature-controlled (accuracy ± 0.01 °C) refrigerated circulators (VWR International, USA, Model 1196D), a test cell, a distilled water reservoir, a vacuum pump, 9 T-type thermocouples, 9 manual valves, and calibrated PFA tubing (Swagelok, Tube size ¼ inch and wall thickness 0.062 inch). Two coolants (distilled water) were circulated through the test cell coolant plates at maximum flow rate (22 ℓ/min) in the counter-flow direction for precise temperature difference uniformity. Three temperature sensors were inserted in the middle of each flow-field plate, located at the inlet, center and outlet positions with respect to the flow direction. These thermocouples (not shown in the Fig. 7-1) were used to control circulator temperature,
enabling proper temperature boundary condition control. Two thermocouples (TC11 and TC21) were inserted in the T-junction of PFA tubing to monitor water temperature inside the tube. The other temperature sensor measured the ambient temperature. The valves and vacuum pump were used to fill water inside the test cell and remove air pockets. For example, after maintaining the test cell below – 750 mmHg with opened valves (V12 and V22) and closed other valves, both sides of the test cell were filled by opening valves (V14, V24, and V31). After the temperature of the flow-field plate reached the desired experimental temperature, water inside the tube was flushed using valve operations (open V31, V11, V21, V13, and V23, close the others) to maintain water temperature below 30°C, providing negligible evaporation loss of water in the PFA tubing. All valves except for V11 and V21 were closed for measurement of thermo-osmotic water flux.

Figure 7-1: Schematic of test cell to measure water transport driven by temperature gradient in PEFCs.
As shown in Fig. 7-1 (b), the test cell consisted of two flow-field plates, two cooling plates, and two end plates. The flow-field plate is made from machined impregnated fuel cell grade graphite with 12 parallel channels (1 mm width and 0.6 mm depth) and 0.75 mm wide lands. The cell active area is 23.75 cm², with identical anode and cathode flow-fields. Flat fluorine rubber gaskets (width 2 mm and thickness 0.7 mm) were attached on the grooved surface in each flow-field plate for sealing. The cooling plate consisted of gold-plated aluminum (thickness 20 mm) and Lexan® (thickness 5 mm). The surface with parallel cooling channels (2 mm depth and 3.1 mm width) was bonded by a Lexan® plate, serving as thermal and electrical insulator. The surface temperature of gold-plated aluminum in contact with flow-field plate was nearly uniform, providing a uniform thermal boundary condition. Stainless steel end plates (thickness 20 mm) were used to provide evenly distributed compression at contact pressures identical to normal fuel cells (e.g. 1 - 1.5 MPa). To prevent localized over-compression, incompressible PTFE-coated fiberglass shims were inserted in the border area of flow-field plates. A fiberglass washer was also inserted for each bolt, ensuring thermal and electrical isolation.

The water transport rate was calculated by measuring the change of water volume in the cold and hot side calibrated tubes. The water volume in the tube was calibrated by measuring different lengths of water weights using an accurate balance (resolution 0.001g). Water transport by hydraulic pressure gradient was negligible, because the tubes in the hot and cold sides were configured symmetrically. Hydrophilic, highly porous (porosity = 88 %) diffusion media (DM) and three different membranes were tested. The membranes tested were non-reinforced Nafion® membrane and two different commercialized reinforced membranes. The material properties are summarized in Table 7-2.
To enhance the temperature uniformity of the membrane surfaces and allow access to the entire active area for thermo-osmotic transport, porous diffusion media, SGL 10AA (SGL Carbon Group, USA), were used. The SGL 10AA has no PTFE content, showing completely hydrophilic behavior. Prior to thermo-osmotic experiment of membranes, a single diffusion medium was tested to separate the possible diffusion media effect from the assembly of membrane and diffusion media. The non-teflonized DM showed no temperature-driven flux when completely saturated with liquid. Thus, the thermo-osmotic water flux of the assembly was ascribed to the membrane. The assembled cell was soaked at 95°C for 9 hours prior to thermo-osmotic measurement, ensuring the membrane was fully saturated and activated. Thermo-osmotic experiments were conducted at average cell temperatures of 80, 65, 45 and 35°C with a temperature difference between flow-field plates of 10, 5, and 3°C. Each test condition was repeated 3 times and the test duration was sufficiently long to minimize the measurement error and assure a steady state had been achieved.

**Thermal Model for Temperature Distribution**

The schematic of the test cell, components, and computational model domain is shown in Fig. 7-2. The model is based on two-dimensional conduction heat transfer. The key assumptions in the model formulation are:

<table>
<thead>
<tr>
<th>Materials</th>
<th>Properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diffusion media</td>
<td>SGL10AA [128] Porosity=0.88, t=0.39 mm</td>
</tr>
<tr>
<td>Membrane</td>
<td>Nafion® 112 EW=1100, t=50µm</td>
</tr>
<tr>
<td>Flemion® SH50 [152]</td>
<td>PTFE fibril reinforced composite membrane EW=910, t=50µm</td>
</tr>
<tr>
<td>Gore-Select® [113]</td>
<td>ePTFE micro-reinforced composite membrane EW &lt;1000, t=18µm</td>
</tr>
</tbody>
</table>
• The heat transfer is considered two-dimensional and has reached steady state.
• All material properties are homogeneous, but can be anisotropic.
• Thermal contact resistance is negligible.
• Heat transfer by convection is negligible.

The governing equation in each component can be written as a Laplace Eqn.:

\[ \kappa_x \frac{\partial^2 T}{\partial x^2} + \kappa_y \frac{\partial^2 T}{\partial y^2} = 0 \]  \[ \text{[7.1]} \]

where \( \kappa_x \) and \( \kappa_y \) are the thermal conductivity in the x and y-direction, respectively. The assumption of negligible convective heat transfer can be justified by considering the Peclet number. The Peclet number is defined as the ratio of convective to conduction heat transfer, and expressed as:

\[ Pe = \frac{VL}{\alpha} \]  \[ \text{[7.2]} \]

where \( V \) is the velocity, \( L \) is the characteristic length scale, and \( \alpha \) is the thermal diffusivity. For example, in the channel of Fig. 7-2 (b), the characteristic length scale is \( 0.6 \times 10^{-3} \) m, the effective thermal diffusivity of water is \( 1.6 \times 10^{-7} \) m\(^2\)/s, and the effective velocity is \( 6 \times 10^{-7} \) m/s (Refer to Results and Discussion section, Gore-Select® membrane at \( T_{cell, \text{avg}} = 80^\circ \text{C} \) and \( \Delta T_{cell} = 10^\circ \text{C} \)). The Peclet number, \( Pe \) is \( 3 \times 10^{-3} \), so convective heat transfer is negligible compared to conduction heat transfer. In other components, the Peclet number is also very minute, so the assumption is valid in the entire computational domain.
Constant temperature boundary conditions are used:

\[ T_{|x=0} = T_H \]  \hspace{1cm} [7.3a]

\[ T_{|x=L} = T_C \]  \hspace{1cm} [7.3b]

where \( T_H \) and \( T_C \) are the temperature of the flow-field plate of hot and cold sides respectively. For the top and bottom boundaries, a symmetrical boundary condition is used.

Base properties of fuel cell components and water are summarized in Table 7-3. Membrane, graphite and water were approximated to be isotropic and homogeneous, but anisotropic thermal conductivity was considered for diffusion media, where its in-plane thermal conductivity was considered to be ten times higher than thru-plane thermal conductivity based on a survey of published values [127]. Because water was filled in the vacuum state and diffusion media, SGL 10AA, is hydrophilic (no PTFE), water is fully saturated in the diffusion media. It should be noted that full saturation and water wetting can justify the assumption of negligible contact resistance for this thermal model.

Figure 7-2: Schematic (not to scale) of computational model cell domain and components for the two-dimensional temperature model.
For diffusion media and membrane, effective properties were estimated by volume averaging. The effective thermal conductivity of diffusion media can be estimated by:

\[ \kappa_{DM,i,\text{eff}} = (1 - \varepsilon_{\text{comp}}) \kappa_{DM,i} + \varepsilon_{\text{comp}} \kappa_w \]  

where \( \kappa_{DM,i,\text{eff}} \) and \( \kappa_{DM,i} \) are effective and base thermal conductivity of diffusion media (DM) in the \( i \) direction respectively, \( \varepsilon_{\text{comp}} \) is compressed porosity of diffusion media, 0.84 for 25% compressed SGL 10AA, \( \kappa_w \) is water thermal conductivity. The effective thermal conductivity of membrane can be estimated by [138]:

\[ \kappa_{PEM,\text{eff}} = \frac{\rho_{PEM}}{\rho_w} \frac{EW}{\rho_{PEM}} \kappa_{PEM} + \frac{\lambda M_w}{\rho_w} \kappa_w \]  

where \( \kappa_{PEM,\text{eff}} \) and \( \kappa_{PEM} \) are effective and base thermal conductivity of membrane, respectively, \( \rho_{PEM} \) (1980 kg/m\(^3\)) and \( \rho_w \) (981 kg/m\(^3\)) are density of dry Nafion\(^\circledR\) membrane and water respectively, \( \lambda \) is the number of water molecules per sulphonic acid site in the membrane. Since the membrane is in the liquid water, \( \lambda = 22 \) is used for this model, The \( EW \) and \( M_w \) are equivalent weight of membrane and water molecular weight, respectively. The estimated effective thermal

<table>
<thead>
<tr>
<th>Component</th>
<th>Compressed thickness(µm)</th>
<th>( \kappa_x ) (W/m-K)</th>
<th>( \kappa_y ) (W/m-K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Graphite plate</td>
<td>2000</td>
<td>20 [140]</td>
<td>20 [140]</td>
</tr>
<tr>
<td>Diffusion media</td>
<td>291</td>
<td>0.48±0.09 [138]</td>
<td>4.8±0.9 [138]</td>
</tr>
<tr>
<td>Nafion(^\circledR) membrane</td>
<td>-</td>
<td>0.15±0.04 [138]</td>
<td>0.15±0.04 [138]</td>
</tr>
<tr>
<td>Water</td>
<td>-</td>
<td>0.66</td>
<td>0.66</td>
</tr>
</tbody>
</table>

Table 7-3: Base material properties of thermal model.
conductivity of diffusion media are 0.63 ± 0.02 and 1.32 ± 0.14 W/m-K for thru-plane and in-plane directions, respectively. The effective thermal conductivities of the Nafion®, Flemion®, and Gore-Select® membrane are 0.36 ± 0.03, 0.39 ± 0.03, and 0.37 ± 0.03 W/m-K, respectively. Note that slightly different effective thermal conductivities of the composite reinforced membranes result from contribution of PTFE fiber (Flemion®, 2.7 wt% [153]), ePTFE (Gore-Select®, porosity 70 ~ 95% [154], thickness 6 µm [114]), and different EW. The effective conductivity was estimated using properties at 65°C, and was approximated to be constant at all temperature ranges for this model.

The effective thermal conductivity of the membrane is 0.38W/m-K. The effective conductivity was estimated using properties at 65°C, and was approximated to be constant at all temperature ranges for this model.

### 7.3 Results and Discussion

The temperature uniformity of the membrane surfaces in contact with liquid water is an important parameter for the static test conditions, where water is not circulated. Interface temperatures were calculated by two-dimensional thermal model for cases where the membrane only was used and where the membrane was sandwiched between two diffusion media (DM). Figure 7-3 shows that, without diffusion media, there is significant temperature difference between channel and land area, which would result in ambiguity in interpretation of the data. However, the diffusion media significantly enhanced the uniformity of the membrane surface temperature. Additionally, the highly porous structure of diffusion media and the small land width (0.75 mm) enabled water transport through the whole surface cross-sectional area of membrane. Note that $\Delta T_{cell}$ (10°C) indicates temperature difference between cold and hot flow-field plates, while the membrane temperature difference is much lower than 1°C because the
highest thermal resistance is from the DM. As mentioned in the section of Method of Approach, hydrophilic diffusion media does not contribute water flow due to temperature difference, and membrane temperature difference is an important parameter for thermo-osmotic water flux in the membrane. Thus in the following figures, membrane temperature difference estimated from modeling is used instead of the controlled cell temperature difference.

As mentioned, temperature-driven water transport was not observed through SGL 10AA hydrophilic diffusion media. This result agrees with the literature that porous membrane with large, non-binding pores shows negligible thermo-osmotic water flux, due to negligible entropy change between bulk water and unbound water in the porous membrane [14]. From the fact that SGL 10AA does not have any temperature-driven flow, the thermo-osmotic water flux of the assembly was ascribed to the membrane. Thermo-osmotic measurement for each test case was conducted at least three times for repeatable data.

*Thermo-osmotic water flux in different membranes*

Figure 7-3: Effect of diffusion media on interfacial temperature profile for $T_{\text{cell, avg}}=65^\circ\text{C}$ and $\Delta T_{\text{cell}}=10^\circ\text{C}$ cases.
Figure 7-4 shows that thermo-osmotic water flux in the Nafion® 112 membrane (termed N112) increases linearly with temperature difference, and increases with membrane average temperature. The three sets of repeated data overlap so well that the data scatter is almost negligible. Error bars denoted estimation errors of membrane surface temperature difference of modeling. The estimation error was found less than 8 %, attributing to variation of effective thermal conductivities. Note that the water flux direction is from the cold to hot side, which agrees with the literature for Nafion® membranes [78, 51].

The thermo-osmotic water flux in Flemion® SH50 and Gore-Select® membranes also linearly increased with temperature difference and increased with membrane average temperature. The water flux direction was also from cold to hot direction.

Figure 7-4: Thermo-osmotic water flux of Nafion® 112 membrane.
Figure 7-5 shows thermo-osmotic water flux of three membranes at the average membrane temperature of 65°C. Flemion® membrane was found to be higher thermo-osmotic water flux than Nafion® membrane. Gore-Select® membrane had significantly higher water flux at the same temperature difference than other membranes because of higher temperature gradient resulting from thin thickness (18 µm for Gore-Select®, and 50 µm for Nafion® 112 and Flemion® SH50) and different membrane properties. It may result from variation errors of thermal conductivity or different composition and structures of membrane. It should be noted that water flux is proportional to temperature difference and inversely proportional to membrane thickness.

Water transport mechanism of thermo-osmosis may be the same as that of mass diffusion, as Figure 6 shows the same activation energy in both diffusion and thermo-osmosis; thus the higher mass diffusion, the higher thermo-osmosis. Membranes with lower equivalent weight (EW) have generally higher water diffusion because of more conductive and connected pathways. A thinner membrane also has higher mass diffusion flux. Although the measured flux is slightly affected by reinforcement type, the net direction of thermo-osmotic water flux was not affected by reinforcement, suggesting that the reinforcement acts as an inert barrier that only affects net path length and not the fundamental transport. For example, reinforced membranes (Flemion® SH50 and Gore-Select®) and non-reinforced Nafion® membrane had slightly different rates of flux, but all showed cold-to-hot behavior.

Even though very small temperature difference across the membrane, water flux is significant; for example, for average temperature of 65°C and difference of approximately 0.3°C in the Gore-Select® membrane, water flux is the equivalent amount of water produced at current density of 400mA/cm² in the PEFC. Thus thermo-osmotic water flows from the anode side to the cathode side because cathode side it typically hotter than the anode side, resulting in more flooding behaviors. At higher current operation of fuel cell, where the membrane temperature
difference across the membrane may be 1 or 2 °C or higher \cite{138,139}, thermo-osmotic water flux should be more important in water balance of fuel cell operation.

\begin{equation}
J_T = -D_T \nabla T
\end{equation}

where $D_T$ is the thermo-osmotic diffusivity, $\nabla T$ is the temperature gradient, and $J_T$ is the thermo-osmotic water flux. In mass diffusion, mass diffusivity is always positive, indicating mass flux by concentration gradient is from higher concentration to lower concentration. However, the thermo-osmotic diffusivity can be positive or negative, depending on membrane hydrophobicity. Water flux direction can be from higher to lower temperature (positive thermo-osmotic diffusivity), or from lower to higher temperature (negative thermo-osmotic diffusivity). It should be noted that negative water flux in this testing indicates negative thermo-osmotic diffusivity because the

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Figure 7-5: Comparison of thermo-osmotic water flux of Nafion\textsuperscript{®} 112, Gore-Select\textsuperscript{®} (18 µm thick), and Flemion\textsuperscript{®} SH50 membranes.
temperature gradient was positive in this experiment and analysis (see temperature boundary
conditions, Eq. 7.3 (a) and 7.3 (b)).

From the observation that thermo-osmotic water flux increases with the average
membrane temperature, all test data were recast by thermo-osmotic diffusivity versus reciprocal
temperature to explore the temperature dependency of thermo-osmotic water transport.
Experimental data for a given material set were collapsed into a single line shown in Fig. 7-6,
similar to temperature dependency of mass diffusivity. Thus thermo-osmotic diffusivity can be
expressed by:

\[ D_T = \frac{\Delta G_{act,T}}{RT} \exp\left(-\frac{\Delta G_{act,T}}{RT}\right) \]  [7.7]

\[ \log_{10}(D_T) = \log_{10}(D_T^0) - 0.4343 \frac{\Delta G_{act,T}}{R} \frac{1}{T} \]  [7.8]

where \( D_T^0 \) is reference thermo-osmotic diffusivity, and \( \Delta G_{act,T} \) is the thermo-osmotic activation
energy. Three membranes show almost identical slopes, indicating the same fundamental water
transport mechanism despite different reinforcement structures. The mass diffusivity of Nafion®
membrane can be expressed by [57]:

\[ D_{\lambda=4} = 1 \times 10^{-6} \exp\left\{ \frac{1}{303} \left( 2.563 - 0.33\lambda + 0.0264\lambda^2 - 0.000671\lambda^3 \right) \right\} \]  [7.9]

where \( \lambda \) is the number of water molecules per sulphonic acid site in the membrane. The
temperature dependency of mass diffusivity was calculated for the liquid-equilibrium condition,
\( \lambda = 22 \). Figure 7-6 shows that mass diffusion has an almost identical slope to the thermo-osmotic
water transport. This indicates that the driving force is different, but water transport mechanism
through the membrane may be the same. The presence of reinforcements and different EW affects
the net flux, but not the underlying physical mechanism.
From the slope and extrapolation in Fig. 6, empirical thermo-osmotic diffusivities for different membranes were drawn and are summarized in Table 4, which can be utilized by fuel cell modelers and design engineers.

**Figure 7-6:** Temperature dependency of thermo-osmotic diffusivity of different membranes and mass diffusivity of Nafion® membrane.

**Table 7-4:** Empirical thermo-osmotic diffusivity of different membranes.

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Empirical relations of thermo-osmotic diffusivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nafion®</td>
<td>$D_T \left{ \frac{kg}{msK} \right} = -\left[1.04 \pm 0.08\right] \times 10^{-5} e^{-\frac{2362 \pm 106}{T}}$</td>
</tr>
<tr>
<td>Thickness=50 µm</td>
<td></td>
</tr>
<tr>
<td>Flemion® SH50</td>
<td>$D_T \left{ \frac{kg}{msK} \right} = -\left[1.30 \pm 0.09\right] \times 10^{-5} e^{-\frac{2298 \pm 70}{T}}$</td>
</tr>
<tr>
<td>Thickness=50 µm</td>
<td></td>
</tr>
<tr>
<td>Gore-Select®</td>
<td>$D_T \left{ \frac{kg}{msK} \right} = -\left[1.66 \pm 0.15\right] \times 10^{-5} e^{-\frac{2297 \pm 36}{T}}$</td>
</tr>
<tr>
<td>Thickness=18 µm</td>
<td></td>
</tr>
</tbody>
</table>
Comparison of diffusion flux and thermo-osmotic flux

Figure 7-7 shows water flux by thermo-osmosis and mass diffusion. Water flux by thermo-osmosis of Gore-Select® membrane is denoted by black lines for two different cases (average membrane temperature of 65 and 80°C, with a temperature difference across the membrane, $\Delta T_{PEM} = 2^\circ C$). Mass diffusion flux was calculated using four different ranges of diffusivity considering the large variation of water diffusivity values in the literature [144]. For typical water content difference, 8 ~ 14, water flux by diffusion ranges from similar to ten times higher than thermo-osmosis, depending on the particular diffusivity value reference used. During fuel cell operation, the cathode side generally has a higher water content and higher temperature, indicating diffusion flux is generally from the cathode to anode, depending on inlet relative humidity conditions. Water flux by thermo-osmosis is therefore typically from the anode to cathode side. Thus, net water flux can be significantly reduced by thermo-osmosis, depending on the material properties of the DM and operating conditions.

![Figure 7-7: Comparison of diffusion flux and thermo-osmotic flux in the Gore-Select® membrane.](image_url)
Water transport by thermo-osmosis can not be neglected under fuel cell operating conditions of high current, or during shutdown or start-up transients. The temperature gradient across the membrane is high at the beginning of shutdown, but asymptotes to a negligible value as time elapses. This also indicates that the net flux of water across the MEA during operation can be dependent on the diffusion media based on temperature boundary conditions. Since the DM represents the major heat transfer resistance, the net water transport across the cell can be altered by selection of a DM with different thermal conductivity and thickness.

i. Importance of Complete Saturation on Net Flow Direction

Interestingly, the net water flux direction was reversed when hydrophobic diffusion media was used instead of hydrophilic diffusion media, or a catalyst layer was used on the membrane. If the gas phase is involved under a temperature gradient, the net water flux was observed to flow from hot to cold, indicating that a phase-change induced effect can dominate transport in these circumstances. When the membrane is sandwiched by hydrophobic diffusion media, the water content of membrane surface in the hot side is different from that in the cold surface. In the hot side, water evaporates, diffuses through the porous media, and then condenses on the membrane surface, resulting in increase of water content, whereas in the cold side, water on the membrane surface evaporates, diffuses via the PM, and condenses in the channel of the cold side, resulting in decrease of water content in the membrane. Water can transport from the hot to the cold side, resulting from concentration gradient. Net water flux in the membrane is determined by competing transport modes of thermo-osmosis (from the cold to the hot side) and diffusion flux. Diffusion flux can be affected by phase-change induced flow in the porous media. Even for very small temperature gradients, in the pure membrane only, flow is driven from the cold to hot locations, with a much weaker flux, in general, than the phase-change induced flow. It should be noted that we have also deduced Arrhenius expressions which describe this phase-change induced flow as a function of materials, average cell temperature, and temperature
gradient. Even for very small temperature gradients, in the pure membrane only, flow is driven from the cold to hot locations, with a much weaker flux, in general, than the phase-change induced flow. Study on the phase-change induced water flow is discussed in Chapter 8.

7.4 Conclusions

Direct thermo-osmotic water flux in different perfluorinated membranes (non-reinforced Nafion® 112 and two different reinforced membranes) was measured. Thermo-osmotic water flux was observed in all membranes, and the direction was from cold to hot side. The water flux was higher in the membranes with lower equivalent weight and increased with thinner membranes. The water flux was proportional to temperature gradient and increased with average temperature of membrane. The temperature dependency of thermo-osmotic diffusivity showed very repeatable Arrhenius behavior in all membranes. Activation energies are similar in different membranes, indicating a similar fundamental water transport mechanism, with some effects of transport path based on material properties such as EW and presence of reinforcement structures. From the Arrhenius plots, empirical thermo-osmotic water flux relations across the membrane were drawn, which can be used by modelers and design engineers to improve fidelity of existing calculations, and help to choose more appropriate material sets to achieve the desired water distribution and enhance durability.

The thermo-osmotic water flux has a similar order of magnitude to diffusion flux and should not be neglected in water balance calculations. The thermo-osmotic water flux can be important under real operating condition as well as during shutdown and startup, due to potentially high temperature gradients across the membrane electrode structures.
Chapter 8

Temperature-driven Water Transport: Phase-change Induced Water Flow

8.1 Introduction

Water transport by electro-osmotic drag, diffusion and hydraulic permeation in the polymer electrolyte membranes has been well explored \[58, 68, 69, 70, 71, 73, 75, 76, 155\]. Capillary and diffusion water transport in the diffusion media has also been well studied \[136, 137, 145, 147, 151\]. However, temperature-driven water transport modes, *thermo-osmosis in the membrane* and *phase-change induced flow* (also known as heat pipe effect, although this is technically not a heat pipe) *in the porous media* are not yet well explored. Temperature-driven water flow is potentially attractive because of the possibility of tailoring material properties to avoid flooding, or for non-parasitic water drainage during shutdown using naturally occurring temperature gradients within the stack \[48, 138, 139\].

As a first approximation, temperature-driven flow in the porous media (phase-change induced flow) can be treated as a gas-phase diffusion process induced by a thermodynamic saturation pressure gradient. However, temperature-driven flow in the membrane (thermo-osmosis) is a fundamentally different transport mode. When a membrane separates liquid water at different temperatures, water flows from hot to cold direction or vice versa, a process known as thermo-osmosis. The direction of water flow depends on the entropy difference between water in the membrane and external to the membrane; for example, water in a hydrophilic membrane can be considered to have a relatively ordered state compared to water existing outside the membrane. Therefore, unbound water transport from the cold to the hot side leads to an increase of total entropy, and is thus thermodynamically favored \[78\]. For hydrophobic membranes, water
typically flows from hot to cold direction, based on a similar entropy-based argument [52, 78].

Despite this established conventional understanding, disagreement in the literature on the direction and magnitude of water flux for different fuel cell materials and combinations of materials still exists, as summarized in Table 8-1.

Table 8-1: Summary of published studies of temperature gradient-driven flow in PEFCs.

<table>
<thead>
<tr>
<th>References</th>
<th>Materials</th>
<th>Observations</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kim et al. [146, 150]</td>
<td>Nafion® 112 Commercial reinforced perfluorinated membranes</td>
<td>$J = 3.3 \times 10^{-4} \text{kg/m}^2\text{s} @ T_{avg} = 65^\circ C$, $\Delta T = 0.28^\circ C$ for commercial reinforced membrane (18 µm thickness) Similar order of magnitude to mass diffusion Empirical thermo-osmosis flux relations Water flows from cold to hot side.</td>
</tr>
<tr>
<td>Villaluenga et al.[51]</td>
<td>Nafion® 117 (t=183 µm, EW=1100)</td>
<td>$J = 7.5 \times 10^{-4} \text{kg/m}^2\text{s} @ T_{avg} = 26.5^\circ C$, $\Delta T_b = 10^\circ C$ Water flows from cold to hot side.</td>
</tr>
<tr>
<td>Tasaka et al.[52]</td>
<td>Nafion® 417 (t=430 µm, EW=1613)</td>
<td>$J = 3.6 \times 10^{-5} \text{kg/m}^2\text{s} @ T_{avg} = 35^\circ C$, $\Delta T = 10^\circ C$ Water flows from cold to hot side.</td>
</tr>
<tr>
<td>Zaffou et al. [49, 50]</td>
<td>Nafion® 112 (t= 51 µm, EW=1100)</td>
<td>No water flow</td>
</tr>
<tr>
<td></td>
<td>PTFE-reinforced Nafion® 112</td>
<td>$J = 4.1 \times 10^{-4} \text{kg/m}^2\text{s} @ T_{avg} = 65^\circ C$, $\Delta T = 1^\circ C$ Water flows from hot to cold side.</td>
</tr>
<tr>
<td></td>
<td>Catalyst-coated Nafion® 112</td>
<td>No water flow</td>
</tr>
<tr>
<td></td>
<td>Catalyst-coated Gore-Select® (5510 MEA)</td>
<td>$J = 6.9 \times 10^{-4} \text{kg/m}^2\text{s} @ T_{avg} = 65^\circ C$, $\Delta T = 1^\circ C$ Water flows from hot to cold side.</td>
</tr>
<tr>
<td>Bradean et al. [48]</td>
<td>MEA (20 cell stack)</td>
<td>$J = 3.0 \times 10^{-4} \text{kg/m}^2\text{s}$ during cooling ($66^\circ C \rightarrow 33^\circ C$ (3 hours)) Water flows from hot to cold side.</td>
</tr>
<tr>
<td>Perry et al.[45, 46]</td>
<td>MEA (30 cell stack)</td>
<td>Water flows from hot to cold side. Freeze-damage of anode end cell</td>
</tr>
</tbody>
</table>
Kim and Mench [146, 150] observed that thermo-osmotic flux of water in three different commercial perfluorinated polymer electrolyte membranes flows from the cold to hot side of the membrane, and that reinforcement did not affect the flow direction. The net flux, however, was altered by the reinforcement structure. The water flux was higher in membranes with lower equivalent weight and decreased thickness. The water flux was proportional to temperature gradient and showed Arrhenius behavior with average temperature dependency, which agrees with literature [51, 52]. Results indicated that the thermo-osmotic water flux has a similar order of magnitude to mass diffusion flux and should not be neglected under high current or startup/shutdown operation. New empirical thermo-osmotic water flux relations were presented, which can be used by modelers and design engineers.

Villaluenga et al. [51] observed that water flows from the cold to hot side in the Nafion® 117 membrane, which agrees with Tasaka’s [51] observation in Nafion® 417. Water flux was proportional to temperature difference and increased with average membrane temperature. The temperature dependency of water flux showed Arrhenius behavior for Villaluenga et al. [51]. However, Zaffou et al. [49, 50] observed that there was hot to cold thermo-osmotic flow in the PTFE-reinforced membrane, but did not observe thermo-osmosis in the non-reinforced Nafion® membranes. Bradean et al. [48] and Perry et al. [45, 46] observed net water flux from hot to cold side in complete membrane electrode assemblies (MEA's) with diffusion media in a real fuel cell stack. It should be noted that Villaluega et al. [51] and Tasaka et al. [52, 78] used bare membranes, but Zaffou et al. [49, 50] used fuel cell fixtures where the membrane was sandwiched between highly porous diffusion media.

Temperature-driven flow during fuel cell operation, as well as at shutdown, can be important, but is still not completely understood. Kim and Mench [146, 150] observed net water

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1 In this work, we refer to MEA as a 3-layer CL | membrane | CL structure.
flux reversal in membranes when hydrophilic DM were replaced with hydrophobic DM. With fully saturated hydrophilic DM and membranes, the net flow was thermo-osmosis through the membrane from the cold to hot side. When hydrophobic DM or a catalyst layer was used with the membrane, the net flux under an imposed temperature gradient was reversed from the hot to cold side, and even with fully liquid filled flow channels. Clearly, the existence of some gas phase plays a key role in determining the net direction of water flux direction.

Contradictions regarding the net flow direction presented in the literature may come from the fact that fuel cell consists of materials with different hydrophobicity. Hydrophobicity prevents complete liquid phase saturation in the porous media (DM and CL), allowing vapor diffusion across a temperature gradient. Vapor diffusion always results in flow from higher saturation pressure (high temperature) to lower saturation pressure (low temperature), but thermo-osmotic water transport in a perfluorinated membrane flows from the cold to the hot side [51, 52, 146, 150].

Thus, the temperature gradient induced water transport in the fuel cell should be considered to be the net flux of phase-change induced flow in porous media and thermo-osmosis in the membrane. We also expect that the phase-change induced flow would be more dominant with increasing temperature, since the saturation pressure is a highly non-linear function of temperature.

Some inclusion of water transport in the DM by the phase-change induced flow based solely on thermodynamics has been implemented in non-isothermal models [139, 140], but temperature-driven flow in an individual fuel cell has not been definitively explored experimentally or numerically validated. This work is motivated by the need to understand and quantify water transport driven by temperature gradient in the fuel cell materials. Using an in-house fuel cell, phase-change induced flow was carefully quantified as a function of materials, average cell temperature, and temperature gradient. Water transport behavior under temperature
gradient was also confirmed and visualized using high resolution neutron radiography at the National Institute of Standards and Technology (NIST).

8.2 Method of Approach

The impact of hydrophobicity on water transport under a temperature gradient in fuel cell materials was explored using direct measurement of water flux as well as visualization by neutron radiography.

Direct Measurement of Water Flux

The test cell utilized was designed for direct measurement of water flux driven by temperature gradient, as well as for fuel cell testing (Fig. 8-1). The test setup consisted of two precisely temperature-controlled (accuracy ± 0.01 °C) refrigerated circulators (VWR International, USA, Model 1196D), the test fuel cell, a distilled water reservoir, a vacuum pump, 9 T-type thermocouples, 9 manual valves, and calibrated PFA tubing (Swagelok®, Tube size ¼ inch and wall thickness 0.062 inch). For precise temperature difference uniformity two separate coolant streams were circulated through the test cell coolant plates at maximum flow rate (22 \( ℓ / \text{min} \)) in the counter-flow direction. Three temperature sensors were inserted in the middle of each flow-field plate, located at the inlet, center and outlet positions with respect to the flow direction. These thermocouples (not shown in the Fig. 8-1) were used to control circulator temperatures, enabling proper boundary condition control. Two thermocouples (TC11 and TC21) were inserted in the T-junction of PFA tubing to monitor water temperature inside the tube. The other temperature sensor measured the ambient temperature. The valves and vacuum pump were used to fill water inside the test cell and remove air pockets. For example, after maintaining the test cell below – 750 mmHg with valves V12 and V22 opened and other valves closed, both sides of the test cell were filled by opening valves V14, V24, and V31. After the temperature of the
flow-field plate reached the desired experimental temperature, the water inside the tube was flushed using valve operations (open V31, V11, V21, V13, and V23, and close the others) to maintain the tube water temperature below 30°C, reducing evaporation loss of water in the PFA tubing to negligible levels. All valves except for V11 and V21 were closed for measurement of water flux.

As shown in Fig. 8-1 (b), the test cell consisted of two flow-field plates, two cooling plates, and two end plates. The flow-field plate is machined impregnated fuel cell grade graphite with 12 parallel channels (1 mm width and 0.6 mm depth) and 0.75 mm wide lands. The cell active area is 23.75 cm², with identical anode and cathode flow-fields. For sealing, flat fluorine rubber gaskets (width 2 mm and thickness 0.7 mm) were attached on the grooved surface in each
flow-field plate. The cooling plate consisted of gold-plated aluminum (thickness 20 mm) and Lexan® (thickness 5 mm). The surface with parallel cooling channels (2 mm depth and 3.1 mm width) was bonded by a Lexan® plate, serving as a thermal and electrical insulator. The surface temperature of gold-plate aluminum in contact with the flow-field plate was nearly uniform, providing a uniform thermal boundary condition. Stainless steel end plates (thickness 20 mm) were used to provide evenly distributed compression at contact pressures similar to those used in normal fuel cells (e.g. 1 - 1.5 MPa). To prevent localized over-compression, incompressible PTFE-coated fiberglass shims were inserted in the border area of flow-field plates. A fiberglass washer was also inserted for each bolt, ensuring thermal and electrical isolation.

The water transport rate was calculated by measuring the change of water volume in the cold and hot side calibrated tubes. The water volume in the tube was calibrated by weighing different lengths of water using an accurate balance (resolution 0.001g). Water transport by hydraulic pressure gradient was negligible, because the tubes in the hot and cold sides were configured symmetrically.

The impact of diffusion media hydrophobicity was investigated with Nafion® 112 (termed N112) and Gore-Select® reinforced membrane (t=18 µm) using SGL 10BB DM (5% PTFE and micro-porous layer (MPL)). The Gore-Select® reinforced membrane (termed R-PEM) has a lower equivalent weight than N112 membrane. The effect of the existence of catalyst layers was explored using Gore-Primea® 5710 series MEA (termed R-MEA) and hydrophilic SGL10AA DM (0% PTFE) as well as hydrophobic DM (SGL10BA (5% PTFE) and SGL10BB (5% PTFE and MPL)). To investigate the effect of membrane reinforcement, an MEA with non-reinforced membrane (termed NR-MEA) was tested. Note that NR-MEA has the identical catalyst layers and equivalent weight to Gore-Primea® 5710 series MEA. The material properties of tested cases are summarized in Table 8-2.
For membrane only test cases, the assembled cell was soaked at 95°C for 9 hours prior to measurement, ensuring the membrane was fully saturated and activated. For 3-layer MEA cases, the assembled cell was electrochemically activated at 65°C and ambient pressure with fully humidified hydrogen/air by repeated cycling between 0.4V and open circuit voltage (OCV) for 2 hours. Measurements were conducted with liquid filled and evacuated flow channels at average cell temperatures of 80, 65, 45 and 30°C with a temperature difference between flow-field plates of 10, 5, and 3°C. Note that for Gore-Primea® 5710 series MEA with SGL 10BB test case, water flux was measured at the average cell temperature of 85, 65, 45, 25 and 10°C. Each test condition was repeated 3 times, and the test duration was sufficiently long to minimize the measurement error and assure a steady state had been achieved.

Table 8-2: Summary of materials used in this work.

<table>
<thead>
<tr>
<th>Membranes / MEA Combinations</th>
<th>DM</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Membrane</strong></td>
<td></td>
</tr>
<tr>
<td>Nafion® 112 (N112)</td>
<td>EW=1100, t=51 µm</td>
</tr>
<tr>
<td>Gore-Select® reinforced membrane (R-PEM)</td>
<td>EW&lt;1000 [113] t=18 µm</td>
</tr>
<tr>
<td><strong>MEA</strong></td>
<td></td>
</tr>
<tr>
<td>Gore-Primea® 5710 series MEA (R-MEA)</td>
<td>Pt 0.4mg/cm² electrode Gore-Select® membrane (t=18 µm)</td>
</tr>
<tr>
<td>NR-MEA</td>
<td>Pt 0.4mg/cm² electrode Non-reinforced membrane (t=18 µm)</td>
</tr>
</tbody>
</table>

SGL10AA [128]: no PTFE content, 0.39mm thickness, 88% porosity
SGL10BA [128]: 5% PTFE, 0.40mm thickness, 88% porosity
SGL10BB [128]: 5% PTFE, MPL(23% PTFE +carbon black), 420 µm thickness

Visualization by Neutron Radiography

The water behavior under temperature gradient was visualized using neutron radiography at the National Institute of Standards and Technology (NIST), where a small field-of-view (2.5 cm²) high resolution (~ 25 µm) neutron imaging system exists. Figure 8-2 shows the schematic of
the test cell, flow-field plates, and visualized zones. The original test cell used in [143] was modified with external coolant flow-field plates and fed by separate coolant baths, to enable temperatures of both flow-field plates to be independently controlled. The same cooling plates and compression end plates used in the direct temperature-driven water flux experiment shown in Fig. 8-1 were used. An additional temperature sensing hole was machined in the center of flow-field plate, away from the contact surface with DM. The flow-field plate has a single serpentine channel (1 mm width and 1 mm depth) with 1 mm land, and has the identical design in both the anode and cathode. The details of high resolution radiography on the unmodified test cell are described in the literature [143].

Figure 8-2: Schematics of test cell used for neutron radiography: (a) flow-field plate [143], (b) assembled modified test cell with independent coolant plates, and (c) side-on-view for visualization, where the left (anode) side of channels was filled with liquid, and the right (cathode) side was initially purged.
The tested materials were Gore-Primea® 5710 series MEAs with SGL 10AA (0% PTFE) and SGL 10BB (5% PTFE and MPL). Prior to testing, the test cell was electrochemically activated by repeated cycling between 0.4V and OCV for 2 hours at fully humidified conditions. After activation, the anode side was filled with liquid water. After the flow-field temperature reached target temperature, the cathode side was dry-purged for one minute by 857 sccm air to remove water inside the channel. An image was recorded every minute (i.e., consecutive images of the fuel cell were taken which were each integrated over one minute), to try to capture water movement. Note that water reservoir was located 1.2 m above the test cell, indicating the anode side has higher pressure (~12 kPa) than the cathode side, which led to leakage flow from the liquid-filled to dry side under some conditions, described below.

8.3 Results and Discussion

**Scale Analysis of Water Transport Mode in Phase-change Induced Flow**

A scale analysis and water balance was conducted on 1D membrane/hydrophobic DM assembly test case shown in Fig. 8-3, to investigate the major parameters in the phase–change induced water flow. The model cell consists of the membrane sandwiched between diffusion media, which are contact with liquid with different temperatures.

The assumptions are:

- The local vapor pressure for unsaturated pores is assumed to be the saturated vapor pressure at the local temperature. Thus the gradient of diffusion flux driven by vapor pressure difference in the control volume is net water accumulated by phase change.
- Heat transfer by the advection is negligible for gas phase and liquid phase. The Peclet number was calculated to be very small to justify this assumption.
An order of magnitude analysis was conducted by considering conservation laws of mass and energy in the porous media as well as membrane:

1) Mass conservation in the porous media:

\[
\rho_w \varepsilon \frac{\partial s_w}{\partial t} = -\nabla \cdot \bar{J}_{D,v} - \nabla \cdot \bar{J}_c
\]

where \( \rho_w, \varepsilon, s_w, \bar{J}_{D,v}, \) and \( \bar{J}_c, \) respectively, denote water density, porosity, saturation, vapor diffusion mass flux, and water flux by capillary force. Vapor diffusion mass flux and water flux by capillary action is defined in Eq. 8.2 and 8.3:

\[
\bar{J}_{D,v} = -D_{eff} \frac{dP_{sat}(T)}{dT} \frac{R_v}{T} \nabla T = -D_{fT} \nabla T
\]
where \( D_{v}^{\text{eff}}, R_{v}, P_{\text{sat}}, \) and \( D_{fg} \), respectively, denote effective water vapor diffusivity, vapor gas constant, saturation pressure, and equivalent diffusion coefficient of water vapor in the gas phase resulting from phase-change induced flow.

\[
\bar{J}_c = -\rho_w k_{rw} \frac{k_w}{\mu_w} \nabla p_w = -\rho_w k_{rw} \frac{k_w}{\mu_w} \nabla p_c \tag{8.3}
\]

where \( k_{rw}, k_w, \mu_w, p_w, \) and \( p_c \), respectively, denote relative water permeability, water permeability, water viscosity, water pressure and capillary pressure.

2) Mass conservation in the membrane:

\[
\frac{\rho_{\text{PEM}} M_w}{EW} \frac{\partial \lambda}{\partial t} = -\nabla \cdot \bar{J}_{D,\text{PEM}} - \nabla \cdot \bar{J}_{TO} \tag{8.4}
\]

where \( \rho_{\text{PEM}}, M_w, EW, \lambda, \bar{J}_{D,\text{PEM}}, \) and \( \bar{J}_{TO} \), respectively, denote density of dry membrane, water molecular weight, equivalent weight of the membrane, water content (the number of water molecules per sulphonic acid site), water diffusion flux, and thermo-osmotic water flux. Water diffusion flux and thermo-osmotic flux in the membrane are defined by Eq. 8.5 and 8.6:

\[
\bar{J}_{D,\text{PEM}} = -D_\lambda \frac{M_w \rho_{\text{PEM}}}{EW} \nabla \lambda \tag{8.5}
\]

where \( D_\lambda \) is water diffusivity in the membrane and is a function of water content and temperature.

\[
\bar{J}_{TO} = -D_{TO} \nabla T \tag{8.6}
\]

where \( D_{TO} \) is thermo-osmotic diffusivity in the membrane and is a function of temperature.

3) Energy conservation in the porous media:

\[
\frac{\rho C_p}{\partial T}{\partial T}{\partial t} = \nabla \cdot \kappa \nabla T + q_{\text{gen}} \tag{8.7}
\]
where $\overline{\rho C_p}$, $\kappa$, and $q_{gen}$, respectively, denote volume average thermal mass of porous media, thermal conductivity and heat generation per unit volume. The heat generation per unit volume can be expressed by phase-change term, and the energy equation can be arranged by:

$$\frac{\overline{\rho C_p}}{\partial t} = \nabla \cdot \kappa \nabla T + \nabla \cdot h_{fg} D_{fg} \nabla T
$$

$$= \nabla \left[ (\kappa + \kappa_{eqv}(T)) \nabla T \right]
$$

$$= \nabla \left[ \kappa_{tot}(T) \nabla T \right] \tag{8.8}$$

where $h_{fg}$, $\kappa_{eqv}$, and $\kappa_{tot}$, respectively, denote heat of vaporization per unit mass, conduction equivalent thermal conductivity resulting from phase-change induced flow, and total thermal conductivity. Note that this energy equation in the porous media was approximated by using equivalent heat conduction thermal conductivity from phase change. Equivalent thermal conductivity, $k_{eqv}$, is defined as:

$$k_{eqv} = h_{fg} D_{fg} = h_{fg} \frac{D_{eff}}{R_v} \frac{d P_{sat}(T)}{dT} \tag{8.9}$$

Equivalent thermal conductivity from phase change can be calculated as a function of temperature by using typical tortuosity ($\tau \approx 1.5$), vapor diffusivity relations (Eq. 8.12 and Eq. 8.13), and $\frac{P_{sat}(T)}{T}$ relations with temperature. Instead of coupled mass (flow) equation and energy equation, decoupled energy equation can be used to estimate the temperature distribution.

4) Energy conservation in the membrane:

$$\frac{\overline{\rho C_p}}{\partial t} = \nabla \cdot \kappa \nabla T \tag{8.10}$$

where $\overline{\rho C_p}$ and $\kappa$ are the volume average thermal mass and thermal conductivity of membrane, respectively.
Liquid water is filled in both anode and cathode channels and the temperature boundary conditions are:

\[ T = T_H \quad \text{at} \quad x = 0 \quad \text{[8.11a]} \]
\[ T = T_C \quad \text{at} \quad x = l \quad \text{[8.11b]} \]

As shown in Fig. 8-3, in the hot side (left side of PEM), water vapor condenses inside the DM and on the surface of the membrane, increasing water content of membrane and liquid water saturation in the DM. In the cold side, water in the membrane evaporates and condenses inside the DM or on the flow-field plate surface. Water saturation increase in the pores of the hydrophobic DM increases capillary pressure, driving liquid water toward locations of lower pressure (e.g. larger hydrophobic pores or hydrophilic locations). To estimate the maximum water flux by phase change, the water flux by vapor diffusion in the DM and water flux in the membrane were estimated by Eq. 8.2, Eq. 8.5, and Eq. 8.6.

From Eq. 8.2, vapor diffusion flux in the DM is proportional to temperature gradient and equivalent vapor diffusivity. The equivalent vapor diffusivity linearly increases with effective vapor diffusivity and is a function of saturation pressure change with temperature. The vapor diffusivity decreases with liquid saturation and tortuous path in the diffusion media [126]. In this analysis, which estimates the maximum vapor diffusion flux, liquid saturation was assumed to be zero. Thus, the effective diffusivity in the diffusion media can be approximated by [126]:

\[ D_v^{\text{eff}} = \frac{D_v}{\tau} \quad \text{[8.12]} \]

where \( \tau \) is tortuosity. Pore structures in the DM increase diffusion path, decreasing effective diffusivity by a factor of tortuosity. Typical tortuosity in the DM is 1.5. Vapor diffusivity in the air, \( D_v \), is a function of temperature and pressure, expressed by [148]:

\[ D_v = D_{v_0} \left( \frac{T}{T_o} \right)^n \left( \frac{P_o}{P} \right) \quad \text{[8.13]} \]
where $D_{v0}$ is the diffusivity at absolute temperature $T_0$ and pressure $p_0$. $D_{v0}$ is $0.226 \pm 0.003 \times 10^{-4}$ m$^2$/s at 273.15K and 1 bar, and $n$ is 1.81. Vapor diffusivity increases almost linearly with temperature in the typical PEFC operation ranges (20 ~ 80°C). Saturation pressure and the derivative of $P_{sat}/T$ with temperature increase nonlinearly with temperature.

Thus, phase-change induced flow in the DM can be more important at high temperatures, above 50°C, and can be strongly affected by the effective diffusivity. It should be noted that effective vapor diffusivity has some variation and can be affected by saturation and material property (porosity and hydrophobicity) of diffusion media.

To estimate water flux by phase-change, the temperature gradient in the DM was estimated by an anisotropic thermal model in the assembly set of Gore-Select® membrane sandwiched between SGL 10BB DM, discussed in Ref. [150]. Total thermal conductivity, sum of phase-change equivalent thermal conductivity (0.33 and 0.6 W/m-K for $T_{cell, avg} = 65$ and 80°C, respectively) and intrinsic material thermal conductivity was used for this thermal model [150]. In the case of steady state with a cell temperature difference of 10°C and a cell average temperature of 65°C, a 2.9~3°C, < 0.5°C, and 1.7~1.8°C temperature drop occurs in each DM, membrane, and each flow-field and water inside the channel, respectively.

Figure 8-4 (a) shows that the estimated water flux by phase-change in the DM increases sharply with temperature, indicating that phase-change induced flow is significant in the high temperature region and is also strongly affected by the effective diffusivity. For typical effective diffusivity relation expressed by Eq. 8.12 and at average cell temperature of 65°C, the estimated water flux is about 0.0015 kg/m$^2$-s, which is a similar order of magnitude observed in measurement (see Fig. 8-5). Use of a lower effective diffusivity represents the realistic effect of increased effective tortuosity from liquid saturation.
Water diffusivity in the membrane is dependent on water content, temperature, and materials. Water diffusivity in Gore-Select® membrane was observed to be about 50% of that in Nafion® membrane [144]. Diffusivity does not change significantly for water content ($\lambda$) between 8 and 19, where ionic conductivity does not change significantly. Water diffusivities of N112 and R-PEM membranes at can be approximately by $2.87 \times 10^{-10}$ and $1.44 \times 10^{-10}$ m$^2$/s, respectively for water content between 8 and 19 [144]. Figure 8-4 (b) shows estimated diffusion water flux in both membranes at average temperature of 65°C as well as estimated net water flux, which is a sum of thermo-osmosis and mass diffusion water flux. Thermo-osmotic water flux is from the cold to the hot side, the opposite direction to mass diffusion. Thermo-osmotic water flux was estimated by empirical relations [146, 150], and is 0.00024 and 0.00047 kg/m$^2$·s for Nafion® 112 and Gore-Select® membranes, respectively.

Diffusion water flux in the membrane and phase-change induced water flux in the diffusion media have a similar order of magnitude. In normal situations it appears neither mode is dominant, and both modes contribute to the net water flux, because there are some variations in the effective vapor diffusivity with saturation ($s_w$) in the DM and CL as well as water diffusivity with water content ($\lambda$) in the membrane. However, the effective vapor diffusivity, membrane diffusivity, average cell temperature, as well as temperature gradient play an important role in parameters in the phase-change induced flow. Water flux can be engineered by tailoring thermal and material properties to suit the desired conditions.
Direct experimental measurement

Figure 8-5 shows measured water flux through the Nafion® membrane without a catalyst layer sandwiched between hydrophobic DM (SGL10BB) or hydrophilic DM (SGL10AA). The net water flux in the assembly with hydrophobic DM and membrane was proportional to the
temperature difference, and the flux amount increased with cell average temperature, as in the hydrophilic DM and membrane assembly. However, the net water flux direction was instead from hot-to-cold direction and the amount of water flux increased by nearly 7 times compared to that of the completely liquid saturated hydrophilic DM and membrane assembly case. It should be noted that the negative value of water flux was chosen arbitrarily, and represents water flow from the cold to hot side.

Figure 8-5: Effect of hydrophobicity of DM on temperature-driven water flux through Nafion® 112 membrane at various average cell temperatures.

For cases with hydrophobic DM, some gas phase saturation in the micro-porous layer (MPL) of SGL10BB contact with membrane exists due to very high capillary pressure, even when the water was filled with a vacuum. As discussed in Chapter 7, Kim and Mench observed negligible water flux through fully saturated hydrophilic DM (SGL10AA) under temperature
gradient, and water flow from cold to hot in the Nafion® 112 membrane. Contrary to hydrophilic DM, in the hydrophobic DM (SGL 10BB), water can evaporate at the higher temperature side, diffuse through unsaturated void volume, and condense on the cold side of the unsaturated pore. For hydrophobic DM and membrane assembly cases, the water transport mode by phase-change induced flow dominates compared to thermo-osmosis in the membrane, which is in the opposite direction.

The Gore-Select® reinforced membrane (R-PEM) without catalyst layer was also observed to have similar behavior. Figure 8-6 shows water flux of Gore-Select® reinforced membrane at 45 and 65°C. Surrounded by hydrophilic DM, water flux of Gore-Select® reinforced membrane was almost twice that of Nafion® 112 membrane at 45 and 65°C. However, sandwiched by hydrophobic DM (SGL 10BB), the Gore-Select® membrane had only 8.5% and 23.5% higher water flux than a similarly situated N112 membrane at 45 and 65°C, respectively. Even if Gore-Select® reinforced membrane has higher thermo-osmotic water flux to the hot side compared to N112, the overall net water flux by phase change was observed to be higher toward the cold side for the Gore-Select® membrane case. This is because the temperature difference across the membrane is small (~0.4°C), leading to small thermo-osmosis, and the diffusion flux in the membrane is non-limiting and high because of significant phase-change induced flow in the diffusion media. As shown in Fig. 8-4 (b), assuming the same vapor-phase water flux in the DM in both Gore-Select® membrane and N112 membrane cases, diffusion flux in the membrane is dominant, and the Gore-Select® membrane has a higher diffusion flux.
The effect of existence of catalyst layers, hydrophobicity of DM, MPL, and non-reinforcement of membrane on water flux was summarized in Table 8-3. The existence of a catalyst layer also results in gas-phase voids, and a net phase-change induced water flux direction toward the cold side, even if the hydrophilic DM (SGL10AA) were used to sandwich the 3-layer MEA. As seen in the activation plot (Fig. 8-8), the slope was similar to other hydrophobic DM cases, indicating water transport mode is dominated by the phase-change induced flow in these situations. The mixed wettability in the catalyst layers creates a gas phase boundary between membrane and porous media (catalyst layer). However, the phase-change induced flow was significantly lower than hydrophobic DM (SGL10BB) with a bare membrane. This is explained by a result of the low effective vapor diffusivity (due to postulated low unsaturated void volume) in the catalyst layer and very thin profile with low temperature gradient to induce flow.

Figure 8-6: Comparison of Gore-Select® reinforced membrane (R-PEM, 18µm) and non-reinforced (Nafion® 112) membranes with different hydrophobic DM at average cell temperatures of 65 and 45°C.
Nevertheless, it is interesting to see that even the catalyst layer contributes to net flow, despite its thickness, and should not be ignored in analysis.

Table 8-3: Comparison of temperature-driven flow at average cell temperature of 65°C in different combination of MEAs and DM.

<table>
<thead>
<tr>
<th>PEM/MEA</th>
<th>DM</th>
<th>Water flux, J (kg/m²-s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>R-PEM (Gore-Select 18 µm thick)</td>
<td>SGL 10AA</td>
<td>J = - 3.502 x 10⁻⁵ ΔT&lt;sub&gt;cell&lt;/sub&gt;</td>
</tr>
<tr>
<td>R-MEA (Gore Primea 5710 series)</td>
<td>SGL 10AA</td>
<td>J = 4.351 x 10⁻⁵ ΔT&lt;sub&gt;cell&lt;/sub&gt;</td>
</tr>
<tr>
<td>R-MEA (Gore Primea 5710 series)</td>
<td>SGL 10BA</td>
<td>J = 7.311 x 10⁻⁵ ΔT&lt;sub&gt;cell&lt;/sub&gt;</td>
</tr>
<tr>
<td>R-MEA (Gore Primea 5710 series)</td>
<td>SGL 10BB</td>
<td>J = 1.486 x 10⁻⁴ ΔT&lt;sub&gt;cell&lt;/sub&gt;</td>
</tr>
<tr>
<td>NR-MEA</td>
<td>SGL 10AA</td>
<td>J = 5.658 x 10⁻⁵ ΔT&lt;sub&gt;cell&lt;/sub&gt;</td>
</tr>
<tr>
<td>NR-MEA</td>
<td>SGL 10BB</td>
<td>J = 1.659 x 10⁻⁴ ΔT&lt;sub&gt;cell&lt;/sub&gt;</td>
</tr>
</tbody>
</table>

From Table 8-3, effect of extent of hydrophobicity on water transport rate shows that water flows from hot to cold side for all cases with hydrophobicity attributable to catalyst layers or DM. From the comparison of water flux in the SGL10BB and 10BA (no MPL) test cases, the MPL layer was observed to have a significant role in water transport rate under temperature gradient. Hydrophobic DM increased water transport rate significantly compared to the 3-layer MEA with hydrophilic DM. There is a phase-change induced flow across the gas voids in the catalyst layer, MPL, and main DM. Overall, the water transport was dominated by the phase-change induced flow in the diffusion media. The difference of water transport rate can be attributed to the availability of void space in the porous media and temperature gradient. SGL 10BB is made by coating mixture of carbon black and PTFE on the one side of SGL 10BA. The MPL thickness is approximately 60–80µm and 23% PTFE content and small pore size, resulting in very high capillary pressure and very low liquid saturation compared to 5% PTFE coated SGL10BA [136]. The MPL layer has very low liquid saturation and high void space for water
vapor diffusion, resulting in a higher water vapor diffusion rate. Higher water saturation in the DM SGL 10BA can reduce effective water vapor diffusivity, leading to decreasing water flux. It was also observed that water flux in the MEA with SGL10AA case had the highest water flux when MEA and DM are in a dry state at the initial condition. However, as time elapsed, the water flux to the cold side decreased to the steady value as water saturation in the DM (SGL10AA) increased.

From Table 8-3, the MEA with non-reinforced membrane (NR-MEA) was observed to have slightly higher net water flux with both hydrophilic and hydrophobic DM than the reinforced membrane. It is expected that non-reinforced membrane has higher water diffusivity than reinforced membrane because non-reinforced membrane has higher water passage than reinforced part. From this observation, net water flux can be affected by diffusion mode in the membrane and the vapor diffusion rate in the unsaturated pores. It should be noted that catalyst layers and ionomers in the membrane are identical for both types of MEA.

Figure 8-7 shows the temperature-driven water flux of R-MEA sandwiched between two SGL10BB DM, which is a typical combination of fuel cell. Within the measured temperature ranges, water flows from hot to cold side, as a result of phase-change induced flow across the unsaturated regions of the CL, MPL, and DM, and shows linear relationships with temperature difference.
Figure 8-8 shows plots of the effective temperature-driven mass diffusivity ($D_{\text{eff},r}$), defined as water flux per temperature gradient ($|\bar{J}_r| / \frac{dT}{dx}$), versus reciprocal of average cell temperature. Test data for a particular material set were collapsed into a single line on the log scale plot, and the slope is constant, which can be considered as activation energy in an Arrhenius rate law expression. Arrhenius rate expressions for different material sets (thermo-osmosis and phase-change dominant induced flow) are also shown in Fig. 8-8. Test cases with hydrophobicity ascribed to CL or DM were observed to have similar activation energy and to be less sensitive to materials, MEA or membrane. However, between thermo-osmotic and phase-change induced flow, the slope (e.g. activation energy) was significantly different, indicating that the fundamental transport mechanism is different between the two modes of temperature-driven transport. Phase-
change induced flow is a net flow of thermo-osmosis and diffusion in the membrane, vapor diffusion in the porous media, and phase change in the porous media or interfaces.

Figure 8-9: Comparison of phase-change induced flow and thermo-osmotic diffusivity of different materials.

If any gas phase and liquid water coexist in the fuel cell materials (typically in DM, CL or MPL) and there is a temperature gradient, water transports by phase-change induced flow through porous media. This is a normal case for fuel cell operation. Figure 8-9 (a) shows
schematic water transport modes and water distribution of actual fuel cell operation. Cathode catalyst layer is hottest and flow-field plates are colder, inducing phase change flow towards flow-field plates through the porous media (water can also transport by capillary flow). In the membrane, thermo-osmotic and electro-osmotic water flows from the anode to cathode, contrary to diffusion flux. Thermo-osmotic water flux is proportional to temperature gradient, and for Gore-Select® (18µm thick) membrane thermo-osmotic water flux is equivalent to product water at 400 mA/cm² for the membrane temperature difference of 0.3°C [150]. At high current operation, thermo-osmotic water flux can be more important because membrane temperature difference may be over 1°C. The importance of thermo-osmotic water transport is also strongly dependent on membrane water diffusivity [150]. Schematic temperature distribution shown in Fig. 8-9 (a) can be applied to all cells in a fuel cell stack, while coolant is circulated through all flow-field plates. During the shutdown, center cells in the fuel cell stack has also similar temperature profile shown in Fig. 8-9 (a), but anode and cathode end cells have heat flow toward end plate as shown in Fig. 8-9 (b). In the anode end cell, liquid water can accumulate in the cathode catalyst layers, resulting in damage in the frozen condition [45, 46].

For this direct measurement of water flux (simulated phase-change induced flow testing), both anode and cathode channels were fully saturated with liquid water and the DM had some saturation (≈ 1 for untreated SGL 10AA case), as shown in the schematic diagram of Fig. 8-3. In this experimental setup (simulated heat pipe testing) applying a temperature difference across the cell, most of the temperature drop occurs in the DM, based on the analysis of two-dimensional anisotropic thermal model [146, 150]. For example, for 10°C cell temperature difference, the temperature difference across the membrane was computed to be less than 0.5°C (0.47 and 0.4 °C for T_{cell, avg} = 80 and 65°C, respectively), resulting in water flux (less than 0.0007 kg/m²·s) in the
hot direction\cite{146, 150}. This flux amount is approximately 30\% of the measured net flux (hot to cold direction). Thus, mass diffusion in the membrane is dominant compared to thermo-osmosis.

The differences between this simulated phase-change induced flow testing and actual fuel cells are described in Table 8-4. While infinite heat and water source (energy and mass source for evaporation) and heat sink are used, the heat source (heat generation by current) and heat sink (cooling) are finite in real fuel cell. Thus, water transport by phase-change induced flow in the...
real application is important in high current operation because of the available heat source. Additionally, in the high current operation, temperature difference in the membrane can also be higher than 1 °C [138, 139], driving water from the anode (cold) to the cathode (hot) side via thermo-osmosis. This corresponds to an equivalent water production at approximately 1.1 A/cm [150]. In addition to transported water to the cathode side via electro-osmotic drag, thermo-osmosis can significantly increase water amount in the cathode side. However, higher temperature at the cathode can significantly enhance water removal away from the cathode through the diffusion media via phase-change induced flow. Note that thermo-osmotic water flux can be significantly reduced due to insufficient liquid water in the anode side, and higher water content in the cathode side can also enhance the back-diffusion. In total, thermo-osmosis, electro-osmosis, back-diffusion and phase-change induced flow should be considered for water balance in fuel cell. Thermo-osmosis and phase-change induced flow can also be important at localized high current regions because of high temperature gradient resulting from local ohmic heating. Note that phase-change induced flow may not occur under dry or low humid operation because of no availability of liquid water source.

Temperature-driven flow can be very important in initial stage of shutdown because of high average cell temperature as well as high temperature difference in the membrane. As time elapses during the shutdown, thermo-osmotic water flux is reduced to negligible levels. In this case, the phase-change induced flow becomes the major water transport mode. However, phase-change induced flow also decreases with decreasing temperature, since saturation pressure is significantly reduced with temperature, especially below 50°C.
Experimental visualization

Neutron images were taken every minute for thirty minutes under conditions of different temperature gradients and material sets. Two main material sets were used: A R-MEA with a non-PTFE treated gas diffusion layer (SGL10AA) with no MPL on the anode and cathode sides, and a diffusion layer set with 5% PTFE and a highly hydrophobic MPL. For cases with the non-PTFE DM set, tests with negligible temperature gradient (≈ 0°C) revealed a slow leakage of water from the liquid to gas sides (See Fig. 8-10) via the static pressure head of liquid in the channel, as well as capillary wicking. When the liquid side was colder, however, the phase-change induced flow reversed and prevented the leakage. When the gas-phase side was colder, the flow from hot to cold was augmented by the phase-change induced flow, and the gas phase side filled much more quickly.

When the DM were switched to a hydrophobic set with MPL, the breakthrough pressure of the DM was increased, and the gravity-induced leakage of water from the anode to cathode side under a negligible temperature gradient (≈ 0°C) condition was completely prevented (Fig. 8-
However, when the initially gas-phase side of the cell was colder, the channels were filled very quickly by the phase-change induced flow. In all cases in which the gas-side of the assembly was colder, phase-change induced flow dominated, and the net flux was to the cold side.

Figure 8-10: Visualized water transport behavior of MEA with hydrophilic DM test set under different temperature gradients.

Figure 8-11: Visualized water transport behavior of MEA with hydrophobic DM test set under different temperature gradients.
The modes of temperature-driven transport in PEFCs can be summarized in Table 8-5. In the pure membrane only, flow is driven from the cold to hot locations. In the porous media with incomplete liquid saturation, the phase-change induced flow is dominant, even for very small temperature gradients and thicknesses. Under high current operation as well as the initial stage of shutdown, thermo-osmosis in the membrane should not be neglected. However, at low current as well as most of shutdown periods, thermo-osmotic flux in the membrane can be neglected, and phase-change induced flow is dominant.

Table 8-5: Differences between thermo-osmosis and phase-change induced flow.

<table>
<thead>
<tr>
<th>Transport mode</th>
<th>Thermo-osmosis</th>
<th>Phase-change induced flow</th>
</tr>
</thead>
<tbody>
<tr>
<td>Materials</td>
<td>Membrane</td>
<td>Porous media (CL or DM)</td>
</tr>
<tr>
<td>Driving force</td>
<td>Entropy change between liquid out of membrane and in membrane</td>
<td>Gradient of saturation pressure with temperature</td>
</tr>
<tr>
<td>Flux direction</td>
<td>Hot-to-cold or cold-to-hot direction, depending on membrane properties; typically for hydrophilic membrane, cold to hot direction.</td>
<td>Always hot-to-cold direction</td>
</tr>
</tbody>
</table>

![Schematic](image)
8.4 Conclusions

Temperature dependent flow in PEFCs was identified to occur in two primary modes: 1) Thermo-osmosis in the pure membrane only, and 2) phase-change induced flow which occurs when there is any gas phase and a temperature gradient in the CL, MPL, or main DM. Both modes are precisely and conveniently fit by Arrhenius expressions with different activation energy, indicating water transport under the phase-change induced mode is fundamentally different than the thermo-osmotic flow in membranes. Although the slope was not affected, the absolute value of the phase-change induced flow was affected by average membrane temperature, temperature gradient, and porous media properties.

Gas phase saturation is a key controlling parameter to determine the water transport mechanism driven by temperature gradient. If some gas phase exists in the CL, MPL, and DM, the phase-change induced water transport was dominant, and the net water flux was observed from the hot to cold side. The existence of catalyst layers and PTFE-coated DM results in incomplete liquid saturation in the fuel cell porous media. In this normal operating case (incomplete saturation), the phase-change induced water transport mode is dominant. Neutron radiography confirmed and visualized the phase-change induced water flow from hot to cold locations in PEFCs with incomplete saturation of porous media.

Thermo-osmotic water transport, showing water flux on the cold-to-hot direction, can be more important when fuel cell is operated in the high current as well as initial stage of shutdown. The importance of thermo-osmotic water transport is strongly dependent on membrane water diffusivity.

Water balance in fuel cells can be engineered by controlling thermal and material properties. Incorporation of thermo-osmosis and evaporative flow into modeling is critical to ensure accurate results.
Chapter 9
Conclusions and Future Work

Physical damage modes of PEFC materials subject to freezing were identified: 1) PEM|CL interfacial delamination, 2) CL|DM interfacial delamination, 3) pore level damage in the porous media (CL and DM). Material selection and design guidelines for freeze-tolerance were proposed. A two-dimensional anisotropic current disruption model has been developed to quantify effect of interfacial delamination on performance. Temperature-driven water transport modes: 1) thermo-osmosis in membrane, 2) phase-change induced water flow in the porous media, in PEFC materials were explored, due to potential to utilize natural water drainage during shutdown to mitigate freeze-damage and to enhance cold start. The conclusions drawn are based on the experimental results obtained in this program.

9.1 Conclusions

The PEFC is a promising alternative power source for future clean energy, but still has technical barriers for commercialization: 1) cost, 2) durability, and 3) rapid cold startup without damage. The overall objective of this work is to elucidate freeze-damage modes of fuel cell materials and determine plausible mitigation methods in terms of materials as well as operation.

In this work, to identify physical damage modes of PEFC materials and material design criteria for freeze-tolerance, micro-structure effects of MEAs and DM were investigated in the worst case conditions (fuel cell in the immersed liquid water), which may occur in the local areas of fuel cell when proper shutdown is not performed. Damage modes of interfacial delamination: 1) between catalyst layer and membrane, 2) catalyst layer and diffusion media, were identified.
The membrane electrode assemblies were found to be a source of water that can damage the catalyst layers under freeze/thaw conditions. Damage was found to occur almost exclusively under the channel, and not under the land (the graphite that touches the diffusion media). Conceptually, the best material to mitigate freeze-damage is a crack free virgin catalyst layer on a reinforced membrane that is as thin as possible, protected by a stiff diffusion media. Pressure uniformity of the diffusion media onto the catalyst layer was determined to be a key parameter to mitigate freeze-induced physical damage. Stiffer diffusion media, enabling more uniform compression under the channels and lands, can mitigate surface cracks, but flexible cloth diffusion media experienced severe catalyst layer surface damage. The thickness of the diffusion media and existence of a micro-porous layer were not observed to be major factors to mitigate freeze-damage when the catalyst layer is in contact with liquid.

Although use of a freeze-tolerable MEA design (negligible virgin cracked catalyst layers with thinner reinforced membrane) with stiff diffusion media can reduce the freeze-damage in the worst case scenario test condition of direct liquid contact, extensive irreversible damage (diffusion media/catalyst layer interfacial delamination) was not be completely prevented. In addition to proper material selection, liquid water contact with the catalyst layer should be removed prior to shutdown to a frozen state to permit long term cycling damage and facilitate frozen start.

A two-dimensional anisotropic model has been developed to investigate the impact of local delamination on PEFC performance. Localized interfacial delamination of the membrane|catalyst layer and catalyst layer|diffusion media were found to increase ohmic resistance significantly. As interfacial delamination width and area fraction increases, the ohmic resistance sharply increases in a non-linear manner. The in-plane resistance and in-plane-to-thru-plane resistance ratio of PEFC components adjacent to the delamination were determined to be the key controlling parameters for increase in ohmic resistance. The membrane is a critical
component because of its relatively low conductivity and very thin cross-section. Finally, it is shown that under frozen conditions, small interfacial delaminations can result in a greater ohmic loss due to significantly low membrane conductivity compared to normal operating conditions.

Water management during the shutdown is a key operational parameter to mitigate freeze-damage and improve rapid cold startup. Temperature gradient driven water transport is attractive because of a potential of non-parasitic water drainage during shutdown. Two water transport modes driven by temperature gradient were explored: 1) thermo-osmosis in membrane, 2) phase-change induced water flow in the porous media (CL and DM). Thermo-osmotic flow was observed in all membranes, and the water flow direction in the membrane was determined to always flow from the cold side to the hot side, as anticipated for a small pore hydrophilic porous medium. The water flux was found to be proportional to temperature gradient, and increase with average membrane temperature. The dependency of the thermo-osmotic diffusivity on average temperature showed predictable Arrhenius-type behavior. True interfacial temperatures of the membrane were estimated using a two-dimensional thermal model, and empirical relations for the thermo-osmotic diffusivity for the membrane types tested were developed. These can be of use to design engineers concerned about achieving optimal water balance during steady and transient operation.

Contrary to thermo-osmotic flow in fuel cell membranes, a net flux of water driven by phase change was found to flow from the hot to cold side of the full membrane electrode assembly. The key to this is the existence of some gas phase in the catalyst layer or other porous media. The measured water transport through the membrane electrode assembly is the net effect of mass diffusion as well as thermo-osmosis in the membrane, which moves counter to the direction of the phase-change induced flow. Arrhenius functions that are dependent on material set, temperature gradient, and average temperature across the materials were developed that describe the net flux. In addition to direct quantification, phase-change induced flow was
visualized and confirmed using high resolution neutron radiography. The flux rates achievable using modest temperature gradients were found to be adequate for drainage of PEFCs with proper design.

9.2 Recommendations for Future Work

As a continuation of the present research work, the following recommendations are proposed in this section based on present experimental results:

1) Diagnostic tools under freezing condition should be developed because damage which is not detected at normal operating condition can be detected under freezing condition (see Fig. 5-8). Fundamental study on electrochemical reaction mechanism, ice formation and distribution, and proton transport will be helpful to diagnose freeze-damage and rapid cold start without freeze-damage.

2) Further studies are recommended on the fundamental studies to quantify water amount in the catalyst layers and membranes during shutdown, including freezing. Water content in the membrane can be assessed indirectly by HFR measurement, but is yet to be elucidated under freezing conditions. Moreover, water amount in the catalyst layers is challenging to quantify. The present study was to characterize freeze-damage modes under worst case conditions. Diagnosis of water amount in the catalyst layer is very helpful to accelerate freeze/thaw durability testing and develop freeze-tolerable fuel cells.

3) In this study, temperature-gradient induced water transport modes were explored in fundamental level and confirmed qualitatively by neutron radiography. Water drainage under real fuel cell shutdown conditions should be investigated to optimize
fuel cell shutdown procedures. The optimized shutdown procedure should be also verified by freeze/thaw cycling test.

4) Water transport rate under shutdown can be controlled by engineering initial conditions (water amount and distribution in the fuel cell), thermal boundary conditions (cooling rate and temperature in the fuel cell stack), and material properties (hydrophobicity, thickness, thermal conductivity) of diffusion media. To mitigate freeze-damage and enhance cold start capability, engineering thermal boundary conditions and material properties is required and should be complemented by modeling work.
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