MODELLING OF FROST HEAVE DURING FREEZING IN POLYMER ELECTROLYTE FUEL CELLS

A Thesis in
Mechanical Engineering
by
Suhao He

© 2007 Suhao He

Submitted in Partial Fulfillment of the Requirements for the Degree of
Doctor of Philosophy

May 2007
The thesis of Suhao He was reviewed and approved* by the following:

Matthew M. Mench  
Assistant Professor of Mechanical Engineering  
Thesis Advisor  
Chair of Committee  

Fan-Bill Cheung  
Professor of Mechanical Engineering and Professor of Nuclear Engineering  

Dan Haworth  
Professor of Mechanical Engineering  

Patrick M. Reed  
Assistant Professor of Civil and Environmental Engineering  

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

*Signatures are on file in the Graduate School
ABSTRACT

With continuous innovation in recent years, fuel cells have the potential to provide the next generation of clean energy. One of the remaining technical barriers for polymer electrolyte fuel cells (PEFCs) is achieving a damage-free cold-start, which is critical for automobile application in cold regions. PEFCs generate water. Upon freezing, ice lens formation in the thin film porous media in the fuel cell can occur, causing irreversible damage. With limited experimental and theoretical analysis available, the detailed mechanisms for the degradation are still unknown.

To better understand the phenomena involved and determine engineering approaches to control and mitigate the degradation, a 1-D transient freezing model based on theories of porous media flow and soil frost heave mechanisms has been formulated to describe the degradation process. The freezing process of a PEFC is a multi-phase porous media flow problem. The porous media can contain both unsaturated and saturated domains. Ice lenses will initialize and grow when the ice phase pressure overcomes the overburden pressure. This work presents an improvement of Harlan’s hydraulic model by integrating the frost heave mechanism from Miller’s rigid ice model. The model’s main improvement and feature most relevant to PEFCs is that it can be applied to both saturated and unsaturated domains, which is critical for PEFC application.

Additionally, detailed discussion on the capillary pressure versus saturation
characteristic curve and the unfrozen water versus temperature characteristic curve, and methods to derive these curves for PEFC components are given. The unfrozen water versus temperature curve for Nafion® can be derived from differential scanning calorimetry (DSC) data via an energy balance approach. For the diffusion media (DM) and catalyst layer (CL), this curve can be predicted through freezing temperature depression and pore size distribution through thermodynamic relations. Through the characteristic curves and formulated model, an ice lens can be predicted to occur only around the CL, either between the CL and the DM, or between the CL and the Nafion® membrane.

The numerical model was coded and solved using the Newton method. Simulation results show the processes controlling ice lens and pore ice accumulation include the drainage rate of the Nafion®, the porous materials, heat dissipation, hydrophobicity of catalyst layer, irreducible water saturation of catalyst layer, electrolyte thickness, and cooling rate. Cycling and inverted end cells effects are also found to be important. Two indices, the ice lens thickness ratio and the catalyst pore ice filling-up ratio, are proposed to characterize simulation results and estimate the possibility that a crack can initialize and grow, especially under cycling conditions. Strategies to control freeze/thaw damage are proposed based on methods that control crack initialization and that control crack development. Basically, any approach that can reduce the final ice saturation in the
Another work presented here is the development of a MEMS-based micro sensor for real-time measurement of the electrolyte temperature. The micron-sized gold thermistor is embedded in parylene film, and fabricated using MEMS technologies. Experimental results show that the sensor has a very linear response, and is robust enough to withstand the severe electrolyte expansion forces that occur during water uptake. It is an improvement compared to the conventional micro-thermocouples, with respect to sensitivity and placement accuracy, and can be used to measure the internal temperature distribution in a PEFC.
TABLE OF CONTENTS

LIST OF FIGURES .................................................................................................................. ix
LIST OF TABLES ..................................................................................................................... xv
LIST OF TABLES ..................................................................................................................... xv
NOMENCLATURE .................................................................................................................... xvi
ACKNOWLEDGEMENTS .......................................................................................................... xxiv

CHAPTER 1  INTRODUCTION .............................................................................................. 1
  1.1 PEFC Technology ......................................................................................................... 1
    1.1.1 Fuel cell introduction ............................................................................................ 1
    1.1.2 Overview of PEFCs ............................................................................................ 4
    1.1.3 Thermal effects ................................................................................................... 11
    1.1.4 Water transport through Nafion® ...................................................................... 13
  1.2 Flow through PM ........................................................................................................... 20
    1.2.1 Fundamentals ..................................................................................................... 20
    1.2.2 The immiscible flow model for multi-phase flow through PM ......................... 26
  1.3 Frost Heave in Soil Science .......................................................................................... 29
    1.3.1 History ............................................................................................................... 29
    1.3.2 Capillary force balance of the three phases within PM ..................................... 32
    1.3.3 Characteristic curves ......................................................................................... 34
    1.3.4 Models of frost heave in soil ............................................................................. 37
      1.3.4.1 Rigid ice model ........................................................................................... 37
      1.3.4.2 Hydraulic model ......................................................................................... 41
  1.4 Motivation for Study – PEFC Freezing Modeling ...................................................... 44

CHAPTER 2  1-D TRANSIENT MODEL FOR FROST HEAVE IN PEFCs:
MODEL FORMULATION ........................................................................................................ 49
  2.1 Introduction ................................................................................................................. 49
  2.2 Model Formulation ..................................................................................................... 52
    2.2.1 Model assumptions ............................................................................................. 52
    2.2.2 Mass/flow equations ......................................................................................... 55
    2.2.3 Energy equations ............................................................................................... 58
    2.2.4 Characteristic curves ......................................................................................... 61
5.4. Results and Discussion.......................................................................................... 140
5.5. Conclusions ........................................................................................................ 148

CHAPTER 6  CONCLUSIONS AND FUTURE WORK ............................................. 150

6.1 Conclusions ....................................................................................................... 150
6.2 Recommendations for Future Work................................................................. 153

REFERENCES.......................................................................................................... 156

APPENDIX A  DERIVATION OF UNFROZEN WATER VERSUS TEMPERATURE CURVE FROM DSC DATA FOR NAFION®.................................. 169
APPENDIX B  NUMERICAL METHOD IMPLEMENTATION.............................. 176
LIST OF FIGURES

Figure 1-1: The schematic of a typical fuel cell [3] ..........................................................4

Figure 1-2: Enlarged cross-section of diffusion media and membrane electrode assembly showing structural details [4]........................................................................5

Figure 1-3: Ionic conductivity of Nafion® as a function of temperature and relative humidity, using the relationship proposed by Springer [5].................................7

Figure 1-4: Ideal and actual PEFC $V_{cel} - i$ curve [3] ..................................................9

Figure 1-5: The structural formula of the Nafion® polymer............................................14

Figure 1-6: Water uptake for Nafion® 117 at 30 °C [17]................................................16

Figure 1-7: Evolution of the membrane structure as a function of water content [18-19]..................................................................................................................17

Figure 1-8: Diffusion coefficient $D_w$ as a function of water content of the membrane at different temperature [24] .................................................................18

Figure 1-9: Illustration of contact angle ........................................................................21

Figure 1-10: Equilibrium at a curved interface [26] ......................................................22

Figure 1-11: Illustration of hysteresis effects [27]..........................................................23

Figure 1-12: Typical wetting/drying curves illustrating hysteresis [26] .........................24

Figure 1-13: Typical relative permeability as a function of saturation [26] .................26

Figure 1-14: Typical configuration of air-water and air-ice-water coexisting in a pore structure with hydrophilic material [74] .........................................................32

Figure 1-15: Similarity between air-free ice-water interface and ice-free air-water interface. The data are from (a) SLS soil sample and (b) SS soil sample with ▽ representing freezing; ○ representing drying; ▼ representing drying; ●
representing wetting [75]...........................................................................................................33

Figure 1-16: Temperature change during freezing [76].................................................................35
Figure 1-17: Typical unfrozen water content of soil as a function of temperature [90]........36
Figure 1-18: Comparison of (a) primary and (b) secondary frost heave [74].......................37
Figure 1-19: Illustration of secondary frost heave [58]...............................................................39
Figure 1-20: Non-homogeneous water distribution in a PEFC, shown by Neutron Image Technique [91] ......................................................................................................................43
Figure 1-21: Schematic showing the potential locations of freeze/thaw damage..........47
Figure 2-1: Comparison of (a) primary and (b) secondary frost heave, following ref. [74]........................................................................................................................50
Figure 2-2: 1-D model PEFC geometry .........................................................................................52
Figure 2-3: Heat conduction for case with ice lens.................................................................61
Figure 2-4: Unfrozen water versus temperature curves derived from Nafion® DSC data of refs. [84, 88-89]..................................................................................................................63
Figure 2-5: Predicted freezing temperature distribution using pore size distribution data of carbon paper (Toray® TGP-H-060) of ref. [111]..............................................................65
Figure 2-6: Dependence of capillary pressure on water content and temperature, in which -x- represents the unfrozen water versus temperature curve, -○- represents the capillary pressure versus saturation curve, -□- represents the thermodynamic relation, the unmarked one is the $p_c(s_w, T)$ curve.........................66
Figure 2-7: Schematic showing the potential locations of freeze/thaw damage. Ice lenses grow mostly likely in location 1-3, less likely in location 4-5, and not likely in location 6-10 ...........................................................................................................................70
Figure 2-8: 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

\[ \lambda = 14 \quad H_2O/\text{SO}_3^- \] .................................73

Figure 3-1: Domain decomposition for unsaturated freezing in porous media. Domains include: A) saturated nonfreezing, B) unsaturated nonfreezing, C) unsaturated freezing, D) saturated freezing, and E) frozen domains. Also shown on the plot are iso-ice-content lines with \( s_i = 0, 0.2, 0.4, 0.6, 0.8, \) and 1.................77

Figure 3-2: Comparison of drainage rate on relative permeability relations................84

Figure 3-3: Transient temperature distribution along the 1-D geometry with (a) bipolar plate and (b) open channel boundary condition.................................87

Figure 3-4: Transient water saturation distribution along the 1-D geometry with (a) bipolar plate and (b) open channel boundary condition.................................88

Figure 3-5: Transient ice saturation distribution along the 1-D geometry with (a) bipolar plate and (b) open channel boundary condition.................................90

Figure 3-6: Illustration showing locations of IL1, IL2, and IL3.............................91

Figure 3-7: Transient ice lens growth with bipolar plate boundary condition with (a) thickness, temperature, water saturation change for IL1, and (b) thickness change for IL1, IL2, and IL3 .................................................................93

Figure 3-8: Transient ice lens growth with open channel boundary condition with (a) thickness, temperature, water saturation change for IL1, and (b) thickness change for IL1, IL2, and IL3 .................................................................94

Figure 3-9: Illustrations show possible damage modes inside catalyst layer. a) Initial state before freeze/thaw. b) Unfrozen water from Nafion® membrane flow into the catalyst layer, freeze inside Nafion® components, and cause swelling of
Nafion® structure. c) Unfrozen water from Nafion® membrane flow into the catalyst layer, come out and freeze on surface of Nafion® components. d) Catalyst pores get filled up with water locally.

Figure 3-10: Effects of drainage speed for (a) bipolar plate boundary condition and (b) open channel boundary condition.

Figure 3-11: Effects of irreducible water content for (a) bipolar plate boundary condition and (b) open channel boundary condition.

Figure 3-12: Effects of initial water content for (a) bipolar plate boundary condition and (b) open channel boundary condition.

Figure 3-13: Effects of contact angle for (a) bipolar plate boundary condition and (b) open channel boundary condition.

Figure 4-1: Comparison on final ice saturation for cases with different material thermal conductivity, when the membrane electrolyte assembly is (a) under the BP and (b) under the CH.

Figure 4-2: Comparison on final ice saturation for cases with different material layer thickness when the membrane electrolyte assembly is (a) under the BP and (b) under the CH. (The three cases are with different layer thickness, so the saturation distribution has been stretched to fit the geometry shown in the bar so that they are comparable.)

Figure 4-3: Illustration showing stack structure and unfrozen water flow in a fuel cell stack.

Figure 4-4: Comparison on final ice saturation for cases with different thermal boundary conditions when the membrane electrolyte assembly is (a) under the BP and (b) under the CH.

Figure 4-5: Comparison on final ice saturation for the base case and the cases with
MPL, when the membrane electrolyte assembly is (a) under the BP and (b) under the CH.................................................................120

Figure 4-6: Illustration showing ice lens growth during cycling.................................122

Figure 4-7: IL2 thickness ratio change with cycles with (a) base and (b) inverted thermal boundary conditions ................................................123

Figure 4-8: Catalyst pore ice filling-up ratio change with cycles with (a) base and (b) inverted thermal boundary conditions .........................125

Figure 4-9: Triangle showing the interrelation between heat transfer, purge, and materials, based on which strategies to control freeze/thaw damages can be developed .................................................................126

Figure 5-1: Thermal sensor design (the right figure is the enlarged view)......................134

Figure 5-2: Sensor setup in a fuel cell ........................................................................136

Figure 5-3: Temperature contours for the case of 1A/cm² and 10 μm thick parylene layer......................................................................................139

Figure 5-4: Plot of the averaged temperature increase in the centerline and error brought by the parylene layer versus global heat generation for different parylene layers thickness..............................................................140

Figure 5-5: Magnified view of thin film sensors: (a) Cracks grow on sensor directly deposited on Nafion® membrane, (b) Water can penetrate the NPPN laminate and destroy the sensor, (c) NPPN laminate with the aid of Epoxy® 301, (d) NPPN laminate with the aid of acrylic adhesive, (e) Cracks grow on sensor with 2 μm thick parylene protecting layer, and (f) Sensor with 1 μm thick parylene protecting layer ..................................................................................................................141

Figure 5-6: Plot of thermistor resistance versus temperature during ex-situ calibration. The test was done at different days to check repeatability .................143
Figure 5-7: Plot of the 5 cm² fuel cell performance with the sensor-MEA sandwich.....145
Figure 5-8: Plot of fuel cell temperature response for (a) heat-up and (b) cool-down....146
Figure 5-9: Plot of fuel cell transient response measured by the sensor. The cell voltage was changed between OCV and 0.2V every five minutes. The heat generation flux was around 0.2W/cm² at 0.2V......................................................147
Figure A-1: DSC data from various literature [84-89].............................................171
Figure B-1: Flow chart of current numerical model shows (a) the main program using Newton solver to get transient results, and (b) the sub program for function evaluation in Newton solver..........................................................178
Figure B-2: Convergence history of one typical calculation.................................181
Figure B-3: Mass and energy balance check with the code for one typical calculation..182
Figure B-4: Temporal discretization error check ..................................................183
Figure B-5: Spatial discretization error check ......................................................184
LIST OF TABLES

Table 2-1: Local overburden pressure .................................................................69

Table 3-1: Domain decomposition criteria for freezing in porous media ..............77

Table 3-2: Freezing point depression for PEFC components .............................79

Table 3-3: Porous media properties used ................................................................81

Table 3-4: Sensitive input parameters controlling ice lens formation and growth ....81

Table 3-5: Empirical relative permeability relations .............................................83

Table 3-6: Parameters used for parametric study ................................................99

Table 3-7: IL Comparison on IL thickness ratio and pore filling-up ratio .............100

Table 4-1: FEFC component thermal parameters .............................................110

Table 4-2: IL Comparison on IL thickness ratio and pore filling-up ratio .............112

Table 4-3: MPL Physical Properties [31, 143-144] .........................................121
NOMENCLATURE

English Symbols

\( A \) Superficial electrode surface area, \( cm^2 \)

\( c \) Molar concentration, \( mol/l \)

\( c_{so_3} \) Mole concentration of sulfonic acid group, \( mol/l \)

\( C_p \) Specific heat capacity, \( J/kg \cdot K \)

\( D \) Diffusivity, \( m/s^2 \)

\( E \) Impedance factor for permeability

\( E_0 \) Electromotive force, \( V \)

\( F \) Faraday’s constant, 96,485 \( C/eq \)

\( g \) Acceleration of gravity, 9.8 \( m/s^2 \)

\( G \) Free Gibbs energy, \( J/mol \)

\( H \) Enthalpy, \( J/mol \)

\( h \) Convective heat transfer coefficient, \( W/m^2 \cdot K \)

\( h_{sf} \) Heat of fusion, \( J/kg \)

\( i \) Current density, \( A/cm^2 \)

\( i_o \) Exchange current density, \( A/cm^2 \)

\( i_n \) Crossover current density, \( A/cm^2 \)
$i_L$  Limiting current density, $A/cm^2$

$J$  J-Leverett function

$k$  Permeability, $m^2$

$k_e$  Effective permeability, $m^2$

$k_r$  Relative permeability

$n$  Number of electrons transfer in half-cell reaction or elementary charge-transfer reaction, $eq/mol$

$M$  Molar weight, $g/mol$

$\text{Nu}$  Nusselt number

$p$  Phase pressure, $Pa$

$p_b$  Bubbling pressure, $Pa$

$p_c$  Capillary pressure, $Pa$

$p^*$  Characteristic pressure

$p_c^*$  Weighted capillary pressure, $Pa$

$P$  Pressure, $Pa$

$\text{Pr}$  Prandtl number

$q$  1-D heat flux, $W/m^2$

$Q$  Heat energy, $J$
\( \dot{Q} \) \hspace{1cm} \text{Heat release rate, } W \\
\dot{Q}_m \hspace{1cm} \text{Heat release rate per unit mass, } W/kg \\
r \hspace{1cm} \text{Area specific resistance, } \Omega \cdot cm^2 \\
r \hspace{1cm} \text{Mean pore size, } m \\
r', r'' \hspace{1cm} \text{Two principle radii of the interface, } m \\
r^* \hspace{1cm} \text{Capillary tube radius, } m \\
R \hspace{1cm} \text{Resistance, } \Omega \\
R \hspace{1cm} \text{Ideal gas constant, 8.314 } J/mol \cdot K \\
Ra \hspace{1cm} \text{Rayleigh number} \\
s \hspace{1cm} \text{Saturation} \\
s_e \hspace{1cm} \text{Effective water saturation} \\
s_u \hspace{1cm} \text{Maximum unfrozen water saturation} \\
s_{w0} \hspace{1cm} \text{Irreducible water saturation} \\
s_{nw0} \hspace{1cm} \text{Residual saturation of the non-wetting fluid} \\
S \hspace{1cm} \text{Entropy, } J/mol \cdot K \\
S_h \hspace{1cm} \text{Heat source, } W/m^3 \\
S_m \hspace{1cm} \text{Mass source, } kg/m^3 \cdot s \\
S_g \hspace{1cm} \text{Temperature coefficient of resistance, } \Omega/K
\[ \begin{align*}
t & \quad \text{Time, } s \\
T & \quad \text{Temperature, } K \\
T_f & \quad \text{Reference freezing temperature, } 273.15 \ K \\
\Delta T & \quad \text{Freezing temperature depression, } K \\
v & \quad \text{Velocity, } m/s \\
v_h & \quad \text{Frost heave rate, } m/s \\
V & \quad \text{Volume, } m^3 \text{ or Voltage, } V \\
w & \quad \text{Work per area, } J/m^2 \\
x & \quad \text{x-dimension, } m \\
\end{align*} \]

\textbf{Greek}

\[ \begin{align*}
\alpha_h & \quad \text{Heat diffusivity, } m^2/s \\
\alpha & \quad \text{Half-cell reaction transfer coefficient} \\
\chi & \quad \text{Weighting factor for soil stress} \\
\delta & \quad \text{Thickness, } m \\
\varepsilon & \quad \text{Porosity} \\
\gamma & \quad \text{Pore size distribution index} \\
\gamma_R & \quad \text{Temperature coefficient of metal} \\
\eta & \quad \text{Overpotential, } V \\
\end{align*} \]
\( \kappa \) Thermal conductivity, \( W/m \cdot K \)

\( \overline{\kappa} \) Averaged thermal conductivity, \( W/m \cdot K \)

\( \lambda \) Water content in Nafion\textsuperscript{®}, \( mol \, H_2O/mol \, SO_3^- \)

\( \lambda_0 \) All the freezable water content in Nafion\textsuperscript{®}, \( mol \, H_2O/mol \, SO_3^- \)

\( \lambda_{\text{drag}} \) Electro-osmotic drag coefficient

\( \mu \) Viscosity, \( Pa \cdot s \)

\( \theta \) Contact angle, degree

\( \rho \) Density, \( kg/m^3 \)

\( \overline{\rho C_p} \) Averaged storage term parameter for energy equation, \( J/m^3 \cdot K \)

\( \sigma \) Surface tension, \( N/m \)

\( \sigma_t \) Tensile strength, \( Pa \)

\( \tau \) Characteristic time, \( s \) or Tortuosity

\( \tau_{sh} \) Shear stress, \( Pa \)

\( \omega \) IL thickness ratio

\( \psi \) Filling-up ratio

\( \zeta \) Stoichiometry, \( A/cm^2 \)

Subscripts

0 Reference point
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>Air phase</td>
</tr>
<tr>
<td>A</td>
<td>Anode</td>
</tr>
<tr>
<td>act</td>
<td>Activation</td>
</tr>
<tr>
<td>acid</td>
<td>Sulfonic acid group</td>
</tr>
<tr>
<td>assm</td>
<td>Assembling</td>
</tr>
<tr>
<td>b</td>
<td>Bubbling</td>
</tr>
<tr>
<td>bc</td>
<td>Boundary condition</td>
</tr>
<tr>
<td>bk</td>
<td>Bulk</td>
</tr>
<tr>
<td>bp</td>
<td>Bipolar plate</td>
</tr>
<tr>
<td>c</td>
<td>Capillary</td>
</tr>
<tr>
<td>C</td>
<td>Cathode</td>
</tr>
<tr>
<td>cell</td>
<td>Fuel cell</td>
</tr>
<tr>
<td>ch</td>
<td>Channel</td>
</tr>
<tr>
<td>cl</td>
<td>Catalyst layer</td>
</tr>
<tr>
<td>diff</td>
<td>Diffusion</td>
</tr>
<tr>
<td>dm</td>
<td>Diffusion media</td>
</tr>
<tr>
<td>elos</td>
<td>Electro-osmotic drag</td>
</tr>
<tr>
<td>e</td>
<td>Effective</td>
</tr>
<tr>
<td>E</td>
<td>Electrolyte</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
</tr>
<tr>
<td>--------------</td>
<td>------------------------------</td>
</tr>
<tr>
<td>en</td>
<td>Environment</td>
</tr>
<tr>
<td>fh</td>
<td>Frost heave</td>
</tr>
<tr>
<td>FC</td>
<td>Forced convection</td>
</tr>
<tr>
<td>g</td>
<td>Gas phase</td>
</tr>
<tr>
<td>GCE</td>
<td>GCE relation</td>
</tr>
<tr>
<td>hyd</td>
<td>Hydraulic</td>
</tr>
<tr>
<td>i</td>
<td>Ice phase</td>
</tr>
<tr>
<td>il</td>
<td>Ice lens</td>
</tr>
<tr>
<td>j</td>
<td>Component $j$</td>
</tr>
<tr>
<td>k</td>
<td>Component $k$</td>
</tr>
<tr>
<td>kin</td>
<td>Kinetics</td>
</tr>
<tr>
<td>l</td>
<td>Liquid phase</td>
</tr>
<tr>
<td>mass</td>
<td>Mass</td>
</tr>
<tr>
<td>NC</td>
<td>Natural convection</td>
</tr>
<tr>
<td>nf</td>
<td>Nafion® membrane</td>
</tr>
<tr>
<td>nw</td>
<td>Non-wetting fluid</td>
</tr>
<tr>
<td>ohm</td>
<td>Ohmic</td>
</tr>
<tr>
<td>ovbd</td>
<td>Overburden</td>
</tr>
<tr>
<td>pel</td>
<td>Peltier</td>
</tr>
</tbody>
</table>
\( pm \) Porous media

\( s \) Solid phase

\( u \) Un-freezable water

\( w \) Freezable water in Nafion\(^\text{®}\); water phase in other case

\( wall \) Porous media backbone material

Superscripts

\( m \) Time step

\( o \) Reference point
ACKNOWLEDGEMENTS

The first person I would like to thank is my advisor Dr. Matthew M. Mench, for his guidance, academic and financial support throughout my entire graduate studies at Penn State University. His great enthusiasm and integral view on research and his mission for high-quality work has made a deep impression on me. I owe him lots of gratitude for his continuous encouragement, excellent teaching, and lots of creative ideas. I would also like to recognize the other members of my advisory committee: Dr. Fan-Bill Cheung, Dr. Dan Haworth, and Dr. Patrick M. Reed for their support and for all their recommendations to my thesis, especially their excellent discussion and very helpful information on the numerical model.

I would like to appreciate Dr. Srinivas Tadigadapa of Department of Electrical Engineering for his guidance and support throughout my first project as my co-advisor. I would also like to appreciate Dr. Anil K. Kulkarni for his guidance on my appointment as a Graduate Teaching Fellow for Department of Mechanical and Nuclear Engineering.

I extend my appreciation to Hyundai Motor Company and Hydrogen Center of Penn State University for their financial support. I would also like to appreciate Department of Mechanical and Nuclear Engineering for their financial support when I worked as Graduate Assistantship and Graduate Teaching Fellow for two semesters.
I would like to sincerely thank Dr. Turgay Ertekin from Department of Petroleum Engineering for his valuable suggestions on the numerical model, thank Dr. Qunlong Dong for his guidance on fuel cell testing and lots of excellent discussion with me, thank Mr. Henry M. Chance and Mr. Daniel Burford for their guidance on DME and thermo-sensor projects, thank Dr. Fuqiang Liu for his guidance on MEA fabrication, and thank Dr. Abhijat Goyal for his guidance on MEMS fabrication techniques. I would also like to thank all my labmates at FCDDL and MEMS group and the entire MNE department staff and faculty for all their help.

I am very grateful for my wife Lingli, for her love and support during my Ph.D. study. I also want to thank our parents and all of our friends who were always there, supporting and sharing with us.
CHAPTER 1 INTRODUCTION

In this chapter, an overview of the PEFC technology is given, the theory of flow in porous media is introduced, soil related frost heave phenomena are reviewed, and the objectives of this thesis are presented.

1.1 PEFC Technology

1.1.1 Fuel cell introduction

A recent review [1] summarized the history of low temperature fuel cell development, and another one [2] addressed the current status of research progress and technical barriers. In recent years, to address the increasing environmental concerns, a transition from fossil fuel energy to hydrogen energy appears to be underway. Many of today’s industries, including automotive manufacturers, are investing considerable resources in developing hydrogen-based power generation technologies. One of these emerging technologies is the fuel cell.

Fuel cells were invented by Sir William Grove in 1839 [3]. In 1959, NASA demonstrated some of their potential applications in providing auxiliary power and potable water during space flights. In 1966, the General Electric Company started to fabricate polymer electrolyte fuel cells (PEFCs) as power supplies in space projects by
NASA. From then on, fuel cell technologies have continuously been innovated and improved. Demonstrations in automotive, stationary generator, and portable power supply are widely ongoing today. For PEFCs, over the last ten years, the size and cost has been cut by an order of magnitude. However, there are still several major technical and economical barriers to overcome. One of the technical barriers of PEFC automotive application is to achieve a damage-free cold-start without requiring large parasitic power loss. The goal is to achieve minimum parasitic energy loss for startup and shutdown of a fuel cell.

Fuel cells are electrochemical devices that convert the chemical energy of fuel oxidation directly to electrical energy. It represents a very different approach for energy conversion, which could replace conventional power generation technologies like heat engines and turbines in applications such as automobiles and power plants. Fuel cells have the following major advantages [2-4]:

1. Different from batteries, fuel cells can produce power as long as fuel and oxidizer are supplied.

2. Fuel cells operate quietly and are relatively compact.

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

4. Fuel cells have higher potential energy conversion efficiency, 40~60%. There
will be a 50 percent reduction in fuel consumption for fuel cell vehicles when compared to a conventional vehicle with a gasoline internal combustion engine (ICE), on a well-to-wheels basis.

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

Depending on the types of electrolyte, fuel cells can be divided into several categories. Phosphoric acid fuel cell (PAFC) and the molten carbonate fuel cell (MCFC) have a liquid electrolyte, while a solid oxide fuel cell (SOFC) has a solid ceramic electrolyte. A PEFC and a direct methanol fuel cell (DMFC) have the same solid polymer electrolyte, but the PEFC uses gaseous hydrogen as fuel and DMFC uses liquid methanol.

The DMFC is very suitable for portable power applications, such as notebooks and PDAs, since it has a low operating temperature and the fuel, liquid methanol solution, has high energy density. The SOFC is envisioned for stationary power plant applications, since it has higher power density and high grade waste heat that can be used for cogeneration. The PEFC is ideal for the automotive application, since it has relatively low operating temperature, high power density, and can start up relatively quickly under normal ambient conditions.
1.1.2 Overview of PEFCs

Figure 1-1 shows a typical fuel cell structure. Fuel and air are provided through flow channels (CH), which are embedded in the bipolar plates (BP), and diffuse to the respective electrode. The anode and cathode are also called catalyst layer (CL), where the partial electrochemical reactions will take place. The electrolyte is between the two electrodes and conducts ions. For PEFC, there’s also a porous diffusion media (DM) on top of CL for electron conduction, reactant diffusion, and water management purposes. The electrons are conducted through the CL, DM, BP, and then the external load.

A schematic of an enlarged structure of the DM, CL, and electrolyte in a PEFC are shown in Figure 1-2. The porous DM is woven carbon cloth or non-woven carbon
paper, both made of carbon fibers, with a thickness of 100~400 μm. The DM also provides an electrical connection between the electrode and the BP, which is the current collector.

Figure 1-2: Enlarged cross-section of diffusion media and membrane electrode assembly showing structural details [4]

The CL is a porous layer with a thickness of 10~15 μm, fabricated using Nafion® dispersion solution, carbon supported platinum particles, and polytetrafluoroethylene (PTFE). The CL is designed to facilitate the transport of protons, electrons, and gaseous reactants. Protons transport through Nafion®, and electrons through carbon and platinum particles, while gaseous reactants can flow through the porous structure and also diffuse into the Nafion®. The half-cell electrochemical reaction ideally occurs at the so-called three-phase interfaces, where the Nafion®, catalyst, and gaseous reactants coexist. The
CL is fabricated either directly on the surface of the membrane or on the DM surface and then hot-pressed onto the membrane. The three-layer CL|electrolyte|CL structure is called the membrane electrode assembly (MEA). The cost of catalyst is a significant, but not dominant portion of the total system cost. The present state-of-the-art of platinum loading is ~0.4 mg/cm$^2$ per MEA, which is using a ~45 nm carbon support structure loaded with ~5 nm platinum particles.

In the anode, hydrogen gas is oxidized into protons and electrons.

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

Protons produced in the anode are then transported through the electrode, into the electrolyte membrane (100–175 μm), and to the cathode. The membrane has low permeability to gas-phase reactants and low electrical conductivity. The membrane has to absorb water to maintain good proton conductivity. Figure 1-3 shows the ionic conductivity of Nafion® as a function of temperature and relative humidity, using the relationship proposed by Springer [5]. If the membrane is dry and local temperature increases to the glass transition temperature of Nafion®, ~130 °C, holes may be generated in the membrane. Through the holes, reactants can cross over the membrane and react directly with each other. In this case, a slight combustion or even more dangerous catastrophic failure could occur. Usually, the anode and cathode inlet gas need very high humidification (≥75% at 80 °C) in order to hydrate the membrane.
Figure 1-3: Ionic conductivity of Naion® as a function of temperature and relative humidity, using the relationship proposed by Springer [5]

At the same time, electrons flow through the external load. A single PEFC can generate ~1.0 A/cm² at 0.6 V. Since most electronic devices operate >>1 V, individual fuel cells are typically connected in series, to form a stack. The current from a cell is proportional to the CL area. Thus, for higher voltage, there are more cells in series; for higher current, the cells are larger.

At the cathode, oxygen gas reacts with protons and the electrons coming from the anode. Water is produced through the oxygen reduction reaction (ORR).

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

When the two half-cell reactions are combined, one can obtain the global fuel cell reaction.
Depending on the local conditions, the water product remains in vapor form or condenses into a liquid. Liquid water flows through the porous media (PM), driven primarily by capillary pressure, not the gravity or convective forces, since through scale analysis,
\[ \rho g \left( \frac{4}{3} \pi r^3 \right) << \frac{2\sigma}{r} (\pi r^2) \] and \[ \frac{C_D}{2} \rho v^2 << \frac{2\sigma}{r} (\pi r^2) \]. Since water production is proportional to the current density, water generation in the cathode increases with current, leading to a phenomenon known as “flooding”. The water may block the cathode diffusion media, thus preventing oxygen from reaching the reaction sites. Flooding can be mitigated through structure or material modification, but the fundamental science behind two-phase flow in these thin-film PM is far from well-defined. Present water management methods include adding a micro-porous layer (MPL) onto the DM next to the CL, and modifying the thickness, pore size distribution, or hydrophobic properties of the DM or CL. For instance, the PTFE added to the CL can make it more hydrophobic and facilitate the water removal for the CL. Upon reaching the gas channels, liquid water is then removed by the bulk gas flow by evaporation or drag forces.

Figure 1-4 shows the cell voltage-current density \( (V_{cell} - i) \) curve of a typical PEFC. The actual voltage of PEFC is lower than its electromotive force (EMF) or ideal voltage, which is determined by thermodynamics [3, 6-7].
Here, $E_0$ is the EMF voltage; $\Delta G$, $\Delta H$, and $\Delta S$ are the free Gibbs energy, enthalpy, and entropy released from the global reaction; $n$ is the number of electrons transferred in the anode reaction, Equation 1.1; $F$ is the Faraday constant; $T$ is the absolute temperature.

The irreversible losses shown in the curve are called polarization or overpotential. There are three basic types of polarizations: activation polarization, ohmic polarization, and concentration polarization. These polarizations dominate different regions of the operating $V_{cell} - i$ curve.

The activation polarization dominates the low current density region. From thermodynamics derivation using electrochemical potential, the relation between
activation losses and current for a single electrode follows the Butler-Volmer equation [8-9].

\[
i = i_0 \left[ \exp\left(\frac{\alpha_A nF}{RT}\eta_{act}^A\right) - \exp\left(-\frac{\alpha_C nF}{RT}\eta_{act}^C\right) \right]
\]  \hspace{1cm} [1.5]

Here, \(i_0\) is the exchange current density; \(\eta_{act}\) is the activation overpotential; \(R\) is the ideal gas constant; \(\alpha_A\) and \(\alpha_C\) are the anodic and cathodic transfer coefficient; \(n\) is the number of electrons transferred in the elementary charge-transfer step (different than Equation 1.4 and typically ranges from 1 to 2; \(i\) is the current density of the cell, which also includes the crossover current, \(i_n\), representing the amount of hydrogen crossed over to the cathode through the membrane;

Ohmic polarization is caused by the ohmic resistance of DM and BP, contact losses, and the ionic resistance of the Nafion® membrane. The later portion is typically dominant and depends on the membrane status. As addressed before, the membrane has to be hydrated to conduct protons. By Ohm’s law,

\[
\eta_{ohm} = ir
\]  \hspace{1cm} [1.6]

Here, \(\eta_{ohm}\) is the ohmic overpotential and \(r\) is the area specific resistance for the respective materials.

The concentration polarization is produced by the decrease of reactant concentration at the reaction sites. This loss becomes prominent at high limiting currents.
because it becomes difficult to provide enough reactant to the cell reaction sites. This effect can be predicted by the Butler-Volmer equation in its full form, which becomes Nernst’s equation at thermodynamic equilibrium [3, 6-7],

\[
\eta_{\text{mass}} = \frac{RT}{nF} \ln \left( 1 - \frac{i}{i_L} \right)
\]  

[1.7]

Here, \( \eta_{\text{mass}} \) is the concentration overpotential and \( i_L \) is the limiting current density, which depends on the mass transfer properties of the DM and CL on each side of the PEFC. Flooding causes a large concentration polarization.

The cell voltage then can be determined by subtracting all the voltage losses from the EMF.

\[
V_{\text{cell}} = E_0 - \sum \eta_{\text{ohm}} - \eta_{\text{act,A}} - \eta_{\text{act,C}} - \eta_{\text{mass,A}} - \eta_{\text{mass,C}}
\]

[1.8]

Here, \( \eta_{\text{act,A}} \), and \( \eta_{\text{mass,A}} \) are the voltage loss in the anode; \( \eta_{\text{ohm,C}} \), \( \eta_{\text{act,C}} \), and \( \eta_{\text{mass,C}} \) are the voltage loss in the cathode; \( \sum \eta_{\text{ohm}} \) is the sum of ohmic voltage losses from all the contacts and components.

### 1.1.3 Thermal effects

Both the temperature and water content in the PEFC have to be precisely controlled for high performance and durability. These two parameters are strongly coupled with each other. The water phase evaporation/condensation and convection tend
to homogenize the temperature distribution for heat pipe effects. For locations with DM flooding, reactants cannot reach reaction sites and the local heat generation will decrease for inhibited reactions. For locations where the membrane is dry, the ohmic resistance of the electrolyte increases significantly, so the ohmic overpotential and respective ohmic heat will increase, if the current remains the same. A review of heat transfer in PEFCs is given by Divisek [10].

The heat source can be calculated through the voltage loss. In PEFCs, all of the chemical energy becomes either electrical energy or waste heat. Theoretically, if all the chemical energy is converted to electric energy, by Nernst equation, the voltage is 1.481 V if the product is liquid water and 1.253 V if the product is water vapor. The difference, 0.228 V accounts for the latent heat. The heat source position for latent heat will depend on the location of condensed water. The output cell voltage, part of the 1.253 V, counts the portion of usable electric energy and the polarizations (1.253-$V_{cell}$) are the portions of waste heat generated. The waste heat can be divided into three parts:

1. Electrode kinetics heat, generated by the overpotential to drive the electrochemical reactions taking place in the electrodes. This includes the activation polarization heat and the concentration polarization heat. For a single electrode,
\[ Q_{\text{kin}} = A i (\eta_{\text{act}} + \eta_{\text{mass}}) \] [1.9]

Here, \( Q_{\text{kin}} \) is the heat generated by the electrode kinetics loss and \( A \) is the surface area of the electrode.

2. Ohmic heat, generated by the current going through the membrane and catalyst layers is written as

\[ Q_{\text{ohm}} = A i \eta_{\text{ohm}} \] [1.10]

Here, \( Q_{\text{ohm}} \) is the ohmic heat.

3. Peltier heat generated by entropy change is written as

\[ Q_{\text{pel}} = A i \left( -\frac{T\Delta S}{nF} \right) \] [1.11]

Here, \( Q_{\text{pel}} \) is the Peltier heat. Actually, the concentration polarization heat can also be treated as one type of the Peltier heat.

The heat dissipates through the DM and BP by conduction, to the cooling channels by forced convection or the environment by natural convection. Study has shown a vast majority of dissipation (~80%) occurs through the BP.

1.1.4 Water transport through Nafion®

Water transport is much more complex than heat transport. The inlet reactants are pre-humidified and the reaction is producing water at the cathode, while the water product can be removed both in liquid and vapor forms. The complexity lies in the
two-phase flow through porous DM and CL, together with the special water transport mechanisms in the electrolyte. During operation, the two-phase flow will become even more complex, since the reactants and products form a multi-component two-phase flow. Section 1.2 discusses the present understanding and models of the flow through PM. This section will focus on the water transport mechanisms in Nafion®, the most commonly used electrolyte in PEFCs.

In 1962 the DuPont Company developed a perfluorosulphonic acid (PFSA) polymer membrane, which was named Nafion®. The polymer is based on a PTFE backbone and has perfluorovinyl ether pendant side chains with sulphonate groups on the ends. The chemical formula of Nafion® is shown in Figure 1-5. This structure represented a vast improvement over less robust hydrocarbon-based electrolyte used before. Besides the PEFCs, Nafion® membranes have also been applied for metal ion recovery, water electrolysis where hydrogen and oxygen is produced, super acid catalyst in organic reactions and different electrochemical devices. Some recent reviews summarized the structure and properties of perfluorinated and alternative membranes [11-12].

\[
\begin{align*}
  & \text{[CF}_2\text{CF-(CF}_2\text{-CF}_2\text{)]}_m \\
  & \text{O-[(CF}_2\text{-CF-O)]}_n\text{-CF}_2\text{-CF}_2\text{-SO}_3\text{H} \\
  & \text{CF}_3
\end{align*}
\]

Figure 1-5: The structural formula of the Nafion® polymer
The Nafion® is quite different from its polymer analogues without ionic groups, PTFE. Yeager and Steck [13] defined three regions within the polymer membrane. The regions are the fluorocarbon phase, interfacial region and ionic clusters. The fluorocarbon phase forms the polymer backbone. The interfacial region is a mix of side chains, water and sulphonate groups that are not active as ion exchange sites. The ionic cluster region is where most of the absorbed water resides. Gierke et al. [14] proposed that the microstructure of Nafion® is a cluster network where the polymer ions and the absorbed water exist in spherical domains and are separated by the PTFE matrix. The 1 nm wide channels that interconnect spherical clusters create a matrix of inverted micelles. The size of the spherical domains grows in size from 2.5 nm to 4 nm when water is absorbed, greatly enhancing ionic and water transport.

The Nafion® membrane has very good chemical, thermal and mechanical stability [15]. For PEFC application, Nafion®’s ionic properties, such as water uptake, proton conductivity, gas permeability, and its microstructure are of special interest. In 1903, Schroeder [16] found that polymeric materials absorb less water from the saturated vapor phase than from the liquid phase. This is called Schroeder’s paradox, which has long been observed in Nafion® as well. Zawodzinski et al. [17] first measured the water uptake of a Nafion® membrane as a function of water activity. The water content of membrane, \( \lambda \), is defined as the number of moles of water associated with a mole of sulfonic groups
in the membrane. As shown in Figure 1-6, $\lambda$ is 14 $H_2O/SO_3^-$ for saturation with water vapor and 22 $H_2O/SO_3^-$ for saturation with liquid water.

![Figure 1-6: Water uptake for Nafion® 117 at 30 °C [17]](image)

Most recently, Weber and Newman [18-19] proposed a physical explanation of the Schroeder’s paradox. They described the four steps during water uptake, as shown in Figure 1-7. 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 a PM. Liquid water
is then flowing into the membrane driven by capillary pressure, instead of the activity gradient. They claimed that Schroeder’s paradox is actually representing a structure and transport mechanism transition.

Figure 1-7: Evolution of the membrane structure as a function of water content [18-19]

Present models of water transport through Nafion® can be categorized to the diffusion model [5, 20-21] and the hydraulic model [22-23]. Springer et al. [5] first proposed the diffusion model. They assumed that the membrane is a homogenous single-phase media, and the water transport is driven by activity gradient. However, if using the activity gradient as driving force, diffusion model cannot describe the water transport in fully hydrated conditions. It might be extended for application when $\lambda > 14$ if the Nafion® is like a water solvent and water content gradient is the driving force, as used by Ge et al. [24]. By Fick’s law
Here, $v_{w,\text{diff}}$ is the water velocity driven by diffusion; $d\lambda/dx$ is the gradient of $\lambda$ in $x$ direction; $M_w$ is the molecule weight of water; $c_{SO_3}$ is the mole concentration of the sulfonic acid group ions in Nafion®; $D_w$ is the diffusivity of water in Nafion®, which is a function of local water content of the membrane. Different values of water diffusion coefficient through Nafion® have been reviewed by Ge et al. [24], also shown in Figure 1-8. Obviously, there is significant variation in the experimentally measured values of this important parameter.

![Figure 1-8](image-url)

**Figure 1-8:** Diffusion coefficient $D_w$ as a function of water content of the membrane at different temperature [24]

Bernardi and Vebrugge [22] first proposed the hydraulic model, which is not suitable for the conditions of low humidity without liquid water. They treated the
membrane as a two-phase porous medium system, where the Darcy’s law applies.

\[
v_{w,\text{hyd}} = -k \frac{dp_w}{\mu \ dx}
\]  

[1.13]

Here, \( v_{w,\text{hyd}} \) is the water velocity driven by capillary pressure gradient; \( \mu \) is the viscosity of water; \( p_w \) is the water phase pressure; \( k \) is the permeability of the electrolyte membrane, which is also a function of water content.

Weber and Newman [18-19] proposed a hybrid model. Between unconnected clusters, water and hydrated proton flow is driven by an activity gradient in a diffusion mode. Whereas between clusters connected by water pathways, hydrated protons are conducted by the Grotthuss mechanism and diffusion, and water is transported by capillary pressure gradient and vehicular mechanism due to the proton hydration effect.

These two velocities are then weighted by the distribution of capillary tubes, with data from standard contact porosimetry.

The vehicular mechanism provides another type of water transport mechanism, the electro-osmotic drag. It is an interaction between the water molecules dissolved in the polymer and the protons being conducted through the polymer. The water flux by electro-osmotic drag is proportional to the proton flux under certain condition of hydration level, temperature, and so on. The relation can be written as

\[
v_{w,\text{elos}} = \lambda_{\text{drag}} \frac{i}{F}
\]  

[1.14]
Here, $v_{w,elos}$ is the water velocity driven by electro-osmotic drag; $\lambda_{drag}$ is the electro-osmotic drag coefficient, which indicates the number of water molecules dragged by each proton and is a function of temperature and with contact in the electrolyte. Dong [25] reviewed the measurement techniques and coefficient values from various literature. The value varies from 1.0 to 2.5 for $\lambda$ at the range of 0–22 $H_2O/\text{SO}_3^-$. Obviously, the two main water transport parameters through Nafion®, diffusivity and electro-osmotic drag coefficient still have large uncertainties.

1.2 Flow through PM

Fluid flow through PM is a common topic in engineering. Practical problems vary from chemical engineering, civil engineering, mechanical engineering, bioengineering and so on. For several decades of work, researchers have developed a theoretical framework on the subject.

This section will introduce the basic concepts for fluid flow through PM and the Immiscible Flow Model. For more details, please refer to reference books [26-27].

1.2.1 Fundamentals

PM is usually composed of a backbone material and void pores. The porosity is defined as $\varepsilon = (\text{total volume of voids})/(\text{bulk volume of PM})$. 
The porosity may change with pressure or temperature with respect to specific conditions. The fluid flowing through the PM can be gas, liquid or multiphase mixture. In the case of multiphase mixture, the saturation of fluid \( j \) is defined as \( s_j = \text{(volume of fluid} j \text{ in PM)/(total volume of voids)}, \) thus
\[
\sum s_j = 1 \tag{1.15}
\]

The interfacial tension \( \sigma_{jk} \) 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
\[
w_{jk} = \sigma_j + \sigma_k - \sigma_{jk} \tag{1.16}
\]

Figure 1-9 shows a droplet of liquid \( l \) on top of solid \( s \), equilibrated with gas \( g \). By balancing the surface tension, one can derive the Young’s equation, written as
\[
\cos \theta = (\sigma_{sg} - \sigma_{sl})/\sigma_{gl} \tag{1.17}
\]

If \( (\sigma_{sg} - \sigma_{sl})/\sigma_{gl} > 1 \), the liquid will spread indefinitely over the solid. The angle \( \theta \), is called the contact angle, and \( \sigma_{gl} \cos \theta \) is called the adhesion tension. If \( \theta < 90^\circ \),
the fluid is called wetting fluid. If \( \theta > 90^\circ \), the fluid is called non-wetting fluid.

The interface of two fluids is balanced by the pressure of the two fluids, together with the surface tension of the interface \( \sigma \). The capillary pressure \( p_c \) is defined as the pressure difference between the non-wetting and wetting fluids, known as the Laplace equation:

\[
p_c = p_{nw} - p_w = \sigma(1/r' + 1/r'') = 2\sigma/r
\]  \[1.18\]

Here, \( r' \) and \( r'' \) are the two principle radii of the interface, as shown in Figure 1-10. \( r \) is the mean radius, which is of the order of magnitude of the pore size.

---

Figure 1-10: Equilibrium at a curved interface [26]

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
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 1-11 shows two hysteresis effects. The ink-bottle effect takes place in pores with non-uniform width, as can be expected in DM and CL. Wetting an initially dry pore or drying an initially wet capillary pore gives two different stable configurations. The raindrop effect shows the different advancing and receding contact angles for a droplet on a declining surface. Hysteresis effects are observed in practical fuel cell operations [28].

\[
p_c = \frac{2\sigma}{r} = \left(\frac{2\sigma}{r^*}\right) \cos \theta
\]  

[1.19]

The process for wetting fluid replacing non-wetting fluid in a PM is called imbibition. The opposite process is called drainage. Figure 1-12 shows a typical capillary pressure and wetting fluid saturation relationship, \( p_c = p_c(s_w) \), during imbibition and drainage for a porous soil medium.
$s_{w0}$ 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, $s_{nw0}$ is called the residual saturation of the non-wetting fluid. Point A shows the bubbling pressure, $p_b$, which means the minimum pressure needed to initiate displacement of wetting fluid by non-wetting fluid.

Leverett [29] proposed a semi-empirical equation to relate the curves, ignoring hysteresis,

$$ J = J(s_w) = \left(\frac{p_c}{\sigma}\right)\sqrt{k/\varepsilon} $$  \hspace{1cm} [1.20]

Here, $\sqrt{k/\varepsilon}$ is the empirical mean pore diameter for a PM. The $J$-Leverett function is not unique because of hysteresis. Leverrett used
Some fuel cell models pick another type of Leverett function [30-31], which is based on the capillary tube model and thus includes the contact angle effect.

\[ J(s_w) = 1.417(1 - s_w) - 2.120(1 - s_w)^2 + 1.263(1 - s_w)^3 \] \[1.21\]

Brooks and Corey [32] proposed another approach. For \( p_c \geq p_b \),

\[ s_e = (p_b/p_c)^\gamma \] \[1.23\]

Where \( \gamma \) here is a factor called the pore size distribution index, determined by experiments, and \( s_e \) is the effective saturation, defined as

\[ s_e = (s_w - s_{w0})/(1 - s_{w0}) \] \[1.24\]

Permeability of a specific fluid \( j \) (could be \( w \) or \( nw \)) changes with the saturation of the fluid \( s_j \). The relative permeability \( k_r \) of fluid \( j \) is defined as

\[ k_{r,j} = k_j/k \] \[1.25\]

Figure 1-13 shows a typical relation of the relative permeability as a function of saturation. Brooks and Corey [31-32] proposed that the relative permeability can be related to the effective saturation,

\[ k_{r,w} = s_e^{(2+3\gamma)/\gamma} \] \[1.26\]

\[ k_{r,nw} = (1-s_e^2)(1-s_e^{(2+\gamma)/\gamma}) \] \[1.27\]

For fuel cell components, there exits no available experimental data of the relative
permeability as function of saturation. Estimations like \( k_{r,w} \propto s_w^3 \) have been used [30]. Also, when a measured value of permeability is unavailable, the Carman-Kozeny equation [33-34] can be used to make an estimate.

Figure 1-13: Typical relative permeability as a function of saturation [26]

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

[1.28]

Here, \( \tau \) is the tortuosity of the PM. This equation can be further simplified using the relation predicted by Salem and Chilingarian [35], which works for high porosity materials with porosity around 0.62 ~ 0.88, appropriate for PEFC materials.

\[
\tau = -2.1472 + 5.2438\varepsilon
\]  

[1.29]

1.2.2 The immiscible flow model for multi-phase flow through PM

The multiphase flow through PM is usually treated as immiscible fluids with the following assumptions [36]:
1) All continuous phases flow simultaneously and do not mix.

2) Every single phase follows its own tortuous path in the pore space.

For phase \( j \), if gravity effects are neglected, the flow rate can be derived through Darcy’s law,

\[
v_j = -k_{r,j} \frac{k}{\mu_j} \nabla p_j
\]

For mass balance,

\[
\frac{\partial (\varepsilon \rho_j s_j)}{\partial t} = -\nabla \cdot (\rho_j v_j) + S_{m,j}
\]

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. Plug in Darcy’s law and assume constant density, porosity, and isotropic PM, one can derive

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

For each phase involved, one can write down such a flow equation to describe the phase’s 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

\[
\frac{D(\rho C_p T)}{Dt} = \nabla \cdot (\kappa \nabla T) + S_h
\]

Here, \( \rho C_p \) and \( \kappa \) are averaged thermal parameters; \( S_h \) is the heat source
term. One approach to obtain the thermal parameters is to use volume averaging, as

\[ \sum_i \left( \varepsilon_i \rho_i C_{p,i} \right) \quad \text{and} \quad \sum_i \left( \varepsilon_i \kappa_i \right) \]. \( C_{p,i} \) is the heat capacity and \( \kappa_i \) is the thermal conductivity of component \( i \). So Equation 1.33 can be written as

\[
\frac{D}{Dt} \left[ \sum_i \left( \varepsilon_i \rho_i C_{p,i} \right) T \right] = \nabla \cdot \left[ \left( \sum_i \varepsilon_i \kappa_i \right) \nabla T \right] + S_h
\]

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 [37]. Then \( \nabla p_g = 0 \) and there’s only one phase flow equation. \( \nabla p_w \) is simply given by

\[
\nabla p_w = -\nabla p_c = -\frac{dp_c}{ds_w} \nabla s_w
\]

The water phase flow Equation 1.32 becomes the Richards equation.

\[
\frac{\partial s_w}{\partial t} + \nabla \cdot \left( k_{\text{r,w}} \frac{k}{\mu_w} \frac{dp_c}{ds_w} \nabla s_w \right) = \frac{S_{m,w}}{\rho_w}
\]

Wang and his students [31, 38-40] took another approach. They averaged the density, velocity, species concentration, enthalpy, and even pressure of the two phases. So they derived only one set of conservation equations for two phases. Their Multiphase Mixture Model (M² Model) strongly resembles the single-phase transport theory. Thus there are fewer nonlinear and coupled differential equations to be solved, but the
accuracy depends on the averaging method significantly, and when applied for freezing modeling, ice lens formation location cannot be found exactly. Recent developments in fuel cell modeling can be found in Lin and Nguyen [41] and Hwang [42].

1.3 Frost Heave in Soil Science

Soil science researchers have studied the phenomenon of frost heave continuously during the last century. The state-of-the-art understanding of the process is that temperature induced freezing changes the capillary force distribution in the soil and, in response, moisture redistributes and forms ice lenses, which can heave soil upward whenever certain criteria are met.

This section will introduce the physical basis of the phenomenon and how the theory was developed. Reviews from O’Neill [43] and Black and Haradenberg [44] are good references for further reading. Most recent developments can be found in Nakano [45], Michalowski and Zhu [46], and Yang et al. [47].

1.3.1 History

In initial research, the frost heave process was explained by the expansion of water during freezing. In 1920, Bouyoucos [48] first found that water in soils does not
freeze at one temperature. He postulated that the unfrozen water was due to the interaction between the mineral matrix and pore water. Schofield [49] presented a method to predict freezing point depression that was a function of negative pore-water pressure. After several decades, people examined the moisture transfer in freezing soils. In 1960, Kemper [50] showed that water transfer in unsaturated soils takes place in a thin liquid film that exists between adjacent soil particles. Later, Dirksen and Miller [51] found that the water transport is impeded by the presence of pore ice. Jame and Norum [52] measured the unfrozen water migration for unsaturated soil. Mizusaki and Hiroi [53] proved that fluids that contract upon freezing also produce heave. Also, it’s been observed that the ice lens layer is perpendicular to the direction of cooling in the specimen [53-54]. All these experimental results prove that thermal and mass transport phenomena play major roles during the process.

For theory development, Everett [55] suggested that the water transport during frost heave is due to the capillary rise, driven by the surface tension at the interfaces between ice and pore water. Based on a similar unfrozen water migration idea, Miller, O’Neill and Black [56-58] proposed a well-known saturated frost heave model, the rigid ice model. In their model, they proposed that the ice lens growing is due to the regelation process, or refreezing motion, as observed in experiments by Hoekstra and Miller [59].

The rigid ice model is based on the Generalized Clapeyron Equation (GCE),
developed by Loch [60-61]. The GCE describes the equilibrium between pore ice and unfrozen water distributed in the fringe. However, the validity of this relation has been argued along the development of the model. T. Forland and S. Ratkje [62] believed that irreversible thermodynamics rejected the suitability of GCE, though it is even more difficult to apply irreversible thermodynamics into frost heave modeling. Newman and Wilson [63] also proposed that the GCE does not apply to soils containing both capillary and adsorptive water forces. The GCE equation was later used by Selvadurai et al. [64] to set up a 3-D frost heave model. Most recently, Rempel et al. [65] modified the GCE by adding the disjoining pressure, through which they determined the fluid pressure from integral force balance.

Harlan [66] took another approach to model the saturated freezing. He used a hydraulic model and assumed that the permeability versus saturation relation is the same for a partially frozen soil and an unfrozen unsaturated soil. But experimental validation shows that the model predicted too much ice accumulated behind the frost front. Jame and Norum [52] modified the model by adding an adjustable impedance factor to the permeability expression to count for effects of ice. This correction was criticized as a “potent and wholly arbitrary correction function” by Black and Haradenberg [44].

However, the hydraulic model was later developed by several researchers and extended to model unsaturated freezing [52, 63, 67-70], because of its numerical
simplicity. The latest development of the model was by Newman and Wilson [63]. By using a functional relationship for permeability versus capillary pressure proposed by Fredlund et al. [71-72], Newman and Wilson claimed that they could calculate the exact water distribution with the exclusion of the impedance factor for calibrating the permeability function.

1.3.2 Capillary force balance of the three phases within PM

Usually, non-wetting fluid dominates larger pores and wetting fluid resides in smaller pores. For the wetting fluid, there is an adsorbed stage on top of the solid, composed of one or more molecular layers. For PM with hydrophilic backbone materials, the water is the wetting fluid. Ice formation is favored further away from the solid surface and the surface of the ice protrudes down into the pores with adsorbed water adjacent to it [73]. Figure 1-14 shows such a configuration of air-water and air-ice-water coexisting in a pore structure with hydrophilic material.

![Figure 1-14: Typical configuration of air-water and air-ice-water coexisting in a pore structure with hydrophilic material [74]](image-url)
PM is introduced here. By Antonov’s rule,

$$\sigma_{ai} = \sigma_{aw} + \sigma_{iw} \quad [1.37]$$

This implies that water is spreading on the surface of ice with a contact angle $\theta_{iw} = 0^\circ$. The surface tensions vary with temperature. The following values are suggested by Miller [74] for the soil frost heave temperature range: $\sigma_{aw} = 0.070 \text{ N/m}$, $\sigma_{iw} = 0.030 \text{ N/m}$, and $\sigma_{ai} = 0.100 \text{ N/m}$.

Koopmans and Miller [75] found the similarity between air-free ice-water interface and ice-free air-water interface, as shown in Figure 1-15.

![Figure 1-15: Similarity between air-free ice-water interface and ice-free air-water interface. The data are from (a) SLS soil sample and (b) SS soil sample with $\nabla$ representing freezing; $\circ$ representing drying; $\blacktriangledown$ representing drying; $\bullet$ representing wetting [75]]

For soils in which solid particles are always separated by an adsorbed liquid film (SLS soil), at the same $s_w$, capillary pressure follows

$$p_a - p_w = p_i - p_w \quad [1.38]$$

For soils in which all particles are normally in solid-to-solid contact with adjacent
particles (SS soil), at the same $s_w$, the capillary pressure follows

$$p_a - p_w = (\sigma_{aw}/\sigma_{lw})(p_l - p_w) \quad [1.39]$$

The best-fit data was obtained when

$$\sigma_{aw}/\sigma_{lw} = 2.20 \quad [1.40]$$

However, it’s questionable whether this can be extended for application of other soil type or hydrophobic PM backbone materials as primarily in PEFCs, since Equation 1.38 is based on the assumption of same osmotic pressure for air-water interface and water-ice interface, and Equation 1.39 is based on the assumption of same curvature for air-water interface and water-ice interface [74]. Actual soil type may fall in the range between these two types [63]. It is unknown whether the hydrophobic PM backbone materials in PEFCs will follow the theories. Also, backbone carbon fiber is hydrophilic, while coating is hydrophobic. These behaviors are not one relationship, and must be modeled at pore scale. This is a bulk approximation.

### 1.3.3 Characteristic curves

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

For freezing in PM, there is usually a freezing-point depression, as shown in the
Figure 1-16. 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 $r$.

Figure 1-16: Temperature change during freezing [76]

Figure 1-17 shows a typical curve for the unfrozen water content of soil as a function of temperature. This curve can be measured using several techniques, including differential scanning calorimetry (DSC) [76-79]. DSC has various applications [76-83] and has also been used to characterize the water composition in Nafion® membrane [84-89]. The sample with high water content had a broad melting peak range from $-30^\circ C$ to $10^\circ C$. Detailed discussion on how to extract the unfrozen water versus temperature curve through the DSC data is given in Appendix A.
Besides the unfrozen water versus temperature curve, another characteristic curve is needed to form a closed equation system. In the hydraulic model [52, 63, 66-70], the measured capillary force versus saturation curve is used. This type of curve has been introduced in Section 1.2. Whereas, in the rigid ice model [56-58], this curve is replaced by the GCE equation. The GCE equation was derived from Gibbs-Duhem equation and the chemical potentials equilibrium between water phase and ice phase [60-61].

\[
\frac{p_i}{\rho_i} - \frac{p_w}{\rho_w} = -h_{sf} \left( \frac{T - T_f}{T_f} \right) = -h_{sf} \left( \frac{\Delta T}{T_f} \right) \tag{1.41}
\]

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.

### 1.3.4 Models of frost heave in soil

#### 1.3.4.1 Rigid ice model

Miller and his students [56-58] proposed the rigid ice model to model the secondary frost heave in saturated soil, which was described by Miller [74]. 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 Figure 1-18.

![Comparison of (a) primary and (b) secondary frost heave](image)

Figure 1-18: Comparison of (a) primary and (b) secondary frost heave [74]

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 1-19 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 [57] 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 [74].

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: \( s_i, s_w, p_i, p_w, v_i, v_w, \) and \( T \).

For the porosity,

\[ s_i + s_w = 1 \]  \[ \text{[1.42]} \]

For ice and liquid water added together, the mass conservation equation is
The energy conservation equation is

$$
\frac{\partial (\sum_j \varepsilon \rho_j s_j)}{\partial t} + \nabla \cdot (\sum_j \rho_j \nu_j) = 0
$$

[1.43]

The energy conservation equation is

$$
\frac{D(\rho C_p T)}{Dt} = \nabla \cdot (\bar{K} \nabla T) + \rho \lambda_s \frac{\partial s_i}{\partial t}
$$

[1.44]

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

$$
\nu_w = -k_{r,w} \frac{k}{\mu_w} \nabla p_w
$$

[1.45]

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.

\[ v_i = v_{fh} \delta \gamma_i \] \hfill (1.46)

Here, \( v_{fh} \) is the frost heave rate. The boundary condition at the ice lens surface next to the frozen fringe is

\[ \rho_i v_{fh} = \rho_i v_i + \rho_w v_w \] \hfill (1.47)

Equation 1.42-1.47, combined with an empirical unfrozen water versus temperature curve, and the GCE equation, 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 reach the overburden pressure,

\[ P_{ovbd} = \chi P_w + (1 - \chi) P_i \] \hfill (1.48)

Here, \( \chi \) is a weighting factor, determined by experimental data, and \( P_{ovbd} \) is the overburden pressure, defined as

\[ P_{ovbd} = P_0 + g \int_0^z \rho(z) dz \] \hfill (1.49)
1.3.4.2 Hydraulic model

As introduced before, there are several unsaturated (air-water-ice three-phase system) models \([52, 63, 66-70]\) for freeze thaw based on Harlan’s hydraulic model. In his original work \([66]\), 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

\[
\frac{\partial (\varepsilon \rho_w s_w)}{\partial t} + \frac{\partial (\varepsilon \rho_i s_i)}{\partial t} = \nabla \cdot (\rho_w k_e \nabla p_e) \tag{1.50}
\]

Here, \(k_e\) is the effective permeability. To account for the reduced flow observed in the frozen zone, Jame and Norum \([52]\) introduced an arbitrary impedance factor

\[
k_e = k \times 10^{-E E_{i}} \tag{1.51}
\]

Here, \(E\) is the impedance factor. Gosnik et al. \([67]\) 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 \([63]\) claimed, by using the relationship for permeability versus suction proposed by Fredlund et al. \([71-72]\), 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 and assuming constant properties, \(s_w \sim T\), they obtained
\[
\varepsilon \frac{\partial s_w}{\partial T} \frac{\partial T}{\partial t} = \nabla \cdot (k_c \nabla p_c) - \varepsilon \frac{\rho_i}{\rho_w} \frac{\partial s_i}{\partial t}
\]  
[1.52]

Plug in this equation into the energy equation, Equation 1.44

\[
\frac{\rho C_p}{\partial T} \frac{\partial T}{\partial t} = \nabla \cdot (k \nabla T) + h_{sf} \rho_w \left[ \nabla \cdot (k_c \nabla p_c) - \varepsilon \frac{\partial s_w}{\partial T} \right] \frac{\partial T}{\partial t}
\]  
[1.53]

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

\[
\frac{\partial p_c}{\partial T} = \frac{\partial p_c}{\partial s_w} \frac{\partial s_w}{\partial T}
\]  
[1.54]

The energy equation can be converted to

\[
(\rho C_p + h_{sf} \rho_w \varepsilon \frac{\partial s_w}{\partial T}) \frac{\partial T}{\partial t} = \nabla \cdot (k \nabla T) + h_{sf} \rho_w \nabla \cdot (k_c \frac{\partial p_c}{\partial s_w} \frac{\partial s_w}{\partial T} \nabla T)
\]  
[1.55]

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 are no concepts of phase pressure. So it cannot directly use the overburden criteria for frost heave, as proposed by the rigid ice model.

1.3.4.3 Application into PEFC freezing

From the previous discussions, one can find that the hydraulic model is relatively straightforward to apply, but it cannot predict the ice lens formation well since it does not provide a mechanism for that. While for the rigid ice model, it expects the ice lens to form when the overburden pressure is overcome, which is more reasonable. However, it
only provides the phase pressure balance between ice and liquid water, which cannot
describe the influence of the air phase during unsaturated freezing. Thus, the rigid ice
model is only seen for frost heave modeling in saturated soil.

In a PEFC, when it shuts down, the DM is typically at an unsaturated status, but
with very non-homogeneous water distribution, with liquid water accumulation favoring
locations under the BP lands, as shown in Figure 1-20 [91]. Practically, it is also possible
that certain areas become saturated. So the model must incorporate the ice phase pressure
change and unfrozen water flow in both saturated and unsaturated domains. Thus, a new
hybrid model capable of dealing with these physics is needed.

Figure 1-20: Non-homogeneous water distribution in a PEFC, shown by Neutron Image
Technique [91]
1.4 Motivation for Study – PEFC Freezing Modeling

The freezing/thawing behavior of polymer electrolyte fuel cells (PEFCs) is an increasingly important topic in fuel cell science and technology based on recent published papers, presentations, and reports to date regarding freeze-thaw induced damage. [92-102] Pesaran et al. [100] summarized some of the most recent developments in this field. There exist some conflicting claims whether there is possible damage during the freeze-thaw operation. Some groups found no performance loss after freeze-thaw cycling. [95-97] Among them, Wilson et al. [95] cycled from –10 °C to 80 °C, while McDonald et al. [96] and Blair [97] cycled from –40 °C to 80 °C. Pivovar et al. [98] also cycled down to –40 °C and did not find performance loss, but when they cycled from –80 °C, they observed delamination of the catalyst layer from the membrane. Some other groups observed some damages. [92-94, 98-99, 101-102] Cho et al. [92-93] cycled from –10 °C to 80 °C. They found that, when the degradation is occurring, the cell impedance increased, and the active electrochemical area decreased concomitant with increasing pore size in the catalyst layer. They concluded that the degradation is related to the residual water in the PEFC. After purging the PEFC, or supplying an anti-freezing solution after cell shutdown, they found the short-term degradation could be prevented. Hottinen [94] also observed irreversible performance loss due to internal water freezing
for a free-breathing PEFC operating at –15 °C, when the heat generated by reaction is not sufficient to prevent freezing. Meyers [99] cycled from –20 °C and observed membrane failure and catalyst delamination from the membrane. Gaylord [101] also showed pictures illustrating membrane failure and breakthrough of the carbon paper after freeze-thaw tests. Similar results on physical damage to diffusion media and catalyst layer materials have also been reported by Guo and Qi [102]. In this thesis, it is hypothesized that the current lack of comprehensive modeling or experimental data to explain the difference is probably the factor differentiating these seemingly conflicting results. Most recently, Patterson reported an interesting phenomenon, which is termed “end cell effects” [103]. He observed performance loss after freeze-thaw cycles, occurring specifically to the anode end cell of a stack, which is another topic to be discussed in this thesis.

As introduced before, the PEFC has a 5-layer structure of DM|CL|Nafion®|CL|DM. The DM and CL are PM and Nafion® can be considered as a special solid-phase water solvent. Similar to frost heave in soil, capillary forces could play a major role during the freeze-thaw process in PEFCs, which means that the moisture could migrate during the freezing process and form ice lenses in specific areas.

The process of freezing a PEFC can be divided into four major steps. Though all the steps can be described as multiphase flow through PM, the actual steps include unsaturated water-vapor flow and unsaturated water-ice flow.
1. The first step is fuel cell operation at normal conditions. This process includes multiphase (water, vapor) and multi-component (H₂, O₂, N₂, H₂O) mass and heat transfer, together with the electrochemical reactions. The liquid capillary pressure distribution has been studied [31] and the two-phase flow has been modeled by several researchers [38-42, 104-108]. Experimental and modeling results both show there are certain areas that are prone to flood, usually at the corner under the lands [91].

2. The second step is cooling down process after the cell is shut down, together with the purging process, which may last from several minutes to several hours depending on the protocols. Droplets in the flow channels are removed, but the remaining liquid water could re-distribute within the diffusion media and MEA.

3. The third step is the freezing process. Since water might redistribute during purging, the operation history must be considered. Also, the overburden pressure and porosity are different below the lands and the channel. There will also be temperature gradient perpendicular to the assembling direction within the MEA, which will drive moisture transport and ice lens growth.

4. The final step is the thaw process. This step should be less complex in physics than the third step, since the fuel cell starts in very short time (a few minutes) and the coupled unfrozen water flow can be neglected. It is thus a basic heat
conduction problem with moving boundary.

The third step, freezing process may cause several problems to a PEFC, as shown in Figure 1-21. Ice lens could possibly grow in position 1~5. The following listed the possible mechanisms for performance degradation.

Figure 1-21: Schematic showing the potential locations of freeze/thaw damage

Position 1~4: Freezing of the residual water can block the flow channels and prevent reactants reaching catalyst layer.

Position 1~5: Freezing ice could increase the thermal mass of the total system and slow down the heat-up process.

Position 2~4: The freezing and ice lens forming could increase the electrical/thermal contact resistance by delaminating the interfaces of DM|BP, DM|MEA, or CL|Nafion®.

Position 4: The process could reduce the active electrochemical surface area by damaging the catalyst layer.
Position 5: The freezing of Nafion® membrane could damage the membrane structure and increase the crossover rate of reactants.

The possible frost heave process in PEFC will be more complex than in soil. There are two consolidated porous materials with very different material properties, under uneven overburden pressure, and a plastic water solvent that can expel water with decreasing temperature. The condensation and evaporation can be neglected due to the low vapor pressure at low temperature. Usually, consolidated materials make it difficult for ice lens to initiate within. So an ice lens can grow more easily at the interface of the materials, such as between the CL and DM. Unevenly distributed overburden pressure also influences the ice lens formation. The ice lens tends to initiate in areas with low overburden pressure, such as areas under channels in PEFCs. Thus, a likely ice lens location is in position 3 or 4 in Figure 1-21.

The goal of this study is to formulate and encode a 1-D model for the frost heave process, predict the ice lens formation position and rate, and provide physical explanations to current test results by different groups. The ultimate motivation is to propose methods to prevent the damage based on the simulation results.
CHAPTER 2  1-D TRANSIENT MODEL FOR FROST HEAVE IN PEFCS:

MODEL FORMULATION

In this chapter, a 1-D transient model has been formulated based on theories of porous media flow and soil frost heave. The model is essentially a modified hybrid of Harlan’s hydraulic model and Miller’s rigid ice model with additional improvements for suitable application to PEFCS. Methods to derive three types of characteristic curves for unfrozen water flow and frost heave modeling are also given. Two modes of physical damage are proposed.

2.1 Introduction

Based on current literature on freeze/thaw damage [92-94, 98-99, 101-102], three physical modes of damage can be documented: 1) membrane failure, 2) delamination between membrane and catalyst, and 3) breakthrough of the diffusion media. However, even the fundamental mechanisms that cause these modes of damage during freeze-thaw cycling are still unclear. One of the goals of this chapter is to explain the last two modes of degradation so that suitable mitigation can be achieved.

As introduced in Chapter 1, soil researchers have studied the frost heave
phenomenon continuously during the last century. Frost heave occurs during the winter and early springtime in cold climates. The noticeable heaving induces uneven support of pavement, forming cracks in the pavement surface layer, which look similar to the “mudcracking” that was observed in the diffusion media and catalyst layer in some PEFC tests. [98-99, 101]

Frost heave is divided to primary heave and secondary heave, depending on whether there is a frozen fringe. As shown in Figure 2-1, the frozen fringe is a two-phase zone where ice content increases from 0% at the freezing front to 100% at the location of the latest lens. [74] The temperature-induced freezing changes the capillary force distribution in the soil and, in response, moisture redistributes and is transported to the freezing front, forming ice lenses. The growth of lenses below the soil surface can heave soil upward whenever certain criteria are met.

![Comparison of (a) primary and (b) secondary frost heave](image-url)

**Figure 2-1**: Comparison of (a) primary and (b) secondary frost heave, following ref. [74]
Two models were developed to model the frost heave process. The hydraulic model [52, 63, 66-67, 69-70] is relatively straightforward to apply, but it cannot predict the ice lens formation well, since it does not include a physical mechanism. For the rigid ice model [56-58], ice lens formation occurs when the overburden pressure is overcome, which is more reasonable. The overburden pressure is a term used in geology to denote the pressure on the ice lens induced by soil weight, since an ice lens will bear the full load being lifted by heave. [57] However, this model only provides the phase pressure balance between ice and liquid water, which is not sufficient to describe the influence of the air phase during unsaturated freezing. Thus, the rigid ice model is useful only for frost heave modeling in completely saturated porous media, while both saturated and unsaturated domains would exist in a typical PEFC diffusion media and catalyst layer.

In this study, a 1-D transient model for the frost heave process in a PEFC was formulated. The model is 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 are integrated into the model. Additionally, methods to derive these characteristic curves for PEFC diffusion media and catalyst layer, which are critical to the simulation, are given in this chapter. Ultimately, this model can be used as a tool to help understand and eventually help mitigate the damage during the freezing process.
2.2 Model Formulation

In a PEFC, upon shut down, the diffusion media is typically partially saturated, but with very non-homogeneous water distribution, and liquid water accumulation favoring locations under the landings of bipolar plates. [91] During freezing, it is possible that certain areas become saturated and ice lenses grow. So the model must incorporate the ice lens initialization in the fully saturated domain, and unfrozen water flow in the unsaturated domain. Thus, a new hybrid model capable of dealing with these physics is needed, and has been formulated.

2.2.1 Model assumptions

The following assumptions are made for this model: 1) It is a 1-D transient model. A BP|BP-CH|DM|CL|Nafion® structure is considered here, as shown in Figure 2-2.

![Figure 2-2: 1-D model PEFC geometry](image)

The diffusion media (DM) and catalyst layer (CL) are considered as porous media, and the Nafion® (NF) membrane is considered to be a water solvent. Bipolar plate (BP) is considered as a solid. The BP-CH represents the 2-D bipolar plate-channel structure,
which is reduced to a 1-D heat conductor here. The diffusion media, catalyst layer, and Nafion® materials are considered homogeneous and isotropic. Also, there is no freezing induced deformation. 2) Gravity effects can be neglected, compared to the capillary effects in porous media, since through scale analysis, \( \rho g (4/3) r^3 \ll (2\sigma/r)(\pi r^2) \) for materials in PEFC. The multiphase flow in porous media is treated as immiscible, so all continuous phases flow simultaneously through their own tortuous path in the pore space. 3) Around and below freezing temperature, the vapor phase pressure is very small and changes little with temperature, which is much different from the case at the 353 K. So it is assumed that there is no transport of water vapor. The condensation/vaporization source term and vapor diffusion are neglected. Additionally, without current flow, there is no electro-osmotic transport of water. 4) The porous media can be divided into the saturated domain and the unsaturated domains. In the unsaturated domain, air phase pressure is assumed to be constant, since there is no significant flow-induced pressure drop for the air phase. In the saturated domain, it is proposed that the ice lens will appear when the ice phase pressure overcomes the overburden pressure, which will be discussed later. No regelation, or ice flux is considered in our model. Instead, the ice lens growth is assumed to be caused by the unfrozen water flow into the ice lens. In this way, both the primary frost heave and secondary frost heave can be modeled. Whether the frost front will propagate depends on the balance between the rate of heat loss and unfrozen water
flow. 5) The unfrozen water versus temperature curve for the Nafion® domain is derived from the best available differential scanning calorimetry (DSC) data for Nafion®. For the diffusion media and the catalyst layer, this curve is calculated using a freezing temperature depression relation and the pore-size distribution. It is assumed that there is always a liquid-like film on the surface of ice, which means the liquid is always the wetting fluid for ice-water flow, even though the backbone material can be mostly hydrophobic. This enables the expected freezing point depression in the hydrophobic porous media. 6) The Nafion® membrane is treated with a pure diffusion model. The diffusion model is chosen based on availability of experimental water diffusivity data. The water content of the membrane, $\lambda$, is defined as the number of moles of water associated with a mole of sulfonic acid group in the membrane. By using the gradient of $\lambda$ as the driving force, the diffusion model can be used for the whole range of $0 < \lambda < \lambda_0 = 22 \text{ H}_2\text{O}/\text{SO}_3^-$. Actually, if the Nafion® can be considered as a porous media with free water at a high water content, (i.e. $22 > \lambda > 14$), through the capillary relation for a two-phase flow in porous media, it can be shown that $\nabla p_w \sim (\tilde{\phi}_w / \tilde{\phi}_w) \nabla s_w \sim \nabla \lambda$. Thus the hydraulic-type model can be simplified to a diffusion-type model, providing unification of the two approaches. When the Nafion® is fully saturated ($\lambda = 14$), the hydraulic-type model is actually the same as a single-phase flow in porous media.
2.2.2 Mass/flow equations

The mass/flow equation differs between porous media domains and Nafion® domain. The porous media domains include diffusion media and the catalyst layer. The saturation of air, water, and ice phases, $s_a$, $s_w$, and $s_i$, respectively have the following relationship:

$$s_a + s_w + s_i = 1 \quad [2.1]$$

From immiscible flow theories, for water phase, the flow equation can be written as: [36]

$$\varepsilon \rho_w \frac{\partial s_w}{\partial t} = \rho_w \nabla \cdot (k_{r,w} \frac{k}{\mu_w} \nabla p_w) + S_{m,w} \quad [2.2]$$

Here, $\varepsilon$ is the porosity, $k$ is the intrinsic permeability, $k_{r,w}$ is the relative permeability of the water phase, which changes with the saturation of the water and is defined as $k_{r,w} = k_w / k$ [109], $\mu_w$ is the viscosity of water, $p_w$ is the water phase pressure, and $S_{m,w}$ is the mass source term for water phase. For the ice phase, a similar equation can be written. The gas phase equation is neglected, since gas pressure is assumed to be constant, $p_a = p_{ch}$. Also by assumption, there is only water mass transfer between ice and liquid interfaces. So when the flow equations of ice and water phases are added together, the source terms cancel and one can derive the following:
The rigid ice model [56-58] assumed a constant ice flux rate, $v_i$, which means $(k_{r,i}/\mu_i)\nabla p_i$ is constant and $\rho_i \nabla \cdot [(k_{r,i}/\mu_i)\nabla p_i] = 0$. The hydraulic model [52, 63, 66-67, 69-70] neglects ice flux, therefore $\rho_i \nabla \cdot [(k_{r,i}/\mu_i)\nabla p_i] = 0$. So both approaches give the same result:

$$\varepsilon \rho_i \frac{\partial s_i}{\partial t} + \varepsilon \rho_w \frac{\partial s_w}{\partial t} = \rho_i \nabla \cdot (k_{r,i} \frac{k}{\mu_i} \nabla p_i) + \rho_w \nabla \cdot (k_{r,w} \frac{k}{\mu_w} \nabla p_w)$$

[2.3]

The relativity permeability of water phase is usually a function of water saturation, e.g. $k_{r,w} = s_w^3$. In frost heave literature, it's usually a function of saturations of both water and ice phase.

$$k_{r,w} = f(s_w, s_i)$$

[2.5]

In this model, the relative permeability from Jame and Norum [52] or O’Neill and Miller [57] may be most appropriate, considering a lack of experimental data. However, other formulations exist. The proper formulation is not yet known for fuel cell applications. Jame and Norum [52] added an impedance term to account for the influence of the ice phase, $k_{r,w} = 10^{-E_{0s}}s_w^3$. Here, $E$ is the impedance factor and should be around 8~10 for PEFC material, based on the estimation by Gosnik et al. [67]. O’Neill and Miller [57] used $k_{r,w} = s_w^9$.

For the boundary conditions, it is assumed that the water migration rate is zero.
when the diffusion media is next to the bipolar plate, \( v_{w,BC} = 0 \). When the diffusion media is adjacent to the gas channel, the water phase pressure is the same as the pressure in the channel, \( p_{w,BC} = p_{ch} \). For interfaces between different porous media layers and the interface between saturated and unsaturated domains, the phase pressure and flow flux are continuous, which means \( p_{w,1} = p_{w,2} \) and \( v_{w,1} = v_{w,2} \) for the neighboring grid 1 and 2.

For the Nafion® domain, water transport has been modeled by many groups. Typically, there are three mechanisms: electro-osmotic drag, diffusion, and capillary flow. During the freezing process, there is no electro-osmotic drag driven by the current flow. In the present model, a pure diffusion model [5,20-21] is used for the Nafion® domain, as introduced in the assumptions:

\[
\frac{\partial c_w}{\partial t} = \nabla \cdot (D_w \nabla c_w) \tag{2.6}
\]

Here, \( D_w \) is the diffusivity of water in Nafion® and \( c_w \) is the water concentration, satisfying \( c_w = \lambda c_{acid} \). \( c_{acid} \) is the molar concentration of sulfonic acid groups in Nafion®.

It has long been established that there are three types of water in Nafion®: strongly bound, loosely bound, and free water.[12] The strongly bound water is also the un-freezable water. In the present study, only freezable water is considered. By introducing \( \lambda = \lambda_w + \lambda_l + \lambda_i \), water in Nafion® can be divided into un-freezable phase,
freezable water phase, and ice phase. The un-freezable water content, \( \lambda_u \), is taken as 2.2 H\(_2\)O/SO\(_3^-\). [87] If the Nafion\textsuperscript{®} is not freezing, the governing equation is:

\[
\frac{\partial \lambda_w}{\partial t} = \nabla (D_w \nabla \lambda_w) \tag{2.7}
\]

As water in the Nafion\textsuperscript{®} starts to freeze, it becomes:

\[
\frac{\partial (\lambda_w + \lambda_i)}{\partial t} = \nabla (D_w \nabla \lambda_w) \tag{2.8}
\]

There are two choices on the boundary condition between the porous domain and Nafion\textsuperscript{®} domain. It can be set to include the effects of Schroeder’s paradox, which is explained by Zawodzinski et al. [17]. When the water saturation of the catalyst layer is positive, \( s_w > 0 \), the membrane is considered to be equilibrated with liquid water with \( \lambda_w + \lambda_i = 22 \). When \( s_w = 0 \), the boundary condition is \( \lambda_w + \lambda_i = 14 \). The second choice is \( \lambda_w + \lambda_i = 14 + 8s_w \).

### 2.2.3 Energy equations

The energy equations have different forms, depending on position. The 1-D energy equation for the BP and BP-CH domain is:

\[
\rho C_p \frac{\partial T}{\partial t} = \frac{\partial}{\partial x} (\kappa \frac{\partial T}{\partial x}) \tag{2.9}
\]

Here, \( \rho \), \( C_p \), and \( \kappa \) are density, heat capacity, and heat conductivity of the BP or BP-CH domain. The boundary conditions of the fuel cell with the environment can be natural convection or forced convection (e.g. coolant flow) with the heat transfer
coefficient \( h = h_{NC} \) or \( h_{FC} \).

In porous media domain, the energy equation is written as:

\[
\frac{D(\rho C_p T)}{Dt} = \nabla \cdot (\kappa \nabla T) + h_s \frac{D(\varepsilon \rho_s \varepsilon_s)}{Dt}
\]  \[2.10\]

Thermal properties are calculated as a mixture:

\[
\overline{\rho C_p} = (\rho_w C_{p,w} s_w + \rho_i C_{p,i} s_i + \rho_a C_{p,a} s_a) \varepsilon + \rho_{pm} C_{p,pm} (1 - \varepsilon)
\]  \[2.11\]

\[
\overline{\kappa} = (\kappa_w s_w + \kappa_i s_i + \kappa_a s_a) \varepsilon + \kappa_{pm} (1 - \varepsilon)
\]  \[2.12\]

Here, the subscript \( pm \) represents both diffusion media and catalyst layer. With the assumptions, there is no ice or gas flux, \( v_i = v_a = 0 \). In addition, the porous media structure is fixed, \( v_s = 0 \). The energy equation in the porous media domain simplifies to:

\[
\frac{\partial (\overline{\rho C_p} T)}{\partial t} + \rho_a C_{p,w} \nabla \cdot (v_w T) = \nabla \cdot (\overline{\kappa} \nabla T) + h_s \varepsilon \rho_s \frac{\partial \varepsilon}{\partial t}
\]  \[2.13\]

The boundary conditions between different domains are continuous, with

\( q_{dm,BC} = q_{bp-ch,BC} \) and \( T_{dm,BC} = T_{bp-ch,BC} \).

In the Nafion® domain, similarly, the thermal properties can also be calculated as a mixture. By averaging based on dry Nafion® volume, the energy storage coefficient is:

\[
\overline{\rho C_p} = c_{Sol} M_w [\lambda_w + \lambda_a] C_{p,w} + \lambda_i C_{p,i} + \rho_{nf} C_{p,nf}
\]  \[2.14\]

Here, \( M_w \) is the molecular weight of water. The averaged thermal conductivity is:
The conductivity of the mixture, $\overline{\kappa}$, changes more with the ice than water content, since the ice has a much higher conductivity, 1.88 W/m·K compared to 0.57 W/m·K for water. While the thermal mass parameter, $\overline{\rho C_p}$, depends more on water content, which has a value of $4.22 \times 10^6$ J/m$^3$·K, much higher than ice phase, $1.88 \times 10^6$ J/m$^3$·K. This conclusion is also valid for the thermal parameters of porous media domain.

The energy equation with volume averaged property in the Nafion® domain is:

$$\frac{\partial (\rho C_p T)}{\partial t} + \rho_w C_{p,w} \nabla \cdot (v_w T) = \nabla \cdot (\overline{\kappa} \nabla T) + h_d c_{SO_i} M_w \frac{\partial \lambda_i}{\partial t}$$  \[2.16\]

When an ice lens grows in the diffusion media, catalyst layer, or between interfacial layers, it will also influence the local heat transfer. Figure 2-3 shows the case when ice lens (IL) grows between diffusion media (DM) and catalyst layer (CL). $v_1$ and $v_2$ are the water flow rate coming into/out the ice lens, $q_1$ and $q_2$ are heat flux coming into/out the ice lens, $T_1$ and $T_2$ are temperatures at boundaries of ice lens, and $\delta_{il}$ is the thickness of the ice lens. The corrected heat flux is given by:

$$q_1 = -\kappa_i \frac{T_2 - T_1}{\delta_{il}} - \rho_w h_g v_1 + \frac{\rho_i C_{p,i} \delta_{il}}{4} \frac{\partial (T_1 + T_2)}{\partial t}$$  \[2.17\]

$$q_2 = -\kappa_i \frac{T_2 - T_1}{\delta_{il}} - \rho_w h_g v_2 - \frac{\rho_i C_{p,i} \delta_{il}}{4} \frac{\partial (T_1 + T_2)}{\partial t}$$  \[2.18\]
Figure 2-3: Heat conduction for case with ice lens

The ice lens growth rate is determined by:

\[ \frac{d\delta_d}{dt} = v_1 - v_2 \]  

[2.19]

### 2.2.4 Characteristic curves

The rigid ice model [56-58] and the hydraulic model [52, 63, 66-67, 69-70] use two of three characteristic curves: 1) the GCE thermodynamic relation; 2) the capillary pressure versus saturation curve; 3) the unfrozen water versus temperature curve. The rigid ice model uses curve 1) and 2), while the hydraulic model uses curves 2) and 3). From soil science studies, calculation results for both models are in reasonable agreement with experimental results, although the thermodynamics of GCE in the rigid ice model, and in the hydraulic model the permeability impedance factor and similarity on capillary relation have been scrutinized.

In the present model, the following characteristic curves are used for the porous media domain: the unfrozen water versus temperature curve for both saturated and
unsaturated domain; the GCE relation for both saturated and unsaturated domain; the water/air capillary relation for unsaturated domain. Only the unfrozen water versus temperature curve is needed for the Nafion\textsuperscript{®} domain, since it is treated as a water solvent.

The capillary relation between the air phase and water phase is: \[ p_{ch} - p_w = \sigma_{aw} \cos \theta_{aw} \sqrt{\varepsilon/k} J(s_e) \] \[
\text{[2.20]}
\]

Here, $\sigma_{aw}$ is the surface tension of air-water interface, $\theta_{aw}$ is the contact angle, and $s_e$ is the effective saturation, $\frac{s_w/\left(1-s_i\right) - s_{w0}}{1-s_{w0}}$. The J-Leverett function, $J(s)$, considering a lack of experimental data, is assumed to be: \[ J(s) = \begin{cases} 
1.417(1-s) - 2.120(1-s)^2 + 1.263(1-s)^3 & \text{wetting fluid} \\
1.417s - 2.120s^2 + 1.263s^3 & \text{nonwetting fluid} 
\end{cases} \] \[
\text{[2.21]}
\]

However, no experimental validation of this J-Leverett function for thin-film media of PEFC has been published.

The phase pressure balance between ice and water phases are represented by the GCE, in which $h_{sf}$ is the heat of fusion and $T_f$ is the freezing temperature:

\[
\frac{p_i - p_w}{\rho_i \rho_w} = -h_{sf} \left( \frac{T - T_f}{T_f} \right) = -h_{sf} \frac{\Delta T}{T_f} \] \[
\text{[2.22]}
\]

The unfrozen water content in soils decreases continuously with temperature. The finer grained a soil is, the greater the freezing point depression from bulk value. This relation for the Nafion\textsuperscript{®} membrane can be extracted from Nafion\textsuperscript{®}'s DSC data.
Differential scanning calorimetry (DSC) is one of the methods to measure the unfrozen water versus temperature curve in soil science. [76-79] Also, it has been used to characterize the water composition in Nafion® membrane. [84-89] Detailed discussions on the methods to derive this curve are shown in Appendix A. Figure 2-4 shows the unfrozen water versus temperature curves from literature [84, 88-89] deemed usable for this purpose.

![Figure 2-4: Unfrozen water versus temperature curves derived from Nafion® DSC data of refs. [84, 88-89]](image)

The empirical equation derived from the data in Figure 2-4 is:

\[
y = \begin{cases} 
  0 & x < -1 \\
  1 + 5.4x + 11.9x^2 + 11.6x^3 + 4.1x^4 & -1 \leq x < 0 \\
  1 & 0 \leq x 
\end{cases}
\]  \hspace{1cm} [2.23]

With \( x = (T - T_f)/\Delta T = (T - T_f)/24.5 \) and \( y = \lambda^u/(\lambda_0 - \lambda^u) = \lambda^u/19.8 \).

For the diffusion media and catalyst layer, the unfrozen water versus temperature
curve can be calculated using their pore size distribution and the freezing temperature depression relation. Through scale analysis, the GCE can be reduced through the following steps.

\[
\frac{\Delta T}{T_f} = -\frac{1}{h_{sf}} \left( \frac{p_i - p_w}{\rho_i} \right) \sim -\frac{1}{h_{sf}} \frac{p_i - p_w}{\rho_i} \sim -\frac{1}{h_{sf}} \frac{p_c}{\rho_i} \sim -\frac{2\sigma_{sw} \cos \theta_{hw}}{h_{sf} \rho_i r^*} \tag{2.24}
\]

This is actually the Gibbs-Thomson equation, which can also be derived from the Gibbs-Duhem equation, but through a different approach. This relationship has been used to determine the crystallization temperature of substance in a confined structure. [110]

With pore size distribution for Toray® carbon paper [111], one can calculate the volume \(\Delta V\) of pores with a specific range of \(\Delta r^*\), in which water has a temperature depression of \(\Delta T\), calculated by Equation 2.24. After integration, the predicted unfrozen water versus temperature characteristic curve can be obtained, as shown in Figure 2-5. Equation 2.23 can also be used here as an empirical curve with \(x = (T - T_f)/\Delta T = (T - T_f)/0.007\), where \(\Delta T\) is calculated by a pore size of 7 \(\mu\)m, and \(y = s_w/s_0 = s_w/1.0\). Similarly, one can use the same equation for catalyst layer with \(\Delta T = 0.49\) K, assuming a pore size of 90 nm. The \(\Delta T\) value used for Nafion®, 24.5 K, actually is equal to the prediction when the Nafion® is treated as a porous media with a pore size of 2 nm.
Figure 2-5: Predicted freezing temperature distribution using pore size distribution data of carbon paper (Toray® TGP-H-060) of ref. [111]

The unknowns of the three characteristic curves are characteristic pressure, \( p^* \), (capillary pressure in capillary relation, \( p^* = p_c = p_i - p_w \) for saturated freezing with only water and ice phases, and \( p^* = p_{GCE} = p_i/\rho - p_w/\rho \) in GCE), saturation of wetting fluid \( s_w \), and temperature \( T \). \( p_c \) is usually a function of both \( s_w \) and \( T \). [112-113] By constructing the unfrozen water relation (Equation 2.23), and capillary pressure relation with \( s_c = s_w \) (Equation 2.20 and 1.21), in a \((p_c, s_w, T)\) space, one can derive the curve \( p_c(s_w, T) \), shown in Figure 2-6. This type of curve has been derived by Haeupl and Xu [112]. They used the curve to calculate the maximum unfrozen water as a function of temperature and water saturation in concrete block.
Figure 2-6: Dependence of capillary pressure on water content and temperature, in which \(-\times\)- represents the unfrozen water versus temperature curve, \(-\circ\)- represents the capillary pressure versus saturation curve, \(-\square\)- represents the thermodynamic relation, the unmarked one is the \(p_c(s_w,T)\) curve.

During freezing, the capillary pressure follows both the capillary force versus saturation curve \(p_c \sim s_w\) and the unfrozen water versus temperature curve \(s_w \sim T\). The importance of the curve is that it will be following a \(p_c \sim T\) relation, which was not discussed by Haeupl and Xu. It actually represents a thermodynamic relation similar to GCE. However it is not exactly the GCE. If one used the GCE \(p_{GCE} = \left(p_i/\rho_i - p_w/\rho_w\right) \sim T\) and \(s_w \sim T\) curve, a similar \(p_{GCE}(s_w,T)\) can be drawn. \(p_c(s_w,T)\) and \(p_{GCE}(s_w,T)\) differ because \(p_c \sim s_w\) and \(s_w \sim T\) are all empirical curves, and data points were fit using \(p_c = p_i - p_w\), instead of \(p_{GCE} = p_i/\rho_i - p_w/\rho_w\).

By further studying the situation for hydrophilic and hydrophobic porous media, they will
have similar curves, which means the liquid phase is always the wetting fluid even for hydrophobic porous media. This result is very compatible with the modern premelting theory [114-115] that there is always a liquid-like film on top of ice with thickness depending on temperature, and thus water trapped in porous media always has a freezing temperature depression. This was also observed through experiments by Sage and Porebska [116], in which hydrophobic and hydrophilic soil samples with same grain size distribution have similar freezing temperature depression.

Thus, for saturated freezing, the three types of characteristic curves actually represent a single relation, \( p^*(s_w, T) \). So it is not unexpected that the rigid ice model and the hydraulic model can both give accurate simulation results, since they interpret the same physics differently by using two of the three characteristic curves. Together with the saturation relation (Equation 2.1), flow equation (Equation 2.4), and energy equation, (Equation 2.10), a closed system for five unknowns can be formed for a saturated system. For the rigid ice model, the unknowns are \( p_w, p_i, s_w, s_i, \) and \( T \). The frost heave rate, \( v_{fh} \), is calculated by assuming an additional boundary condition, constant ice flux. For the hydraulic model, the unknowns are then \( p_c, s_w, s_i, T, \) and \( v_{fh} \). By modifying the flow equation (Equation 2.4), the frost heave rate can also be solved, though this approach has not been published to our knowledge. Harlan [61] only used one characteristic curve for his saturated model, so his model is not able to solve the frost
heave rate.

For an unsaturated system, there is an additional unknown, $s_a$. The hydraulic model is able to deal with the problem by solving a system of $p_c$, $s_w$, $s_i$, $s_a$, and $T$, since ice lens is not supposed to appear in unsaturated zone and $v_{fb}$ can be neglected. The rigid ice model has not been applied in unsaturated zone. In this study, their concept of phase pressure and similar frost heave initialization criteria are used, which will be discussed next. The PEFC system modeled then has seven unknowns: $p_w$, $p_i$, $p_a$, $s_w$, $s_i$, $s_a$, and $T$. By assuming constant gas phase pressure and using the capillary relation between air and water phase (Equation 2.20), one can extend the rigid ice model for the unsaturated case of the PEFC diffusion media and catalyst layer with seven equations total.

### 2.2.5 Ice lens initialization

The initialization of ice lens occurs when the ice pressure reaches the local overburden pressure, $P_{ovbd}$. The concept of overburden pressure here is actually a critical ice lens formation pressure. Only when the ice phase pressure is greater than the critical ice lens formation pressure, the ice lens can initialize.

$$P_{ovbd} = p_i$$ \[2.25\]

This also serves as the boundary condition for the capillary flow at ice lens
surface. The local overburden pressure will depend on the location. All the possible cases for overburden are listed in Table 2-1, where \( P_{\text{assm}} \) is the assembling pressure for PEFC, \( \sigma_s \) is the material tensile strength, and \( \tau_{sh} \) is shear stress, generated by the diffusion media deformation in the through-plane direction, which also depends on the ice lens thickness.

<table>
<thead>
<tr>
<th>Position</th>
<th>Under BP</th>
<th>Under CH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Within diffusion media (DM), catalyst layer (CL), or Nafion®</td>
<td>( P_{\text{ovbd}} = P_{\text{assm}} + \sigma_s + P_{ch} )</td>
<td>( P_{\text{ovbd}} = P_{ch} + \sigma_s + \tau_{sh} )</td>
</tr>
<tr>
<td>At interface between bipolar plate (BP)</td>
<td>DM, DM</td>
<td>CL, or CL</td>
</tr>
</tbody>
</table>

### 2.3 Discussion

The freezing process may cause several problems to a PEFC. Possible ice lens positions are shown in Figure 2-7. Ice could block the flow channels and prevent reactants reaching catalyst layer; increase the thermal mass of the total system and slow down the heat-up process; increase the electrical/thermal contact resistance by delaminating the interfaces of PEFC components; reduce the active electrochemical surface area by damaging the catalyst layer; or increase the crossover rate of reactants by damaging the membrane structure.
2.3.1 Predictions on ice lens location (Why diffusion media can suffer breakthrough damage)

By Equation 2.20 and Equation 2.21, $|p_0 - p_w| = \sigma_{aw} \cos \theta_{aw} \sqrt{\varepsilon/k} J(s_e) < 0.6 \sigma_{aw} \sqrt{\varepsilon/k}$. For typical diffusion media $k = 5.5 \times 10^{-11}$ m$^2$ and $\varepsilon = 0.7$, $[111]$ together with $\sigma_{aw} = 0.07$ Pa·m$^2$ and $0.35 \text{ MPa}$. For catalyst layer, there is no published data for permeability. By using Carman-Kozeny equation, $k = \frac{(r^*)^2 \varepsilon^3}{18 \tau (1 - \varepsilon)^2}$, with $\varepsilon = 0.7$, $r^* = 270$ nm, and $\tau = 1.52$, $[35]$ it is estimated $k = 1.0 \times 10^{-14}$ m$^2$ and $|p_0 - p_w| < 0.35 \text{ MPa}$. So the water phase pressure should be less then 0.11 MPa for diffusion media and 0.45 MPa for catalyst layer. By Equation 2.22, ice phase pressure can be estimated by $p_i = \rho_i (\frac{p_w}{\rho_w} - h_{sf} \frac{\Delta T}{T_f})$. The freezing temperature
depression is 0.007 K for diffusion media and 0.545 K for catalyst layer, so \( p_i \) is less than 0.11 MPa for diffusion media and 1.1 MPa for catalyst layer. The assembling pressure of a typical fuel cell, \( P_{asm} \), is usually >1 MPa of bipolar plate landings onto the diffusion media \([117]\), so the ice lens is not likely to grow under the lands, location 6-10 in Figure 2-7. The tensile strength of diffusion media is 0.01 ~ 0.1 MPa \([118]\), and data for catalyst layer is expected to be less or similar, so the ice lens is less likely to grow within the diffusion media (DM) and catalyst layer (CL) under the channels, location 4-5 in Figure 2-7. For interface of CL|Nafion\(^\circledR\) and DM|CL under channel, or DM|channel, location 1-3 in Figure 2-7, the ice lens is most likely to occur, since the overburden pressure is relatively small.

Thus, the ice lens formed around the catalyst layer under the channel can grow and break through the DM into the channel by shear forces. A thick ice lens means large deformation and large stress force on the diffusion media. Additionally, the carbon paper is easier to damage via this mode since it is more brittle in shear than carbon cloth.

### 2.3.2 Water expelled from Nafion\(^\circledR\) (Possible explanation for delamination between Nafion\(^\circledR\) and catalyst layer)

From the unfrozen water relation, the Nafion\(^\circledR\) has a relatively large freezing temperature depression (\(~24.5\) K), so the unfrozen water can flow out of the Nafion\(^\circledR\),
well below the freezing point of the catalyst layer. Liquid water coming out would freeze instantly in the catalyst layer, and an ice lens can grow when pores are saturated with ice and ice phase pressure overcomes the overburden pressure. An estimation can be made for the maximum thickness of ice lens formed from only water ejected from Nafion® on freezing. The maximum thickness produced by this effect is a function of initial water content and membrane type, as shown in Figure 2-8. The boundary of Nafion® is assumed to be saturated with water vapor with \( \lambda = 14 \). Since the catalyst layer is \( \sim 15 \) \( \mu \text{m} \), while lens thickness can reach the same magnitude from Figure 2-8, the ice lens formed by this mode could be a significant source for damage, while the Nafion® thickness has direct effects on the potential damage in this mode.

### 2.3.3 Factors affecting ice lens growth

During the frost heave process, there usually exists a frozen fringe, with ice content from 0% to 100%. The unfrozen water flow takes place mostly in the frozen fringe. The wider the frozen fringe, the thicker an ice lens can grow. The thickness of the frozen fringe increases with lower overburden pressures and low temperature gradients. Also, residual water saturation and distribution play key roles to the frost heave process. With greater initial water saturation, the frost heave will occur more readily, thus, proper purging of the fuel cell on shut down is critical. Finally, higher water permeability of the
porous media can permit greater water flux to the ice lens location, increasing the frost heave rate. Thus, steady state residual water content in diffusion media and catalyst layer is a critical issue for mitigation of freeze-thaw damage.

![Figure 2-8: 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 $\lambda=14$ $H_2O/\text{SO}_3^-$]

There are several methodologies to influence the ice lens formation in a PEFC, which include: 1) control the temperature gradient after shutdown, 2) control the overburden pressure to influence the freezing fringe range and ice lens growth rate, 3) modify purging protocols to reduce residual water to acceptable levels, 4) engineer the flow fields or modify material properties for bipolar plates, diffusion media, and catalyst layer, to reduce the residual water at shutdown.
2.4 Conclusions

In this chapter, a 1-D transient freezing model to describe the water migration and ice lens formation process has been formulated, based on theories of porous media flow and soil frost heave mechanisms. The freezing process in a PEFC is mostly an unsaturated freezing process, although it is also possible that certain areas become saturated and then ice lenses grow. The present model is a hybrid and extension of Harlan’s hydraulic model and Miller’s rigid ice model for frost heave in soils, which can be applied to both saturated and unsaturated domains in PEFCs. The model also relies on several characteristic curves derived, or used from literature to describe the $p_c$, $s_w$, and $T$ relationships. It is found that the three types of characteristic curves for unfrozen water flow and frost heave modeling can be well unified. For Nafion®, the unfrozen water versus temperature curve can be derived from available DSC data. For the diffusion media and the catalyst layer, this curve can be predicted through freezing temperature depression and pore size distribution data. Through the characteristic curves and formulated model, ice lens formation is most likely around the catalyst layer, either between catalyst and diffusion media, or between catalyst layer and Nafion® membrane, under the channel but not the lands. This mode can explain breakthrough damage observed in carbon paper after freeze-thaw tests. Additionally, the unfrozen water can
continuously flow out of the Nafion®, though at a relatively small rate. The ice lens formed from this water source could be a significant source for delamination damage between Nafion® and catalyst layer, while the Nafion® thickness and initial water content has a direct effect on the potential damage by this mode.
CHAPTER 3  1-D TRANSIENT MODEL FOR FROST HEAVE IN POLYMER ELECTROLYTE FUEL CELLS: PARAMETRIC STUDY

In this chapter, the formulated model is solved and a parametric study has been done. The parametric study was performed to understand the key factors in ice lens growth and damage in PEFCs, and the differences between the ice accumulation and distribution under the channels and lands in a fuel cell.

3.1 Model Development

Upon freezing, porous media can be in different states according to the water phase pressure and temperature. It can be in saturated nonfreezing, unsaturated nonfreezing, unsaturated freezing, saturated freezing, or in a frozen state, as shown in Table 3-1. These criteria are plotted in a non-dimensionalized pressure-temperature-saturation coordinates in Figure 3-1. With these criteria, given a temperature and pressure, one can determine the state in the porous media. Water phase pressure \( p_w = f(s_w, s_i) \) is derived from the capillary relation in porous media with \( s_w \) representing water phase saturation and \( s_i \) representing ice phase pressure. Capillary pressure between gas phase \( p_g \) and water phase \( p_w \) is given by
\begin{equation}
 p_c - p_w = \sigma_{ww} \cos \theta_{sw} \sqrt{\epsilon/k} J(s_c)
 \end{equation} \hfill (3.1)

<table>
<thead>
<tr>
<th>Domain</th>
<th>Criteria</th>
</tr>
</thead>
<tbody>
<tr>
<td>A. Saturated nonfreezing</td>
<td>Single phase with ( s_w = 1, s_i = 0 )</td>
</tr>
<tr>
<td>B. Unsaturated nonfreezing</td>
<td>Two phase with ( p_w = f(s_w, s_i) ) and ( s_i = 0 )</td>
</tr>
<tr>
<td>C. Unsaturated freezing</td>
<td>Two phase, together with freezing, with ( p_w = f(s_w, s_i) ) and ( s_w = g(T) )</td>
</tr>
<tr>
<td>D. Saturated freezing</td>
<td>Single phase, together with freezing, with ( s_w = g(T) ) and ( s_i = 1 - g(T) )</td>
</tr>
<tr>
<td>E. Frozen</td>
<td>Single phase with ( s_w = g(T) = 0 )</td>
</tr>
</tbody>
</table>

Figure 3-1: Domain decomposition for unsaturated freezing in porous media. Domains include: A) saturated nonfreezing, B) unsaturated nonfreezing, C) unsaturated freezing, D) saturated freezing, and E) frozen domains. Also shown on the plot are iso-ice-content lines with \( s_i = 0, 0.2, 0.4, 0.6, 0.8, \) and 1.
Here, $\sigma_{aw}$ is the surface tension between air and water phase. The contact angle is $\theta_{aw}$, $\varepsilon$ is the dry porosity, $k$ is permeability, $J(s_e)$ is the Leverett function [30] used to relate capillary pressure to saturation in the porous media, and $s_e$ is the effective water saturation, defined here to account for the liquid and ice saturation, as

$$s_e = \frac{s_w/(1-s_i) - s_{w0}}{1-s_{w0}}$$  \[3.2\]

Here, $s_{w0}$ is the irreducible water saturation, $s_i$ is ice saturation, and water saturation $s_w$, which can be derived by the unfrozen water versus temperature curve, $s_w = g(T)$, which is derived from DSC data or the Gibbs Thomson Equation.

In Figure 3-1, the saturations of water and ice phases vary from 0 to 1. The non-dimensional capillary pressure is actually the Leverett function $J(s_e)$. The non-dimensional temperature is defined as $(T - T_f)/\Delta T$, where $T$ is the absolute temperature, $T_f$ is reference freezing temperature, 0 °C, and $\Delta T$ is the freezing point depression for the porous material. In porous media, the liquid freezing point can be depressed due to capillary or cohesion forces. It can be derived using the following equation, originally reduced from Gibbs-Thompson equation [110, 119-121]

$$\frac{\Delta T}{T_f} \sim -\frac{2\sigma_{iw}}{h_{sf}\rho_w r}$$ \[3.3\]

Here, $h_{sf}$ is the heat of fusion, $\sigma_{iw}$ is the surface tension between ice and water phase, the contact angle is $\theta_{iw}$, $\rho_i$ is density of ice, and $r$ is the mean pore size of the
porous media. Table 3-2 shows the predicted freezing point depression of PEFC components. One important conclusion from this calculation is that the pore size in the catalyst layers and diffusion media are too large to cause a significant freezing point depression in these media, although surface energy characteristics can play an additional role in delaying condensation and freezing, which could result in significant additional temperature depression for hydrophobic surface in these media. [122]

<table>
<thead>
<tr>
<th>Materials</th>
<th>Mean pore size</th>
<th>Freezing point depression from Equation 3*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diffusion media</td>
<td>6 µm[118]</td>
<td>0.008 °C</td>
</tr>
<tr>
<td>Catalyst layer</td>
<td>40 nm[123]</td>
<td>1.225 °C</td>
</tr>
<tr>
<td>Nafion®</td>
<td>2 nm[124]</td>
<td>24.5 °C</td>
</tr>
</tbody>
</table>

* The presence of supercooled water on GDL & CL surface has been observed in dry startups by Ishikawa et al. [125]

In Figure 3-1, Domain A is saturated nonfreezing, meaning the porous media is filled up with water only, like a single phase flow through porous media. In Domain B, unsaturated nonfreezing, ice phase saturation is zero, air phase and water phase satisfy two phase capillary relation, \( p_w = f(s_w, s_i) \) with \( s_i = 0 \). In Domain C, unsaturated freezing, there are three phases coexisting: ice, water, and air phase. Two equations are used to describe the phase balance, the capillary relation \( p_w = f(s_w, s_i) \) mentioned before, and the unfrozen water versus temperature curve \( s_w = g(T) \). In Domain D (saturated freezing), the porous media is saturated, which means there’s no gas phase, \( s_w + s_i = 1 \). Here, one also has \( s_w = g(T) \). In Domain E, everything is frozen, and there
is only the ice phase, with \( s_w = g(T) = 0 \). These five domains compose a unified continuous surface in the non-dimensional \( p_w \sim T \sim s_w \) space, which provides a theoretical basis for applying Newton solvers to the computational code.

The model formulation is described in previous studies. [119-121] The energy and flow equations are strongly coupled with each other, with several strongly nonlinear terms, including a moving freezing front (Stefan’s problem). [126-127] Additionally, Richard’s equation for flow in the porous media has a highly nonlinear permeability relationship. Mixed saturated and unsaturated flow makes the problem even more complex. [128-129] Finally, the characteristic curves discussed to describe capillary flow and phase equilibrium also contain non-linear terms. Some weakly nonlinear, but significant, terms include advection/diffusion and mixture properties. The numerical model was coded in Fortran and solved using various numerical libraries. The numerical method has been briefly discussed in a previous publication. [121] The code is robust for all normal test conditions. Numerical convergence, mass and energy balance checks [130] were also successfully implemented, as shown in Appendix B.

Some important material properties and model input are given in Table 3-3 and Table 3-4 as the baseline of our parametric study. There is still much work to be done by the experimental community to verify some of the relationships used. In particular, \( J(s_e) \) and \( k_{r,w} \) need to be verified for fuel cell media, as the current relationships are
based on antiquated relationships from soil science. Recent work has shown that the Leverett function is not appropriate for fuel cell materials. [131] In this study, however, the commonly used J(s) relationship is used.

<table>
<thead>
<tr>
<th>Table 3-3: Porous media properties used</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Property</strong></td>
</tr>
<tr>
<td>ε, porosity</td>
</tr>
<tr>
<td>θ, contact angle, degree</td>
</tr>
<tr>
<td>k, permeability*, m²</td>
</tr>
<tr>
<td>r, mean pore size*, m</td>
</tr>
</tbody>
</table>

* $\sqrt{k/\varepsilon}$ is used to estimate mean pore size or permeability.

<table>
<thead>
<tr>
<th>Table 3-4: Sensitive input parameters controlling ice lens formation and growth</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Property</strong></td>
</tr>
<tr>
<td>Water diffusivities of NF [24]</td>
</tr>
<tr>
<td>Relative permeability of porous media [57]</td>
</tr>
<tr>
<td>Initial residual water saturation inside porous media at onset of cooldown</td>
</tr>
<tr>
<td>Contact angle of fuel cell components</td>
</tr>
<tr>
<td>Temperature boundary conditions</td>
</tr>
<tr>
<td>Bipolar plate/open channel boundary conditions</td>
</tr>
<tr>
<td>Boundary conditions between CL and NF</td>
</tr>
<tr>
<td>Irreducible water content in porous media</td>
</tr>
</tbody>
</table>
A parametric study was conducted to determine the controlling parameters in the frost heave and ice lens formation process. The water drainage from Nafion® is controlled by the water diffusion in Nafion®. The water diffusivity used was derived from Ge et al. [24] by fitting room temperature diffusivity, since data below water freezing point is currently unavailable from literature. It’s expected that the drainage rate of Nafion® below the water freezing point would be smaller than at room temperature. An estimate of the time scale of water drainage from saturated Nafion® membrane was determined from scale analysis. The characteristic time scale $\tau \sim \delta^2 / D$ varies from 12 s to 250 s by varying diffusivity from $2 \times 10^{-10}$ m$^2$/s to $1 \times 10^{-11}$ m$^2$/s for Nafion® 112. These time scales are all rapid enough to be essentially instantaneous in the context of a fuel cell stack or individual cell cool-down.

Water drainage rate from other porous media depends on the relative permeability, which is also not well defined in literature. As shown in Table 3-5, there are various empirical relative permeability relations which can be found in PEFC modeling [31,105], civil and petroleum engineering applications [26, 32, 128], and soil frost heave modeling [52, 57, 63, 66]. For soil frost heave, water phase transport is significantly impeded due to the presence of the ice phase. Thus different methods were used to account for this effect. [52, 57, 63]
Table 3-5: Empirical relative permeability relations

<table>
<thead>
<tr>
<th>Relations</th>
<th>Notes</th>
<th>Literature Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_{r,w} = s_w^3$</td>
<td></td>
<td>Pasaogullari and Wang [31], You and Liu [105]</td>
</tr>
<tr>
<td>$k_{r,w} = s_e^3$</td>
<td>$s_e = (s_w - s_{w0})/(1 - s_{w0})$</td>
<td>Bear [26]</td>
</tr>
<tr>
<td>$k_{r,nw} = (1 - s_e^2)(1 - s_e^{(2\gamma)/\gamma})$</td>
<td>$s_e = (p_b/p_c)^\gamma$ $p_b$ is bubbling pressure $\gamma$ is pore size distribution index</td>
<td>Brooks and Corey [32]</td>
</tr>
<tr>
<td>$k_{r,w} = \sqrt{s_e[1 - (1 - s_e^{(1/\gamma-1)}^{(\gamma-1)/\gamma})]^{2}}$</td>
<td>$s_e = (s_w - s_{w0})/(1 - s_{w0})$</td>
<td>Farthing et al. [128]</td>
</tr>
<tr>
<td>$k_{r,w} = s_w^9$</td>
<td></td>
<td>O’Neill and Miller [57]</td>
</tr>
<tr>
<td>$k_{r,w} = s_e^3$</td>
<td>$s_e = (s_w - s_{w0})/(1 - s_{w0})$</td>
<td>Harlan [66]</td>
</tr>
<tr>
<td>$k_{r,w} = 10^{-E_{sn}} s_e^3$</td>
<td>$s_e = (s_w - s_{w0})/(1 - s_{w0})$ $E$ is impedance factor counting for the effect of ice phase</td>
<td>James and Norum [52]</td>
</tr>
<tr>
<td>$k_{r,w} = f(p_c)$</td>
<td></td>
<td>Fredlund et al. [71], Newman and Wilson [63]</td>
</tr>
</tbody>
</table>

To illustrate the impact the selection of this parameter has, Figure 3-2 shows change of the drainage rate of the diffusion media with respect to the relative permeability relationship used. The time required to achieve a steady state can be within a second or in a few hours, depending on the relative permeability chosen. Therefore, selection of the proper relationship is necessary for design-based simulation.
Figure 3-2: Comparison of drainage rate on relative permeability relations

The heat loss rate depends on the thermal boundary conditions. Since a fuel cell stack is generally insulated and can require tens of hours to reach a frozen state, the heat transfer rate from the cell should be sufficiently low. The convective heat transfer coefficient applied to the model boundary in this study is calculated based on a stack which has a characteristic time of about a day to reach a frozen state.
3.2 Results and Discussions

Frost heave in PEFC is related to the following processes among others: 1) drainage of diffusion media and catalyst layer, 2) drainage of the electrolyte, and 3) heat loss direction and rate of the MEA. At the heart of the frost heave process is a balance between the heat loss and unfrozen water flow in MEA. On one extreme if the heat transfer rate is infinitely high, ice will be frozen in place, and no ice lenses will be formed and only pore-ice damage from expansion can result. At this point it is important to delineate between an ice lens and pore ice. An ice lens is a result of ice formation and growth resulting from pulling in local water via capillary action. This can cause physical damage by displacing materials, as long as the overburden pressure is overcome. Thus, an ice lens can cause damage independently of the expansion of water on freezing. Pore ice is a result of local freezing of water and can only cause damage via expansion, but not motion or accumulation of water. In general, water will flow towards colder locations by these effects, which will occur on shut down.

On the bottom of Figure 3-3(b), a BP|BP-CH|DM|CL|Nafion® structure can be found that corresponds to the x-scale in Figure 3-3(a) and 3-3(b). The diffusion media (DM) and catalyst layer (CL) are considered as porous media, and the Nafion® (NF) membrane is considered to be a water solvent. The bipolar plate (BP) is considered as a
solid. The BP-CH (BH) represents the 2-D bipolar plate-channel structure, which is reduced to a 1-D heat conductor here. By changing the boundary conditions at this location, the model can simulate under-the-land and under-the-channel situations. The diffusion media, catalyst layer, and Nafion® materials are considered homogeneous and isotropic. For all the domains, the initial temperature is set at 5 °C and the initial pressure is set at 101,325 Pa, and the environment temperature at the left side boundary is set at –40 °C. Figure 3-3 shows the transient temperature and water saturation distribution for the baseline conditions. Figure 3-3(a) is for under-the-land situation and Figure 3-3(b) is for under-the-channel. At the initial state, the cell is uniformly at 5 °C. As time proceeds, the temperature decreases. The heat loss rate is determined by the thermal boundary conditions and thermal diffusivity of the materials. For domains that are undergoing phase change, the temperature distribution is within a very small range. The sharp slope change observed in the plot on top of the DM is induced by the water layer forming on top of diffusion media in the channel. The model allows a water layer outside of diffusion media in the open channel.

Figure 3-4(a) and 3-4(b) show the time-dependent water distribution with a land or channel left-side boundary condition, respectively. From Figure 3-4, the liquid drainage process can be observed from the initial water saturation, arbitrarily chosen to be 0.6 for this simulation.
Figure 3-3: Transient temperature distribution along the 1-D geometry with (a) bipolar plate and (b) open channel boundary condition.
In operating cells, the residual distribution in diffusion media is usually not homogeneous, [91] which is not considered in the current simulation, but is easily
implemented within the current model framework. Change of the water content in Nafion® is also shown in the plot. This overall drainage process is highly dependent on relative permeability of porous media and water diffusivity of Nafion® membrane. In this 1-D model, when diffusion media is under bipolar plate, drainage to the channel is blocked. Also noted is that, this 1-D simulation does not allow lateral movement of water, so there is no drainage from under the land into the channel, which overestimates the initial water content under bipolar plate.

Figure 3-5(a) and Figure 3-5(b) show the time dependent ice distribution with a land or channel boundary condition, respectively. As Figure 3-5(a) and Figure 3-5(b) show, the ice distribution is quite different when the diffusion media is next to bipolar plate or an open channel. In addition to the ordinary drainage flow, there is also unfrozen water flow driven by the capillary pressure change, induced by the temperature difference which occurs between freezing and non-frozen hydraulically connected water. Due to this effect, and the fact the bipolar plate is the coldest location, diffusion media grids next to the bipolar plate will become highly saturated with ice. Note that this is not an ice lens, but pore ice filling, since the ice phase pressure is not significant to overcome the overburden pressure of ~1.5 MPa from the land. The overburden pressure is a term used in geology to denote the pressure on the ice lens induced by soil weight, since an ice lens will bear the full load being lifted by heave. [56]
Figure 3-5: Transient ice saturation distribution along the 1-D geometry with (a) bipolar plate and (b) open channel boundary condition.

Therefore, there is no interfacial separation, and as long as the diffusion media can support the expansion of ice in the pores, there should be no permanent damage from
this occurrence, although the presence of ice should significantly impede start-up times. When the diffusion media is under the channel, a large portion of water drains and freezes out of diffusion media in the channel, due to both capillary drainage and unfrozen water flow effects for these thermal boundary conditions. Also observed from modeling results is that most water inside the Nafion® would freeze without drainage. The volume expansion of Nafion® could also be a possible reason for catalyst layer damage and PTFE washout, as observed in freeze/thaw experimental testing. [133] Note that it is also possible that damage is caused by sudden freezing of super-cooled water droplets, which is not considered in this model, since this model assumes thermodynamic equilibrium.

### 3.2.1 Ice lens formation

Figure 3-6 is a schematic of the ice lens location identified by modeling. As shown in Figure 3-6, IL1 represents a water layer/ice lens at DM|BP or DM|BH interface, IL2 is located at the DM|CL interface, and IL3 is located at the CL|NF interface.

---

**Figure 3-6:** Illustration showing locations of IL1, IL2, and IL3
Figure 3-7 and Figure 3-8 show the initialization and growth of ice lens for the two cases in both Figure 3-4 and Figure 3-5 for water under a land and under a channel, respectively. For diffusion media under the bipolar plate (Figure 3-7), there is no ice lens initialization at interface of DM|BP and DM|CL, since the freezing temperature depression is too small for diffusion media to generate an ice phase pressure exceeding the assembling pressure (typically ~ 1.5 MPa). But an ice lens can still initialize at interface of the CL|NF due to the large freezing temperature depression in the Nafion®. When temperature is very low, e.g. ~-10 °C, the ice phase pressure at this interface can increase to overcome the overburden pressure.

For diffusion media under the open channel (Figure 3-8), the ice lens can form in all three locations. It is interesting that the maximum thickness of ice lens at CL|NF are only on the scale of microns, which could be responsible for some cracks and catalyst delamination observed in MEA, but is probably small enough to avoid any catastrophic damage in a single cycle. The ice lens on top of the diffusion media in the channel would cause no damage and is a favorable location for frost accumulation, except that it can block the surface from reactant penetration and potentially cause carbon corrosion due to local fuel starvation on start-up. [134]
Figure 3-7: Transient ice lens growth with bipolar plate boundary condition with (a) thickness, temperature, water saturation change for IL1, and (b) thickness change for IL1, IL2, and IL3
Figure 3-8: Transient ice lens growth with open channel boundary condition with (a) thickness, temperature, water saturation change for IL1, and (b) thickness change for IL1, IL2, and IL3.
Additionally, the presence of ice in the channel at startup has been linked to a higher temperature product water freezing. [125] One important conclusion is that, even when the thickness of ice lens at CL|NF and CL|DM are combined, it is still not significant enough to create any punch through damage of the diffusion media, as has been observed by some. [98-99, 102] The reason for this damage is likely the accumulated effects of cycling, or large residual slugs in the channel. With each cycle, the growing ice lens will eventually become thick enough to punch through the diffusion media. This will predominantly take place in the IL2 position under CH, so it is important to compare the IL thickness ratio $\omega$ defined in Equation 3.4 for under open channel condition.

$$\omega = \frac{\text{IL thickness for test CH case}}{\text{IL thickness for baseline CH case}}$$  \[3.4\]

For cycling damage, a small delamination between the layers could be non-recoverable. Residual water will tend to accumulate at these locations where any gap exists due to lower water phase pressure. After each cycle, the gap at interface can accumulate more and more water, leading to gap expansion. This is similar to lateral crack expansion that occurs in roads and other structures under repeated freezing conditions, and can also occur in cracking the CL caused by Nafion® freeze/thaw cycling.

It is not likely that the observed delamination or cracking in catalyst layer [98-99, 102] is solely caused by the small quantity of ice lens. Considering the 3-D structure in
catalyst layer, unfrozen water is transported from the Nafion® membrane to the Nafion® components in catalyst layer based on current diffusion model. If unfrozen water comes out of Nafion® components, ice lens forms on the surface of Nafion® components inside catalyst pores. If unfrozen water stays and freezes inside Nafion® components, expansion of these components are expected. For both cases, local delamination stresses could cause loss of C or Pt particles or NF connectivity with catalyst. This situation can be exacerbated when the catalyst pores are locally filled with ice, since ice phase pressure will definitely overcome the overburden pressure at the temperature level of Nafion®'s freezing point depression. These effects are shown schematically in Figure 3-9. Figure 3-9(a) shows the initial state before freeze/thaw. Figure 3-9(b) shows unfrozen water flow from Nafion® membrane into the catalyst layer, freeze inside Nafion® components, and cause swelling of Nafion® structure. It is also possible that unfrozen water flows out and freezes on surface of Nafion® components, as shown in Figure 3-9(c). Figure 3-9(d) shows the catalyst pores getting filled up with water locally. For all the situations illustrated from Figure 3-9(b) to 3-9(d), interfacial delamination can happen due to local stress. Loss of carbon and platinum particles means loss of reaction sites and performance degradation. A single parameter, catalyst layer filling-up ratio, is used to describe these important effects. The filling-up ratio $\psi$ is defined as
Figure 3-9: Illustrations show possible damage modes inside catalyst layer. a) Initial state before freeze/thaw. b) Unfrozen water from Nafion® membrane flow into the catalyst layer, freeze inside Nafion® components, and cause swelling of Nafion® structure. c) Unfrozen water from Nafion® membrane flow into the catalyst layer, come out and freeze on surface of Nafion® components. d) Catalyst pores get filled up with water locally.

\[ \psi = 1 - \frac{\text{remaining pore space}}{\text{original pore space}} \]  

[3.5]

To get a realistic filling-up ratio, one has to consider the final ice saturation in catalyst layer, ice lens formed at CL|NF interface from the calculation, and the expansion of Nafion® components due to water freezing inside.
\[ \psi = s_{i,d} + \frac{\delta_{il2} + \delta_{il3}}{\varepsilon_{cl} \delta_{cl}} \]  

Here, \( s_{i,d} \) is final ice saturation in catalyst layer. \( \delta_{il3} \) is the calculated ice lens thickness at the NF|CL interface, which is also possibly contributing through expansion. \( \delta_{il2} \) is the ice lens thickness at DM|CL, included here since the interface at DM|CL is also not distinct. \( \varepsilon_{cl} \) is the porosity of catalyst layer and \( \delta_{cl} \) is thickness of catalyst layer. The second part, from calculation, is usually a very small value, \(~0.01\), but can be large due to cycling or catalyst layer cracking effects. The magnitude of \( \psi \) actually relates to the total ice content around the catalyst layer, either in the form of ice lens or pore ice, although pore ice dominates. Ice content from ice lens is included simply because there’s no distinct boundary defined between the catalyst layer and other layers.

### 3.2.2 Parametric study: drainage rate

A parametric study was conducted to determine the controlling parameters on the final water saturation in the catalyst layer and the ice lens thickness. As shown in Table 3-6, two porous media drainage rates, two Nafion® diffusivity values, three irreducible water saturation combinations, three residual water profiles, and five contact angle combinations are tested.
Table 3-6: Parameters used for parametric study

| PM drainage          | Fast: $k_r=s_w^3$  
|                     | slow: $k_r=s_w^9$  
| NF diffusivity      | $D_{w, 303K}$    
|                     | $D_{w, 303K}\exp(2416(1/303-1/T))$  
| Irreducible water saturation | $s_{w0, dm}=0.1$ and $s_{w0, cl}=0.1$  
|                     | $s_{w0, dm}=0.15$ and $s_{w0, cl}=0.1$  
|                     | $s_{w0, dm}=0.1$ and $s_{w0, cl}=0.15$  
| Initial water       | Dry: $s_{w, dm}=0.1$, $s_{w, cl}=0.1$, and $\lambda_w=14.8$ for NF  
|                     | Median: $s_{w, dm}=0.35$, $s_{w, cl}=0.15$, and $\lambda_w=17.4$ for NF  
|                     | Wet: $s_{w, dm}=0.6$, $s_{w, cl}=0.2$, and $\lambda_w=20$ for NF  
| Contact angle       | DM150° and CL145°  
|                     | DM125° and CL145°  
|                     | DM105° and CL145°  
|                     | DM150° and CL125°  
|                     | DM150° and CL105°  
| Flow b.c.            | Under-the-land  
|                     | Under-the-channel  

Table 3-7 shows a comparison on the IL thickness ratio and catalyst filling-up ratio for different cases. Figure 3-10 shows the test result for the baseline case, case with fast porous media drainage speed, and case with corrected diffusivity, which has an additional activation energy term similar to Ge et al. [24] to account for temperature. It is found that fast drainage speed of porous media will significantly reduce the final ice saturation in catalyst layer. Interestingly, despite reducing the final pore filling in the catalyst layer, fast drainage induces the highest IL2 thickness ratio, since the water can most easily drains fast, but move rapidly towards the ice lens, contributing to the growth. It is expected that in-plane water transport would also help reduce the final ice saturation.
calculated under bipolar plate. The temperature-corrected diffusivity decreases the IL thickness at CL|NF interface for less drainage at lower temperature, while it almost has no effects on the catalyst pore filling-up.

| Table 3-7: IL Comparison on IL thickness ratio and pore filling-up ratio |
|-----------------------------|-----|-----|-----|
| Change from the base case   | $\omega$ | $\psi$ |
| Base                        | IL2 | IL3 | BP  | CH  |
| $k_r=s_w^3$                  | 1.00| 1.00| 0.366| 0.366|
| $D_w,303K \cdot \exp(2416(1/303-1/T))$ | 1.00| 0.37| 0.356| 0.356|
| Drainage                    |     |     |     |
| Initial water               |     |     |     |
| $s_{w,cl}=0.1, s_{w,cl}=0.1, and \lambda_w=14.8$ for NF | 0.11| 1.00| 0.281| 0.281|
| $s_{w,cl}=0.35, s_{w,cl}=0.15, and \lambda_w=17.4$ for NF | 1.18| 1.00| 0.374| 0.375|
| Irreducible water saturation|     |     |     |
| $s_{w0,cl}=0.15$ and $s_{w0,cl}=0.1$ | 1.00| 1.00| 0.366| 0.366|
| $s_{w0,cl}=0.1$ and $s_{w0,cl}=0.15$ | 2.14| 1.00| 0.423| 0.423|
| Contact angle               |     |     |     |
| DM125°, CL145°              | 1.00| 1.00| 0.366| 0.366|
| DM105°, CL145°              | 1.00| 1.00| 0.365| 0.366|
| DM150°, CL125°              | 1.20| 1.00| 0.378| 0.378|
| DM150°, CL105°              | 1.85| 1.00| 0.407| 0.407|
Figure 3-10: Effects of drainage speed for (a) bipolar plate boundary condition and (b) open channel boundary condition
3.2.3 Parametric study: irreducible water saturation

Figure 3-11 shows the effect of irreducible water saturation. With higher irreducible water in porous media, higher ice saturation and ice lens accumulation is expected, especially in catalyst layer. This can be directly seen in Table 3-7 as well. With infinite time, the cell would drain to nearly the irreducible saturation, which is related to the fraction of the porous network consisting of connected hydrophilic surfaces. Recent work has shown typical DM has an irreducible saturation from 0.15~0.3, which depends strongly on PTFE content. [131]

3.2.4 Parametric study: initial water saturation

Figure 3-12 shows the effects of initial water saturation. Overall, the lower initial water saturation, the lower final ice saturation. Interestingly, the initial water content in diffusion media is not very critical for CL final ice saturation, since it drains to nearly the irreducible volume before freezing.
Figure 3-11: Effects of irreducible water content for (a) bipolar plate boundary condition and (b) open channel boundary condition.
Figure 3-12: Effects of initial water content for (a) bipolar plate boundary condition and (b) open channel boundary condition.
3.2.5 Parametric study: contact angle

Figure 3-13 shows the effects of DM and CL contact angles, which are included in the Young-Laplace relationship. The DM contact angle doesn’t matter much to IL accumulation or pore filling in the CL. This indicates that some PTFE washout during cycling will have a minimal effect on freeze/thaw damage. The CL contact angle is related to the final catalyst pore ice saturation (Table 3-7). An increase in CL contact angle (hydrophobicity) would help reduce the final ice saturation distribution in CL.

To control frost heave damage, one key strategy would be control the final ice saturation in the catalyst layer, or the filling up ratio, to prevent the delamination/crack initialization. As discussed, fast drainage could help reduce the final ice saturation in catalyst layer, however it speeds up the ice lens growth at DM|CL. A drier initial condition, lower irreducible water content, and higher hydrophobicity of the catalyst layer would also help avoid damage. Other effects might not be significant. One major parameter that is the focus of another publication is the effect of temperature gradient, also recently addressed by Bradean. [135] The direction of heat flux has a profound effect, since water will generally move towards the cold, which is towards the bipolar plate, away from the catalyst layer in all the simulations here. Significant water redistribution can occur with reversed heat transfer profiles. This will be detailed in Chapter 4. Additionally, cycling effects and micro porous layer effects will be discussed.
Figure 3-13: Effects of contact angle for (a) bipolar plate boundary condition and (b) open channel boundary condition
3.3 Conclusions

A numerical model was developed to simulate the frost heave process in fuel cell components during freeze/thaw cycling. A physical domain decomposition method is proposed to describe the capillary force, temperature, and saturation relation for freezing in porous media. It has been implemented into a Newton solver to solve the highly nonlinear problem, as shown in Appendix B. A parametric study was performed to understand the key factors in ice lens growth and damage in PEFCs, and the differences between the ice accumulation and distribution under the channels and lands in a fuel cell. The results are consistent with the physical modes of damage observed by some other work: [98-99, 102]

1) Ice lens induced damage could occur at CL|NF interface due to the large freezing temperature depression of the electrolyte and unfrozen water movement in the electrolyte. 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, 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|NF could be considered as reversible. A key parameter, the catalyst pore filling up ratio, is proposed to determine when the damage could occur. A drier initial membrane condition, lower irreducible water content, and higher hydrophobicity of the catalyst layer would help to reduce this ratio.

2) Ice lens induced delamination could also occur at the CL|DM interface only under the channel. The ice lens is negligible from the calculation for one cycle. This indicates the initialization of punch-through DM damage could be caused by a delamination/crack initialization location, which can grow over many cycles due to water accumulation and eventually cause punch through on diffusion media.

3) The final ice distribution in DM is strongly related to the drainage speed of the porous media and the boundary condition. Under the lands where water motion is prevented, a high ice saturation can occur.
CHAPTER 4  COMPUTATIONAL MODEL OF PHYSICAL DAMAGE DURING FREEZE/THAW OF PEFCS: THERMAL/GEOMETRY/CYCLING EFFECTS

In this chapter, a more detailed case study has been conducted. Computational results with varied layer thickness, layer thermal conductivity and thermal boundary conditions are presented. Moreover, cycling, end cell, and micro porous layer (MPL) effects are discussed in this chapter. Strategies to mitigate freeze/thaw damage based on present understanding are also proposed.

4.1 Introduction

The heat dissipation of fuel cell components is mainly determined by heat transfer boundary conditions, thermal parameters, and geometry. In this chapter, the “end cell effects”, as reported by Patterson [103] will be discussed. Patterson observed performance loss after freeze-thaw cycles, occurring specifically to the anode end cell of a stack. The performance loss after freeze-thaw cycle is connected to the catalyst flooding post cold start. Patterson claimed that the problem could be solved by switching materials. With current frost heave model, the underlying physics of this phenomenon can be explained very well.
In addition, the effects of ice lens growth with cycles are detailed, which is similar to what has been observed in soil science, such as the study by Setzer [136]. As known from previous chapters, small cracks can provide locations with reduced capillary water phase pressure. Water tends to accumulate and freeze in such locations. Although a single cycle would induce too small an ice lens to punch through the DM, repeated cycling of the cell could cause the gap (delamination between DM and CL under CH) to grow. Punch through damage may occur after many cycles in this way.

4.2 Numerical Model

Details on the model formulation and discussions on flow parameters can be found in Chapter 2 and Chapter 3. Figure 2-2 shows the typical BP|BH|DM|CL|NF 1-D structure for the model. The baseline is shown in Table 3-4 and Table 4-1.

<table>
<thead>
<tr>
<th>Table 4-1: FEFC component thermal parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>DM</td>
</tr>
<tr>
<td>$\kappa$, heat conductivity, W/m K</td>
</tr>
<tr>
<td>$\delta$, thickness, m</td>
</tr>
</tbody>
</table>

* CL’s properties are calculated as a mixture of Pt, C, and Nafion® with Pt:C:Nafion® = 0.32:0.48:0.2 (wt%) [139-140]

The original thermal boundary condition for the 1-D model is convective heat transfer at BP side and zero heat flux at NF side. To study the end cell effects, zero heat
flux is set at BP side and convective heat transfer at the NF side. To study the influence of geometry, thermal conductivity, and the micro porous layer (MPL), the respective parameters in the numerical model are changed.

For the cycling study, delamination at the CL|DM interface under CH boundary condition is considered as unrecoverable. For simulation at each cycle, an initial gap is set at CL|DM interface with its thickness equal to the final ice lens thickness from last cycle. It is assumed that the gap is initially filled with water, due to low local water phase pressure. During freezing, the water inside the gap is assumed to have a small freezing temperature depression of 0.005 °C. From 0 °C to –0.005 °C, ice saturation in the gap is assumed to increase from 0 to 1 linearly. The purpose for this assumption is to make the freezing front not so abrupt, so that the Newton solver is much more stable.

IL thickness ratio and CL filling-up ratio are used to evaluate the ice accumulation around the catalyst layer, defined in Equation 3.4 and 3.5. Table 4-2 shows values of these two parameters of all the simulation tests done in this chapter.

To help to read this table, it might be necessary to mention the difference between ice lens and pore ice again. An ice lens is a result of ice formation and growth resulting from pulling in local water via capillary action. This can cause physical damage by displacing materials, as long as the overburden pressure is overcome. Thus, an ice lens can cause damage independently of the expansion of water on freezing. Pore ice is a
result of local freezing of water and can only cause damage via expansion, but not motion or accumulation of water.

<table>
<thead>
<tr>
<th>Table 4-2: IL Comparison on IL thickness ratio and pore filling-up ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
</tr>
<tr>
<td>Base</td>
</tr>
<tr>
<td>DM, ( k=10 \times k_0 )</td>
</tr>
<tr>
<td>CL, ( k=10 \times k_0 )</td>
</tr>
<tr>
<td>NF, ( k=10 \times k_0 )</td>
</tr>
<tr>
<td>DM, ( \delta=10 \times \delta_0 )</td>
</tr>
<tr>
<td>CL, ( \delta=10 \times \delta_0 )</td>
</tr>
<tr>
<td>NF, ( \delta=10 \times \delta_0 )</td>
</tr>
<tr>
<td>h=24*( h_0 )</td>
</tr>
<tr>
<td>Inverted b.c.</td>
</tr>
<tr>
<td>MPL</td>
</tr>
</tbody>
</table>

4.3 Results and Discussions

4.3.1 Parametric study: thermal conductivity

The thermal conductivities of fuel cell components have been reported by various studies \([138, 141-142]\). Data from existing literature show a big variety with respect to different material suppliers. In this study, the base case (shown in Table 4-1) is compared with the cases when the conductivity of diffusion media (DM), catalyst layer (CL), or Nafion\textsuperscript{®} (NF) has been changed to ten times the base value, respectively. Figure 4-1 shows the comparison results. Since the DM has the biggest thickness, it has a greater
Figure 4-1: Comparison on final ice saturation for cases with different material thermal conductivity, when the membrane electrolyte assembly is (a) under the BP and (b) under the CH impact on the final ice distribution. From Table 4-2, there is no big difference caused by thermal conductivity change, since higher thermal conductivity always leads to lower
thermal gradient. From GCE equation (Equation 1.41), when unfrozen water is equilibrated with ice, if ice phase pressure is assumed constant (e.g. $p_i=p_{ovbd}$), one can derive

$$\nabla p_w = \frac{h_f \rho_w}{T_f} \nabla T$$ \[4.1\]

The gradient of water phase pressure is proportional to the gradient of temperature. With higher temperature gradient, one can expect more water flux driven by the water phase pressure.

4.3.2 Parametric study: diffusion media, catalyst layer, and electrolyte thickness

Figure 4-2 shows the comparison between the base case and the cases with doubled material layer thickness, for DM, CL, and NF layer respectively. Results show that the ice saturation in CL decreases with doubled CL thickness and increases with doubled NF thickness, which are also shown in Table 4-2. This results from the fact that water accumulation in CL is mainly from the electrolyte. Doubled NF thickness means a greater water source and doubled CL thickness means more storage room for ice accumulation.
Figure 4-2: Comparison on final ice saturation for cases with different material layer thickness when the membrane electrolyte assembly is (a) under the BP and (b) under the CH. (The three cases are with different layer thickness, so the saturation distribution has been stretched to fit the geometry shown in the bar so that they are comparable.)
4.3.3 Parametric study: thermal boundary conditions/end cell effects

The boundary conditions for the base case are convective heat transfer at BP side and zero heat flux at NF side. The convective heat transfer coefficient is chosen so that the cell has a characteristic time of 24 hours to simulate the real stack cooling-down. With a convective heat transfer coefficient 24 times of the original value, the cell has a characteristic time of 1 hour, which is like the single cell test condition.

In a real stack, heat dissipates towards the end cell, as shown in Figure 4-3. So the heat transfer is not always towards the bipolar plate as has been the simulated case to this point. Here, the thermal boundary condition is inverted to simulate the case when heat transfer is from bipolar plate towards the catalyst layer.

Figure 4-3: Illustration showing stack structure and unfrozen water flow in a fuel cell stack

Figure 4-4 shows results of a parametric study with these two types of thermal boundary conditions. For fast cooling, one can observe more water flux towards the cold side induced by the higher temperature gradient. For inverted heat transfer, unfrozen water flow is now towards the CL, which gives a higher ice accumulation in the CL.
Figure 4-4: Comparison on final ice saturation for cases with different thermal boundary conditions when the membrane electrolyte assembly is (a) under the BP and (b) under the CH
This situation can be linked to the end cell effects observed in Patterson’s study. As addressed by Patterson, the anode end cell suffered more performance loss than the cathode end cell. This is strong evidence that residual water and temperature gradient have direct impacts on the freeze/thaw-induced damage. Also note that this model does not allow flux through the NF layer. In practice, water would flow through to the other side. The result in extreme case is a flow of water toward the cold location.

For heat transfer in a fuel cell stack, the end cells always have the highest temperature gradient, which means the highest unfrozen water flux. So let focus on the anode end cell and the cathode end cell. From Chapter 1, water is generated at the cathode catalyst layer and appears in liquid form if relative humidity is over 100%. One of the major roles of diffusion media is to remove this water product. When water product accumulation reaches a certain level, reactant gas is then blocked from penetrating to the catalyst surface. So flooding more frequently occurs in the cathode. Upon shut down, the cathode will usually have more residual water than the anode.

Due to the unfrozen water flow driven by the temperature field, this could make a big difference between the anode end cell and cathode end cell. In the anode end cell, the residual water in the cathode will flow towards the catalyst layer. In the cathode end cell, the residual water in the anode will flow towards the catalyst layer. However, one can expect more residual water for the first case. Thus more unfrozen water flow towards the
catalyst layer for the first case. As discussed in Chapter 3, water accumulation in catalyst layer directly relates to potential catalyst site loss and cracks in catalyst layer. One would also expect more potential damage in catalyst layer in the anode end cell.

With respect to fuel cell performance, the loss of reaction sites and cracks in catalyst layer are long-term effects. While the short-term effect is that with more ice accumulation in catalyst layer, there is more melted water after cold start, when flooding can occur at catalyst layer.

### 4.3.4 MPL study

An MPL is sometimes used for water management purpose [31, 143-144] but has not been included in simulations so far. Since the MPL has much smaller pores than the DM, it works by increasing water phase pressure and facilitates water drainage from catalyst layer. Table 4-3 shows some typical values for MPL as used in the present study.

By changing from the original 400 μm DM to a 370 μm DM combined with a 30 μm MPL, the effects of the MPL layer can be examined. Figure 4-5 shows final residual ice with and without MPL. There is not much difference for final ice accumulation around the catalyst layer from the base case. With inverted thermal boundary condition, MPL shows a slight help by blocking unfrozen water flow into the catalyst layer.
Figure 4-5: Comparison on final ice saturation for the base case and the cases with MPL, when the membrane electrolyte assembly is (a) under the BP and (b) under the CH.
### Table 4-3: MPL Physical Properties [31, 143-144]

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thickness, μm</td>
<td>30</td>
</tr>
<tr>
<td>Porosity</td>
<td>0.4 or 0.5</td>
</tr>
<tr>
<td>Pore Size, nm</td>
<td>250</td>
</tr>
<tr>
<td>Permeability, m²</td>
<td>2.5e-14</td>
</tr>
<tr>
<td>Contact Angle, degree</td>
<td>150</td>
</tr>
<tr>
<td>Thermal Conductivity, W/m.K</td>
<td>0.4</td>
</tr>
<tr>
<td>Specific Heat, J/kgK</td>
<td>710</td>
</tr>
<tr>
<td>Freezing Temperature Depression, °C</td>
<td>0.96</td>
</tr>
</tbody>
</table>

### 4.3.5. Cycling effects

As explained in Chapter 3, when the fuel cell is cycled, a small delamination between the layers could be non-recoverable. Residual water will tend to accumulate at these locations due to lower water phase pressure. After cycles, the gap at interface can accumulate more and more water, leading to gap expansion. This is similar to lateral crack expansion that occurs in roads and other structures under repeated freezing conditions, and can also occur in cracking the CL caused by Nafion® freeze/thaw cycling.

Figure 4-6 shows the simulation results on cycling effects for the base case and inverted boundary condition case. IL1 (at CH|DM) and IL3 (CL|NF) are positions where ice lens growth is recoverable. IL2 (at DM|CL) is the place where delamination is considered as non-recoverable. The delamination grows with cycles almost linearly. The more ice lens growth for single cycle, the faster the total delamination grows.
From previous parametric study results, for single cycle, CL hydrophobicity, porous material drainage speed, CL irreducible water content, NF thickness, cooling rate, and MPL addition are more important for ice accumulation around the catalyst layer than other factors. Calculation of cycling effects with change on these factors has been conducted. Figure 4-7 shows the change of IL2 thickness ratio with cycles. The IL2 thickness ratio is an index showing the delamination at DM|CL interface under channel boundary condition. The growth of this index directly relates to the growth of delamination or cracks. It’s found that, among so many parameters, rapid drainage and cooling especially facilitate the growth of delamination, which should be avoided in design by engineering material properties and better thermal management.
Figure 4-7: IL2 thickness ratio change with cycles with (a) base and (b) inverted thermal boundary conditions.
Figure 4-8 shows the change of catalyst pore ice filling-up ratio with cycles. From Equation 3.6, the pore ice filling-up ratio actually considers not only the pore ice, but also the ice lens at DM|CL and CL|NF interfaces, so that it can exceed 1.0. It’s an index addressing the total amount of ice around the catalyst layer. The higher the index, the higher possibility damage will occur or cracks will initialize. From Figure 4-8, except for fast drainage speed and fast cooling rate, the case with MPL and inverted heat transfer also has high filling-up ratio after cycles. The reason is that for the same amount of water, MPL tends to have higher water phase pressure than DM. So there will be more unfrozen water flow into the IL at MPL|CL interface than the DM|CL interface when heat transfer conditions are inverted.
Figure 4-8: Catalyst pore ice filling-up ratio change with cycles with (a) base and (b) inverted thermal boundary conditions.
4.3.6 Controlling strategies

From previous discussions, the initialization of damage could be caused by the damage of CL layer due to pore ice filled up. Then this provides a delamination/crack location. The gap can grow with cycles due to capillary effects. The ultimate solution to avoid any freeze/thaw damage would be purging out all the water, although it’s not very applicable in real situations. Strategies to control these damages can be designed based on the triangle shown in Figure 4-9.

![Figure 4-9: Triangle showing the interrelation between heat transfer, purge, and materials, based on which strategies to control freeze/thaw damages can be developed](image)

1) Heat Transfer. As explained in previous discussion, the temperature gradient directly relates to the unfrozen water flow. To control the temperature gradient and direction becomes important, especially around the places where ice lens is likely to form. This is because higher temperature gradient will induce more
unfrozen water flux into that location. If an ice lens is formed, higher local temperature gradient will further facilitate ice lens growth during cycles. Slow cooling rate and insulation layer would help a stack to reduce temperature gradient. However, thermal management on the fuel cell stack under normal operation conditions should also be considered. A stack model might help to optimize the design.

2) Purge. After shutdown of a fuel cell, there is residual water in the flow channel, within porous materials, and inside the electrolyte. To dry out the cell components, especially the electrolyte, would definitely help prevent freeze/thaw damage. This is simply because the electrolyte has a huge freezing temperature depression, which means a big range when unfrozen water flow could occur. High frequency resistance measurement on the electrolyte may be used to define the safe level of residual water inside electrolyte.

3) Materials. When freeze/thaw damage is mentioned, one can easily think of the cracks and delamination in catalyst layer. To control freeze/thaw damage, one can take steps to control the crack initialization and crack development. The porous structure of diffusion media and catalyst layer contains unevenly distributed pores. When different fluids are inside, curved interface forms and capillary pressure plays an important role. For fuel cell porous materials, things are even complex
since they usually are not homogeneous in hydrophobicity. Hydrophilic locations tend to be the same places where water phase pressure is lower and initial crack can grow. Cracks are less likely to initialize in porous materials that are homogeneous in pore size distribution and hydrophobicity. Porous material with less irreducible water saturation is always favored. Similarly, an electrolyte material is favored, when it drains to less irreducible water content and is with less expansion, since from previous discussion, the expansion of Naifon® could also be a source of damage and ice lens initialization. Also, reducing the thickness of the electrolyte would help due to less unfrozen water source. Porous materials and electrolytes with fast drainage ability means less time spent on purging to a safe level. If purging is not very successful, fast drainage ability could be detrimental since it also facilitates unfrozen water flow and ice lens growth. MPL shows some combined effects. It has less pore ice inside and may help to block unfrozen water flow towards CL from DM. However, MPL also facilitates the IL growth rate and can cause a high filling-up ratio after cycles.
4.4 Summary

This chapter discussed the effects of thermal parameters, geometry, MPL, and cycling on freeze/thaw damage. It’s found that several factors can facilitate the crack initialization and growth. In addition, the end cell effects and the underlying physics were explained. Control strategies were proposed based on the simulation results, which include methods to reduce residual water content by purging, control the heat transfer during shutdown, and engineer materials to facilitate purging and prevent crack initialization and growth.
CHAPTER 5  THIN FILM TEMPERATURE SENSOR FOR REAL-TIME MEASUREMENT OF ELECTROLYTE TEMPERATURE IN A PEFC

This chapter describes a technique for the measurement of electrolyte temperature in an operating polymer electrolyte fuel cell (PEFC). This technique can be used to determine the thermal transport properties for PEFC components and enable future validation of the frost heave model by monitoring the temperature change during the freeze-thaw process.

A patterned thin film gold thermistor embedded in 16 µm thick parylene film was laminated in the Nafion® electrolyte layer for in-situ temperature measurements. Experimental results show that the sensor has a linear response of $(3.03 \pm 0.09) \times 10^{-3} \, ^\circ C^{-1}$ in the 20-100 °C temperature range and is robust enough to withstand the electrolyte expansion forces that occur during water uptake. The temperature sensitivity of the present sensor is an order of magnitude better than conventional micro-thermocouples that have been reported. Additionally, use of microfabrication techniques allows for accurate placement of the temperature sensor within the fuel cell. Simulation results show that the sensor has no significant effect on the local temperature distribution.
5.1. Introduction

Temperature measurement of an operating PEFC is critical to understand cold start, water balance and degradation. This chapter describes development of a thin film thermal sensor for the real-time measurement of temperature in an operating PEFC. A patterned thin film gold thermistor embedded in 16 µm thick parylene film was laminated in the Nafion® electrolyte layer for in-situ temperature measurements.

Temperature distribution in a PEFC is of critical importance because of the close ties to water management at the PEFC operating temperature of 80 °C. The electrolyte, Nafion® membrane, has to be saturated with water to conduct protons, but too much water can lead to local flooding. With poor thermal management, short-term effects will be performance loss due to either membrane dry-out or diffusion media flooding, and long-term effects will be the sulfonate group decomposition due to the high temperature, which could increase the fuel crossover rate through the electrolyte, thus degrading the cell performance. At extreme case, pin-holes formed will lead to membrane failure [145-146]. Thermal management is also important for cold start cycling, when residual water freeze-thaw could degrade the cell performance [92-93]. Researchers have been engaged in real-time temperature measurement in a PEFC for some time, especially the electrolyte temperature. A review of various methods for achieving temperature
distribution including infrared technology is given by Wang et al. [147]. Vie and Kjelstrun [138] placed a millimeter sized thermocouple at various locations on a membrane electrolyte assembly (MEA). Mench and his students [137, 141] laminated eight 50 μm thermocouples directly into two Nafion® 111 membranes. With this method, placement of the thermocouples in exact positions is difficult. Also, possible interference with local temperature distribution has to be considered, since the thermocouple wire diameter is equivalent to the electrolyte membrane thickness.

In order to achieve higher spatial resolution and sensitivity, further reduction in the sensor size is required. Thin film thermal sensors have been developed for an array of applications. Most of them are fabricated on solid substrates, such as silicon and glass. Brunco et al. [148] used lithographic technology to fabricate thermistors to measure the interface temperature between a polymide film and a quartz substrate to study laser-induced heating and ablation. Debey et al. [149] also used lithographic technology to fabricate thin film thermocouples with 10 measurement points in 2 mm on polymide and ceramics substrates. Krishnan et al. [150] fabricated thin film thermocouples on flexible polymer and paper substrates by thermal evaporation to measure the properties of thin film. However, the temperature measurements for PEFC application have to be performed on a Nafion® (E. I. du Pont de Nemours) substrate, a perfluorinated polymer that contains connected islands of sulfonic ionic functional groups and has a linear
expansion of 10% from 50% relative humidity to fully water saturated at 23 °C [15]. Therefore, one critical challenge is to design a sensor that will withstand the stretching force during electrolyte water uptake. Such a sensor should work at any environment similar to a PEFC: acidic, electrochemical, and with unstable polymer substrate.

To protect thin film sensors from degradation, researchers have utilized Al₂O₃, TaO, borosilicate, and polymer materials as insulating films. Ruff and Kreider [151] emphasize the following properties for insulation application: adhesion, low electrical conductivity, high strength and hardness. Polymer insulation, especially parylene, has been widely applied for thermistor, thermopiles, and microheaters for thermo sensor [152-153], flow sensor [154], chemical sensor [155-156], stress sensor [157], and so on [158-159]. Wolgemuth [160] has listed the desirable properties of parylene, which includes a simple vapor deposition process capable of producing uniform coating, stability, and low residual stress.

This chapter describes the fabrication process and the performance of a thin film based temperature sensor for monitoring the temperature in a fuel cell during its operation. The chapter also includes a modeling analysis of sensor interference with the local temperature distribution.
5.2. Design and Fabrication Process

Figure 5-1 depicts the sensor design layout used. The 5 cm² fuel cell flow channels are in the middle, as represented by dashed lines. They are composed of 3 parallel gas channels. Protons transport through this area of Nafion® membrane from the fuel cell anode to the cathode. Reaction inefficiency, entropy change, and joule heating result in an increase in the temperature of the Nafion® membrane. To measure the membrane temperature at different location of the flow channels, the temperature sensors are located precisely within the flow channel area and connection legs are placed outside the area.

Figure 5-1: Thermal sensor design (the right figure is the enlarged view)

The design uses thermistors to directly measure the temperature of the PEFC reactant flow inlet and outlet. Parylene layers are used to protect the sensor from the
stretching force of Nafion® membrane. As shown in the Figure 5-1, the closed lines surrounding the sensor set are the parylene cover area.

The fabrication process includes two major steps, one is to fabricate the sensor on the Nafion® membrane and the other is to integrate the Nafion® membrane with the sensor into a fuel cell. The fabrication began with a cleaning of the Nafion® 112 membrane (50 μm thick), using 5% wt H₂O₂ at 80 °C for an hour and washing with de-ioned water for half an hour, followed by the same process with 1 M H₂SO₄ and drying the membrane. A 8 μm thick parylene layer was deposited on the Nafion®, using a metal shadow mask with rubber seals. This was followed by the deposition of the thermistor metal, a 150 Å Cr /2000 Å Au layer, accomplished using e-beam evaporation while the patterns were transferred by a shadow mask. Another 8 μm thick parylene layer was deposited to cover all the sensor area, except the legs for the connection wire bonding. Then, the sample was laminated with another clean Nafion® 112 membrane, and the two electrodes at 125 °C and 100 Kgf/cm² for 3 minutes.

A 10 μm catalyst layer was sprayed on the diffusion media (DM) using an airbrush. The catalyst was prepared using E-TEK® 40% wt carbon-supported Pt and Nafion® 5% wt solution. The Pt loading is 0.3 mg/cm². The DM used is E-TEK® 400 μm carbon cloth. Figure 5-2 shows the position for each part in the fuel cell.
5.3 Thermal Analysis

The two Nafion\(^\circledast\) 112 membranes are 102 \(\mu\text{m}\) thick, while the parylene insulating layer is 16 \(\mu\text{m}\) thick. It’s necessary to study whether the parylene layer will influence the local temperature distribution. Divisek [10] gave a review on current status of research on low temperature fuel cell heat transfer.

A simplified 2-D heat conduction model was set up to calculate the heat transport process with more details shown in He et al. [139]. A major assumption for the model is
that the parylene layer is small enough that it will not block the proton transport. Also, mass transfer and two-phase porous flow have not been considered and all water product exists in vapor phase. Many more detailed fuel cell models can be found in literature equations [38-40, 104-108]. Typically, a PEFC consists of two bipolar plates, flow channels, DMs, electrodes, and electrolyte membrane, as shown in Figure 5-2. Heat is generated in the electrodes and the electrolyte and dissipated through the DMs, flow channels, and backing plates. Isothermal boundary conditions (BCs) are used at the outside walls of the backing plates and symmetric BCs in the other walls, except for the flow channel walls with forced convection BCs [161].

The operating voltage of a hydrogen fuel cell $V_{cell}$ at a current density $i$ can be calculated by reversible open circuit voltage $E^\circ$ from Nernst equation and ohmic, activation, and mass voltage loss $\eta$ at the cell assembly [6], which can be written as:

$$
V_{cell} = E^\circ - \eta_{ohm,E} - \eta_{ohm,A} - \eta_{ohm,C} - \eta_{act,A} - \eta_{act,C} - \eta_{mass,A} - \eta_{mass,C} \\
= E^\circ - (i + i_n)r_E - (i + i_n)r_A - (i + i_n)r_C - (RT/2F)(i + i_n)/i_{0,A} - \\
- (RT/\alpha_C F) \ln[(i + i_n)/i_{0,C}] + (RT/2F) \ln[1 - (i + i_n)/i_{L,A}] \\
+ (RT/4F) \ln[1 - (i + i_n)/i_{L,C}] 
$$

where $i_n$ is the crossover current; $i_{0,A}$ and $i_{0,C}$ are the exchange current density at the anode and the cathode; $i_{L,A}$ and $i_{L,C}$ are limiting current densities at the anode and the cathode; $\alpha_C$ is the cathode cathodic charge transfer coefficient; $r_E$, $r_A$, and $r_C$ are the resistance of the electrolyte (ionic), the anode, and the cathode; $T$ is the temperature;
\( R \) is gas constant; and \( F \) is Faraday’s constant. The expression for \( \eta_{\text{act},C} \) is valid when \( (i + i_n) > i_{0,C} \).

The 2-D steady energy equation is expressed as

\[
\frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2} + \frac{S_b}{\kappa} = 0
\]  

[5.2]

Heat is generated three ways: 1. Activation polarization heat, generated by the electrochemical reactions taking place in the electrodes; 2. Ohmic heat, generated by the current going through the membrane and catalyst layers; 3. Peltier heat generated by entropy change. Thus, most of the heat is generated within the very thin membrane and catalyst layers. The heat source in the anode \( S_{h,A} \) is

\[
S_{h,A} = (i + i_n)(\eta_{\text{ohm},A} + \eta_{\text{act},A} + \eta_{\text{mass},A})/\delta_A + S_{h,pel}
\]  

[5.3]

the heat source in the electrolyte \( S_{h,E} \) is

\[
S_{h,E} = (i + i_n)\eta_{\text{ohm},E}/\delta_E
\]  

[5.4]

and the heat source in the cathode \( S_{h,C} \) is

\[
S_{h,C} = [(i + i_n)(\eta_{\text{ohm},C} + \mid \eta_{\text{act},C} \mid + \eta_{\text{mass},C})]/\delta_C + S_{h,pel}
\]  

[5.5]

The Peltier heat source is assumed to be evenly distributed in the anode and the cathode:

\[
S_{h,pel} = (i + i_n)(-T\Delta S/nF)/(\delta_A + \delta_C)
\]  

[5.6]

\( \Delta S \) is the entropy change of the global reaction. \( \delta_A \), \( \delta_E \), and \( \delta_C \) are the
thickness of the anode, the electrolyte, and the cathode.

Figure 5-3 gives the temperature contours for the case of 1 A/cm² current density and 10 μm thick parylene layer, which shows that the temperature gradient concentrates in the MEA area. The calculated average temperature $\Delta T$ in the centerline of MEA, where the sensor is located, is 9 °C higher than the flow channel temperature. This temperature difference $\Delta T$ is influenced by the fuel cell operation conditions and component properties, especially the DM properties.

Dong et al. [28] indicated that $\Delta T$ is proportional to the global heat generation $S_{h,global}$, which is defined as

$$S_{h,global} = (i + i_n)(1.25 - V_{cell})$$  \[5.7\]

Figure 5-4 confirms the linear relation. It also shows the error of $\Delta T$ brought by the parylene layer versus $S_{h,global}$ for different parylene layer thickness. There is only a
minor temperature change caused by the insertion of parylene layer protected sensors, with absolute value less than 1 °C, though it could be significant for the case of low global heat generation.

![Graph showing influence of parylene layer thickness on ΔT](image)

Figure 5-4: Plot of the averaged temperature increase in the centerline and error brought by the parylene layer versus global heat generation for different parylene layers thickness

5.4. Results and Discussion

Initial attempts to deposit the thermistor metal directly on the Nafion® membrane were unsuccessful. The thin film metal became discontinuous very quickly during swelling of the Nafion® membrane in water as shown in Figure 5-5(a). Several approaches were attempted to resolve this issue. First, a polyethylene terephthalate (PET)
Figure 5-5: Magnified view of thin film sensors: (a) Cracks grow on sensor directly deposited on Nafion® membrane, (b) Water can penetrate the NPPN laminate and destroy the sensor, (c) NPPN laminate with the aid of Epoxy® 301, (d) NPPN laminate with the aid of acrylic adhesive, (e) Cracks grow on sensor with 2 μm thick parylene protecting layer, and (f) Sensor with 1 μm thick parylene protecting layer

film was deposited and patterned with the sensor thin film and then laminated with another PET (P) film. Then the P-P laminate was laminated between two Nafion® (N) membranes to form a N-P-P-N laminate. Though this arrangement was able to resist the stretching force during hydration of the Nafion®, Figure 5-5(b) indicates that water still penetrated and damaged the sensor. Epotek® Epoxy 301 and acrylic adhesive were used to keep the PET membranes sealed, shown in Figure 5-5(c) and (d). Although we were able to achieve stable thermistors using these techniques, the advantages over using conventional macroscopic thermal sensors was lost, since the minimum thickness of the sensor set approached ~75 μm. Since parylene is known to be hydrophobic, this material
was used to embed the thermistor. Initially, the results seemed inconsistent, because a thin film protected by 2 μm parylene layers showed cracks, shown in Figure 5-5(e), while another with 1 μm parylene layers didn’t, shown in Figure 5-5(f). It was later found that the robustness of the sensor depends on the parylene layer thickness and its ability to detach from the Nafion® during water uptake. Whenever the parylene was not subject to the stretching forces, the sensor remained intact. A sacrificial layer between the Nafion® layer and parylene layer was used to promote successful delamination. A 15 nm Cr or Al layer as sacrificial layer and two 8 μm parylene layers was determined the best and repeatable combination to protect the embedded sensor.

Since the thermistors are not standard components, an ex-situ calibration was studied. A standard K-type thermocouple and the thin film thermistor were submerged in a water bath and kept in close proximity. The K-type thermocouple was connected to a FLUKE 52II Thermometer and the thin film thermistor was connected to a FLUKE 8840A multimeter. The water bath was heated by a hot plate. Before calibrating, the water bath was boiled for a few minutes to remove any air dissolved in the water and prevent the formation of two-phase flow below 100 °C, thus extending the stable range for calibration. The calibration was completed during the cooling-down process.

Calibration results are shown in Figure 5-6, a plot of the thermistor resistance versus temperature during calibration. The curves show that the resistance has a linear
The resistance in Figure 5-6 is calculated as

$$ R = R_{\text{leg}} + R_{25^\circ C} [1 + \gamma_R (T - 25)] $$  \[5.8\]

$R_{25^\circ C}$ is calculated by thermistor geometry, $R_{\text{leg}}$ is estimated, which includes the resistance of the leg and wires and contact resistance, and $\gamma_R$ is the temperature coefficient for the thin film metal used.

The ex-situ calibration results were later confirmed with respect to linearity and dependence on temperature and the slope remains constant even after 10 days, though the y-intercept shifts slightly, which is caused by the change in the bonding wires contact resistance. The calibration measurement error is expected to be caused by flow in the water bath, especially when the temperature approaches boiling point, and to be less than 1 °C. The theoretical resistance in Figure 5-6 is calculated as

$$ R = R_{\text{leg}} + R_{25^\circ C} [1 + \gamma_R (T - 25)] $$  \[5.8\]
durability by an in-situ calibration in an operating fuel cell. For in-situ conditions, the sensor output is still highly linear within the fuel cell operation temperature. There’s also similar y-intercept shift of the total resistance. The sensor is robust and the slope kept constant after at least 5 cycles in 12 days. The longer-term performance is expected to be stable, since results from applications of packaging industry [162] show that the parylene coating can help release the strain force and extend solder lifetime significantly under thermal cycling conditions. By supplying nitrogen gas at $T_1$ to the fuel cell setup until thermal equilibrium is reached, the resistance $R_1$ is measured. Then, the same steps are repeated at a temperature $T_2$, and $R_2$ is measured. So, the slope for the $R$-$T$ curve is

$$S_R = (R_2 - R_1)/(T_2 - T_1)$$

[5.9]

When using the sensor, the temperature measured by the sensor will be

$$T = 25 + (R - R_{25^\circ C})/S_R$$

[5.10]

where $R_{25^\circ C}$ is the resistance at $25^\circ C$.

The sensitivity of the sensor, $\Delta R/(R \cdot \Delta T)$, is calculated to be $(3.03 \pm 0.09) \times 10^{-3}$ $^\circ C^{-1}$ from the experimental results. There is a 9% difference between $\Delta R/(R \cdot \Delta T)$ and the temperature coefficient of resistance of pure gold (99.999+), $3.5 \times 10^{-3}$ $^\circ C^{-1}$ [163]. Here $\Delta R/(R \cdot \Delta T)$ was calculated based on the total resistance of the sensor and only the working part of the sensor is subject to temperature change. Also, the temperature coefficient of pure metal decreases sharply with increasing impurity or alloy content.
This sensitivity is an order of magnitude better than micro-thermocouples developed by the authors in previous study [137, 141], with precise location control.

The performance of the fuel cell with embedded sensor was tested in 100% anode and cathode humidification at 80 ºC and room pressure with a stoichiometry of 2 A/cm². The V-i curves are shown in Figure 5-7. Since the parylene layer blocks almost 1/3 of proton transport area for these small active area cells, the performance of the MEA with sensor is not as high as the one without sensor. However, these tests were conducted to demonstrate feasibility of using the sensor in fuel cells. Operation in large area cells with a much lower fraction of affected active area should yield nearly identical performance between cells with and without sensor.

Figure 5-7: Plot of the 5 cm² fuel cell performance with the sensor-MEA sandwich
Besides the thin film sensor, commercially available thermocouples were also inserted into the backing plates of the PEFC. Figure 5-8(a) shows fuel cell shutdown temperature response. The temperature of electrolyte, measured by the sensor, followed exactly the same trend as backing plate temperature change, as the cell cooled by natural convection.

This type of test can also be used for in-situ calibration. Figure 5-8(b) shows fuel cell start-up temperature response. Since cartridge heaters were working in the backing plates, the profile of the temperature followed the PID control. The electrolyte temperature was also influenced by inlet gas from humidifiers. Temperature jumps can be seen from the figure, which represent inlet gas temperature jump.

Figure 5-9 shows fuel cell transient response measured by the sensor. The cell voltage was changed between open circuit voltage (OCV) and 0.2 V every five minutes. With this technique, the heat generation flux fluctuated between around 0.2 W/cm² at 0.2
V and 0 W/cm² at OCV. The temperature jump is at least 1.5 °C. From calculation result in Figure 5-4, the ΔT is around 2.5 °C and the error brought by parylene is around –0.5 °C for 16 μm thick parylene layer at 0.2 W/cm². They give an estimated sensor temperature of 2 °C. There’s a less than 0.5 °C difference between the theoretically estimated temperature and the measured one and this could be generated by the blockage of parylene on local proton transport, thus local heat generation is reduced.

Figure 5-9: Plot of fuel cell transient response measured by the sensor. The cell voltage was changed between OCV and 0.2V every five minutes. The heat generation flux was around 0.2W/cm² at 0.2V

It is the first report of a thin film thermistor integrated into a polymer electrolyte fuel cell for in-situ temperature measurement. While this study clearly demonstrates a path to making such temperature measurement, the current size of the sensor in relation
to the fuel cell active area has resulted in a reduced overall performance of the fuel cell. By further minimizing the sensor size this method could produce series of more practical sensors for fuel cell applications.

5.5. Conclusions

This chapter describes the development of a thin film thermal sensor for application in an operating PEFC. The sensor set is around 16 µm thick and is fabricated using micro-fabrication techniques. By using a Nafion®|Parylene|Sensor|Parylene|Nafion® laminated structure, the sensor can be protected from the electrolyte expansion forces. The thickness of parylene stress insulation layer and the delamination of parylene layer from Nafion® membrane are key to the survival of the sensor in PEFC environment.

Calibration results show that in the 20-100 °C temperature range the sensor has a linear response of (3.03 ± 0.09)×10⁻³ °C⁻¹. Temperature sensitivity of the sensor is an order of magnitude better than micro-thermocouples developed in a previous study, with precise location control. Modeling results also show that the sensor has limited effects on the local temperature distribution.

Moreover, the thin film sensor has the potential to be further minimized using
photolithography and etch technologies. Future work will be concentrated on the application of the sensor in a 50 cm$^2$ fuel cell with high performance electrodes to conduct steady-state and dynamic heat transfer study.
A frost heave model has been formulated and coded to simulate the freeze/thaw-induced degradation of fuel cell components. A MEMS-sensor has been developed to measure the electrolyte temperature of an operating fuel cell. The conclusions drawn are based on the simulation and experimental results obtained in this program.

6.1 Conclusions

In recent years, fuel cells have developed into a potential energy supplier of the next generation of clean energy. One of the remaining technical barriers for PEFC in automotive application is damage-free and rapid cold-start.

In this work, a 1-D transient freezing model to describe the water migration and ice lens formation process has been developed, based on theories of PM flow and soil frost heave mechanisms. The present model is a hybrid and extension of Harlan’s hydraulic model and Miller’s rigid ice model for frost heave in soils, which can be applied to both saturated and unsaturated domains in PEFCs. The model also relies on several characteristic curves derived, or used from literature, to describe the \( p_c \), \( s_w \), and \( T \) relationships for PEFC components. The unfrozen water versus temperature curve for
Nafion® was derived from DSC data available in literature. For DM and CL, this curve can be predicted through freezing temperature depression and pore size distribution. Through the characteristic curves and formulated model, it is predicted that ice lens can occur only around the CL layer, either between CL and DM, or between CL and Nafion® membrane.

The numerical model was coded and solved using the Newton method together with a physical domain decomposition method. As proposed, porous materials undergoing freezing can be in different states, which form a continuous surface in the 3-D pressure-temperature-saturation coordinates. Simulation results show the processes controlling ice lens and pore ice accumulation include drainage rate of the Nafion® and the porous materials, heat dissipation, hydrophobicity of catalyst layer, irreducible water saturation of catalyst layer, electrolyte thickness, and cooling rate.

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 or freeze inside Nafion® and cause expansion. This causes detachment of carbon particles and platinum particles, especially when the pores of catalyst layer are all filled up with ice locally. A key parameter, the catalyst pore filling up ratio, is proposed to determine when the damage could occur. The ice lens is negligible from the calculation for one cycle. This indicates the initialization of punch-through DM damage could be caused by a delamination/crack
initialization location, which can grow over many cycles due to water accumulation and eventually cause punch through on diffusion media.

The ultimate solution to avoid any freeze/thaw damage would be purging out all the water, although it’s not very applicable in real situations. Control strategies were proposed based on the simulation results, which include methods to reduce residual water content by purging, control the heat transfer during shutdown, and engineer materials to facilitate purging and prevent crack initialization and growth.

Other work presented is the development of a MEMS-based micro sensor for real-time measurement of the electrolyte temperature. The thin film gold thermistor is embedded in parylene film, fabricated using MEMS technologies. Experimental results show that the sensor has a very linear response and is robust enough to withstand the electrolyte expansion forces that occur during water uptake. It is an improvement over the conventional micro-thermocouples, with respect to sensitivity and accurate placement, and may be used to determine the thermal transport properties for PEFC components and enable future validation of the frost heave model by monitoring the temperature change during the freeze-thaw process.
6.2 Recommendations for Future Work

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

1. Further studies are recommended on the fundamental studies of freezing in porous material and electrolyte. There are still spaces to develop and improve, such as the transition from state E to other states as shown in Figure 3-3. There might be a better approach to describe the underlying physics.

2. The current model is using a volume-based approach to quantify the extent of damage. The real frost heave damage can occur locally, when a portion of the pores get filled up. It is recommended to explore the usage of a microscopic model, in which water freezing and movement in a single pore can be simulated. The results would be even more interesting, when the parameters of pore size distribution and hydrophobicity are integrated into that model.

3. In present study, the Newton solver with domain decomposition was successfully used to solve the coupled problem with porous media flow and moving boundary condition. It is recommended to further exploit its application in other disciplines, when nonlinear processes are strongly coupled together.

4. It is recommended to measure those critical parameters for fuel cell components
and integrate into the model to get more accurate prediction and validate the model with test results. These in-lab measured data include contact angle, permeability, relative permeability, capillary relation, freezing temperature depression, water diffusivity in Nafion® electrolyte, and thermal parameters of MEA components.

5. It is highly desired to further extend the single-cell frost heave model to a stack one, since the heat transfer pattern for the real case could be very different from the thermal boundary set for the current study. Also it’s recommended to add in a water generation term so that water generated during cold start and their effects on freeze/thaw damage can be studied. The stack model is also a very useful tool for design purpose and can be used to develop strategies to start up a cell quickly and efficiently, without damage to fuel cell components.

6. It is recommended to further extend the 1-D frost heave model to a 2-D one to include the in-plane effects, from which one could find more accurate prediction and study the effects induced by cell geometry. This 2-D model would also enable a further study to develop efficient purging protocols.

7. It is recommended to carefully study the Nafion® electrolyte. The polymer is so critical to fuel cell performance and freeze/thaw damage control. A thorough understanding on the water existence and transport inside the electrolyte would be very helpful.
8. It is recommended to further exploit the usage of MEMS fabrication techniques in fuel cell sensor design, catalyst engineering, and electrochemistry testing.
REFERENCES


29. M. C. Leverett, “Capillary behavior in porous media”, Trans. AIME, 142, 341 (1941)
90. S. A. Grant and R. S. Sletten, “Calculating capillary pressures in frozen and ice-free
102. Q. Guo and Z. Qi, “Effects of freeze-thaw cycles on the properties and performance


147. M. H. Wang, H. Guo, C. F. Ma, F. Ye, J. Yu, X. Liu, Y. Wang, and C. Y. Wang, “Temperature measurement technologies and their applications in the research of...


160. L. Wolgemuth, “Accessing the performance and suitability of parylene coating”,


It has long been established that there are three types of water in Nafion®: strongly bound, loosely bound, and free water [11-12]. The first type is usually related to the plastic properties of Nafion®, while the later two types relate more to the transport properties of Nafion® [87]. During freezing, the strongly bound water exits in the hydration shells around the cation (H⁺ or Na⁺) in Nafion® (H⁺ form or Na⁺ form), and won’t freeze, so it is also called nonfreezing water. The binding energy associated with hydration of water differs with the cation type.

As introduced in Section 1.1, there are three mechanisms for water transport within Nafion®: electro-osmotic drag, diffusion, and hydraulic flow. During the freezing process, there is no current driven electro-osmotic drag. The water phase pressure at the anode and cathode are at the same scale, so hydraulic flow can also be neglected. The diffusion becomes the dominant driving force. The only characteristic curve needed for Nafion® membrane is then the unfrozen water versus temperature curve.

Differential scanning calorimetry (DSC) is one of the methods to measure the unfrozen water versus temperature curve in soil science [76-79]. Also, it has been used to characterize the water composition in Nafion® membrane [84-89]. Pineri et al. [165] believed the melting/freezing of water in Nafion® is coupled with water into or out of the
ionic phase, which means the temperature depression is a bonding and not a pore-size effect. They used the DSC curve, with an upward scanning direction, to estimate the relative amounts of desorbable and nondesorbed water. With the theory, the heat of fusion of water in Nafion® could be quite different from bulk water. Sivashinsky and Tanny [166] measured the heat of fusion in Nafion® as only ~84,000 J/kg. They related the change on heat of fusion to the polymer pore size. However, their DSC curves are also upward scanning curves with large scanning rates. I have reasons to question their results: the scanning rate is a key factor to obtain stable DSC curve, and the upward curve and downward curve show totally different trends. Both of these two effects can be observed in the recent DSC tests by Newman [88]. Our study will use DSC data from available literature to extract the unfrozen water versus temperature curve for the Nafion® membrane using a constant heat of fusion, which is assumed to be 334,000 J/kg. This can be verified through more complete experimental data.

People used different units for their DSC results. Among them, some used the heat release rate [84] and some used arbitrary units [85-86], which are shown in Figure A-1(a). Some used the heat release rate per unit mass [87-89], as shown in Figure A-1(b). The curves using arbitrary units don’t contain enough info for extracting the unfrozen water versus temperature characteristic curve. Also, only scanning in the downward direction is useful to calculate the unfrozen water versus temperature curve for our study.
By comparing the DSC curves with different cooling rates and sample preparation methods, it can be found that slower cooling rate always gives more stable results. DSC tests using a scanning rate of 1/6 °C/s always give a declining baseline [86-88], while
data with a scanning rate of 1/12 or 1/60 °C/s are quite stable \[85, 88-89\], which also validate the assumption that the heat capacity of Nafion® and water phase may be treated as constants in the temperature range.

After applying these criteria, only half of the literature found \[84, 88-89\] are deemed to be useful for the input of our calculation.

DSC measures the amount of energy absorbed or released by a sample as it is heated, cooled or held at a constant temperature. By energy balance, the heat release rate \( \dot{Q} \) includes both storage term and phase change term, written as

\[
\dot{Q} = V_{nf} \{ [\rho_{nf} C_{P,nf} + c_{SO_3^-} M_w (\lambda_w C_{P,w} + \lambda_i C_{P,i})] \frac{\partial T}{\partial t} + h_{nf} c_{SO_3^-} M_w \frac{\partial \lambda_w}{\partial t} \} \tag{A.1}
\]

Here, \( \lambda_w \) and \( \lambda_i \) are water and ice content in the Nafion® membrane; \( V_{nf} \) is the volume of dry Nafion®; \( c_{SO_3^-} \) is the concentration of sulfonic acid group in Nafion®.

If the scanning rate, \( \frac{\partial T}{\partial t} \), is a constant, then

\[
\frac{\partial \lambda_w}{\partial t} = \frac{\partial \lambda_w}{\partial T} \frac{\partial T}{\partial t} \propto \frac{\partial \lambda_w}{\partial T} \tag{A.2}
\]

So one has

\[
\dot{Q} = V_{nf} \{ [\rho_{nf} C_{P,nf} + c_{SO_3^-} M_w (\lambda_w C_{P,w} + \lambda_i C_{P,i})] \frac{\partial T}{\partial t} + h_{nf} c_{SO_3^-} M_w \frac{\partial T}{\partial t} \frac{\partial \lambda_w}{\partial T} \} \tag{A.3}
\]

To derive the unfrozen water versus temperature curve, there are two methods depending on the type of available data.
A.1 Method #1

This method works for DSC curves with the heat release rate known [84]. From energy balance,

\[
\dot{Q} = V_{nf} \left\{ \rho_{nf} C_{P,nf} + c_{SO} M_w (\lambda_w C_{P,w} + \lambda_i C_{P,i}) \right\} \frac{\partial T}{\partial t} 
+ h_{nf} c_{SO} M_w \frac{\partial T}{\partial t} \frac{\partial \lambda_w}{\partial T} = V_{nf} \frac{\partial T}{\partial t} (a + b \frac{\partial \lambda_w}{\partial T}) \tag{A.4}
\]

If all the freezable water is \( \lambda_v \), including the free water and loosely bound water, then

\[
\lambda_i = \lambda_v - \lambda_w \tag{A.5}
\]

The calculation doesn’t include the non-freezable water, which is considered as a portion of the Nafton® structure. During the freezing, water content changes from \((\lambda_w = \lambda_v, \lambda_i = 0)\) to \((\lambda_w = 0, \lambda_i = \lambda_v)\).

When \( \lambda_w = 0 \) and \( \lambda_i = \lambda_v \), \( \frac{\partial \lambda_w}{\partial T} = 0 \) and

\[
\dot{Q}_0 = a_0 V_{nf} \frac{\partial T}{\partial t} = (\rho_{nf} C_{P,nf} + c_{SO} M_w \lambda_v C_{P,i}) V_{nf} \frac{\partial T}{\partial t} \tag{A.6}
\]

Then,

\[
\dot{Q} = V_{nf} \frac{\partial T}{\partial t} (a + b \frac{\partial \lambda_w}{\partial T}) = \frac{Q_0}{a_0} (a + b \frac{\partial \lambda_w}{\partial T}) \tag{A.7}
\]

So

\[
\frac{\partial \lambda_w}{\partial T} = \frac{a_0 \dot{Q} - a \dot{Q}_0}{b \dot{Q}_0} \tag{A.8}
\]

with
\[ a_0 = \rho_{nf} C_{P,nf} + c_{SO_i} M_w \lambda_0 C_{P,i} \]  \textbf{[A.9]} \\
\[ a = \rho_{nf} C_{P,nf} + c_{SO_i} M_w (\lambda_w C_{P,w} + (\lambda_0 - \lambda_w)C_{P,i}) \]  \textbf{[A.10]} \\
\[ b = h_{nf} c_{SO_i} M_w \]  \textbf{[A.11]}

Here, \( \dot{Q} \) and \( \dot{Q}_0 \) can be determined from the DSC curve. By integration of Equation \textbf{A.8}, the unfrozen water versus temperature curve can be derived.

**A.2 Method #2**

This method works for DSC curves with heat released per unit mass data \([88-89]\).

From energy balance, the heat released rate per unit mass, \( \dot{Q}_m \), is expressed as

\[ \dot{Q}_m = \frac{\hat{Q}}{\rho_{nf} V_{nf}} = \frac{1}{\rho_{nf}} \left[ \rho_{nf} C_{P,nf} + c_{SO_i} M_w (\lambda_w C_{P,w} + \lambda_i C_{P,i}) \right] \frac{\partial T}{\partial t} \]

\[ + \frac{1}{\rho_{nf}} h_{nf} c_{SO_i} M_w \frac{\partial T}{\partial t} \frac{\partial \lambda_w}{\partial T} \]  \textbf{[A.12]} \\

Same as Method #1, when \( \lambda_w = 0 \) and \( \lambda_i = \lambda_0 \), \( \frac{\partial \lambda_w}{\partial T} = 0 \) and

\[ \dot{Q}_{m,0} = C_{P,nf} + \frac{c_{SO_i} M_w \lambda_0 C_{P,i}}{\rho_{nf}} \frac{\partial T}{\partial t} \]  \textbf{[A.13]}

Then,

\[ (\dot{Q}_m - \dot{Q}_{m,0}) = \frac{c_{SO_i} M_w \lambda_w (C_{P,w} - C_{P,i})}{\rho_{nf}} \frac{\partial T}{\partial t} + \frac{h_{nf} c_{SO_i} M_w}{\rho_{nf}} \frac{\partial T}{\partial t} \frac{\partial \lambda_w}{\partial T} \]

\[ = c + a \frac{\partial \lambda_w}{\partial T} \]  \textbf{[A.14]}

So
\[
\frac{\partial \lambda_w}{\partial T} = \frac{(\dot{Q}_m - \dot{Q}_{m,0}) - c}{d} \quad \text{[A.15]}
\]

with

\[
c = \frac{c_{SO_3} M_w \lambda_w (C_{p,w} - C_{p,i})}{\rho_{nf}} \frac{\partial T}{\partial t} \quad \text{[A.16]}
\]

\[
d = \frac{h_{sf} c_{m,SO_3} M_w}{\rho_{nf}} \frac{\partial T}{\partial t} \quad \text{[A.17]}
\]

Here, \((\dot{Q}_m - \dot{Q}_{m,0})\) can be determined from the DSC curve. By integration of Equation A.15, the unfrozen water versus temperature curve can be derived.
In current model, the energy and flow equations are strongly coupled with each other, with several strongly nonlinear terms, including a moving freezing front. Problems with moving boundary conditions, such as a melting/freezing front is called Stefan’s problem. The Stefan’s problem has been studied over decades. Good summaries can be found by Fukusako and Seki [167], Voller et al. [126, 168], and Alexiades and Soloman, [169]. The commonly used methods to solve Stefan’s problems with fixed grids include the basic enthalpy method, apparent heat capacity methods (used by Harlan [66] for frost heave modeling), source update methods, and Newton methods.

Frost heave in fuel cell is also a problem of multiphase flow through porous media. As explained in Chapter 1, there are several models for multiphase flow modeling. In petroleum engineering, oil-gas-water three-phase flow is modeled using the immiscible theory, as in Aziz and Settari, [170] and Ertekin [171]. Numerical methods applied include implicit pressure-explicit saturation method (IMPES), simultaneous solution method (SS), and sequential method (SEQ). In civil engineering, immiscible flow theory is also used to model the air-water two-phase flow in soil. Since the air phase pressure can be assumed as constant due to low velocity, the flow equations are simplified to Richards equation as explained in Chapter 1. There are several numerical
methods to solve Richards equation, including Picard iteration, Newton iteration, and some other method [128-129, 172-175]. What is popular in fuel cell modeling is the so-called multiphase mixture model, as used by Wang et al. [31, 38-40] and You and Liu [105]. In this approach, air and water flow are treated as a mixture. The flow equations are simplified to a single-phase equation. Mass-averaged mixture velocity and a diffusive flux are used. Standard numerical procedures for single-phase flow are then used.

The frost heave model developed in this work is also based on immiscible flow theories. The final flow equation derived is like the Richard’s equation for both saturated and unsaturated domains, and the final energy equation has a phase-change term, which represents a moving freezing front. The characteristic curves, such as the unfrozen water versus water curve, have very small slopes at a large range. Some weakly nonlinear but significant terms includes advection/diffusion terms and mixture properties.

IMPES method is tried first, which comes out to be very unstable. Then a SS method with domain decomposition is used. Figure B-1 shows the structure of the code. A Newton solver with global line search ability from Press, et al. [176] is used. Water phase pressure and temperature of all the nodes, $p_{w,i}$ and $T_i$, are treated as primary unknowns. They are strongly coupled with the water phase saturation $s_w$ and ice phase saturation $s_i$. The energy and flow equations can be written as a set of differential algebraic equations (DAEs).
Figure B-1: Flow chart of current numerical model shows (a) the main program using Newton solver to get transient results, and (b) the sub program for function evaluation in Newton solver

\[
F(\Delta t, T, T', s_i, s_w, s_i', T^{old}) = 0 \quad \text{[B.1]}
\]

\[
G(\Delta t, s_i, s_w, s_w', T, P_w, s_w^{old}) = 0 \quad \text{[B.2]}
\]
The porous material under freezing can transit from freezing to frozen, from saturated to unsaturated, and vice versa. For different states, they might have slightly different governing equations, which are updated differently during function evaluation. Appropriate capillary relations are chosen so that all these states form a continuous surface in the capillary pressure-temperature-saturation surface. This also serves as the basis for successful implementation of a Newton solver [178].

So in each iteration, given temperature and water phase pressure, from the “phase diagram”, Figure 3-1, I have

\[ s_i = f(T, p_w) \] \[ s_w = g(T, p_w) \]

All the other unknowns, such as \( \kappa \), \( c_p \), \( p_i \), and \( s_a \), are evaluated implicitly and get updated during function evaluation. Power-law scheme is used for the advection terms. [177]

The Newton-Raphson method works by minimizing the residuals of the energy equation and flow equation.

\[
\begin{align*}
\{ R^{(a)}[T^{(k)} + \Delta T, p_w^{(k)} + \Delta p_w] = 0 \\
R^{(b)}[T^{(k)} + \Delta T, p_w^{(k)} + \Delta p_w] = 0
\end{align*}
\] \[ \text{[B.5]} \]

From Taylor’s expansion, \( \Delta T \) and \( \Delta p_w \) can be solved from
current method, a numerical Jacobian is used. Another challenge is the abrupt transition step jumps. The accuracy of the Jacobian is also critical for convergence of the solver. In pressure and temperature field for the very initial time step were smoothened to avoid last time step iteration results are used as the initial guess for the current time step. The solve any problem. However, it appears not so critical for present application, when the guess or a goold globalization technique, the Newton-Raphson method can be used to grids, the Newton direction can be solved as

\[
\frac{\partial R^{(a)}(T, p)}{\partial T} \quad \frac{\partial R^{(a)}(T, p)}{\partial p} \quad \frac{\partial R^{(a)}(T, p)}{\partial p} \quad \frac{\partial R^{(a)}(T, p)}{\partial p} \quad \ldots \quad \frac{\partial R^{(a)}(T, p)}{\partial p} \quad \frac{\partial R^{(a)}(T, p)}{\partial p} \quad \frac{\partial R^{(a)}(T, p)}{\partial p} \quad \ldots \quad \frac{\partial R^{(a)}(T, p)}{\partial p} \quad \frac{\partial R^{(a)}(T, p)}{\partial p} \quad \ldots \quad \frac{\partial R^{(a)}(T, p)}{\partial p} \quad \frac{\partial R^{(a)}(T, p)}{\partial p} \quad \ldots 
\]

The primary variables are then updated with

\[
\begin{aligned}
T^{(k+1)} &= T^{(k)} + \lambda \Delta T \\
p^{(k+1)}_w &= p^{(k)}_w + \lambda \Delta p_w
\end{aligned}
\]

The line searches and backtracking strategy from Press [176] is used to determine the value of \( \lambda \). The iteration is repeated until \( \Delta T = \Delta p_w = 0 \) is achieved. With multi grids, the Newton direction can be solved as

\[
\begin{bmatrix}
\frac{\partial R^{(a)}(T, p)}{\partial T} \\
\frac{\partial R^{(a)}(T, p)}{\partial p} \\
\frac{\partial R^{(a)}(T, p)}{\partial p} \\
\frac{\partial R^{(a)}(T, p)}{\partial p} \\
\frac{\partial R^{(a)}(T, p)}{\partial p} \\
\frac{\partial R^{(a)}(T, p)}{\partial p} \\
\frac{\partial R^{(a)}(T, p)}{\partial p} \\
\frac{\partial R^{(a)}(T, p)}{\partial p} \\
\frac{\partial R^{(a)}(T, p)}{\partial p} \\
\end{bmatrix}
\begin{bmatrix}
\Delta T_1 \\
\Delta p_{w,1} \\
\Delta T_2 \\
\Delta p_{w,2} \\
\Delta T_3 \\
\Delta p_{w,3} \\
\Delta T_4 \\
\Delta p_{w,4} \\
\Delta T_n \\
\Delta p_{w,n}
\end{bmatrix}
= 
\begin{bmatrix}
R^{(a)}(T, p)^{(k)}_1 \\
R^{(a)}(T, p)^{(k)}_2 \\
R^{(a)}(T, p)^{(k)}_3 \\
R^{(a)}(T, p)^{(k)}_4 \\
R^{(a)}(T, p)^{(k)}_n \\
\end{bmatrix}
\]

Newton's method processes quadritic local convergence. With some good initial guess or a goold globalization technique, the Newton-Raphson method can be used to solve any problem. However, it appears not so critical for present application, when the last time step iteration results are used as the initial guess for the current time step. The pressure and temperature field for the very initial time step were smoothened to avoid step jumps. The accuracy of the Jacobian is also critical for convergence of the solver. In current method, a numerical Jacobian is used. Another challenge is the abrupt transition
locations in the “phase diagram”, Figure 3-1, such as the transition from state E to other states. Except for these locations, the Newton solver with line search can proceed very fast and robust. When the porous media is approaching that abrupt transition, the Newton solver can experience stagnation. An enlarged time step is then used to let the solver jump over the point to smooth domains.

Figure B-2 shows the convergence history of one typical calculation. Most of the time, convergence is achieved in less than 10 steps, when function evaluation or primary variable error is less than $1 \times 10^{-15}$. A case with 39 spatial grids and 36000 time steps would take around 20 min on a PC with Intel Pentium 1.7 MHz CPU and 512 Mb memory.

Figure B-2: Convergence history of one typical calculation
Figure B-3 shows a typical mass and energy balance check with the calculation. The total mass and total thermal energy are well conserved throughout the calculation time period, since all of the schemes are derived from a conservative finite volume method. This serves as part of the verification of the code.

![Figure B-3: Mass and energy balance check with the code for one typical calculation](image)

Verification on temporal and spatial discretization errors [130, 179-180] was also completed and shown to be negligible. In Figure B-4, with three separate temporal grids (h_1=0.05 s, h_2=0.5 s, and h_3=5 s), the empirical order of the discretization p can be calculated as around 1.0 by assuming asymptotic regime.

\[ p = \frac{\ln(x_3 - x_2)}{\ln(x_2 - x_1)} / \ln(r) \]  

[B.9]
The temporal discretization errors are estimated to be less than 0.03%.

$$
\epsilon_i = x_i - x_{\text{exact}} = \frac{x_2 - x_1}{r^p - 1}
$$

[\text{B.11}]

I used a base time step of 0.5 s in the program. In the extreme case, when the iteration crossed the abrupt transitions, a time step of less than 50 s can be observed. By using $p=1$, one can estimate the error for that extreme case, with 50 s as time step, is still less than 0.1%.

![Figure B-4: Temporal discretization error check](image)

In Figure B-5, with three separate spatial grids (the scale factors are $h_1=1/9$, $h_2=1/3$, and $h_3=1$), the spatial discretization error for primary variables is estimated to be less than 0.25% for current grid selection.
Figure B-5: Spatial discretization error check
VITA

EDUCATION:
Ph.D. in Mechanical Engineering, Penn State University, University Park, PA, 2007
M.S. in Thermal Power Engineering, Tsinghua University, Beijing, P. R. China, 2002
B.S. in Thermal Engineering, Tsinghua University, Beijing, P. R. China, 2000

SELECTED JOURNAL PUBLICATIONS AND REFEREED PROCEEDINGS
PEFC Freeze-Thaw Degradation Modelling:
2. S. He and M. M. Mench, (to be submitted pending sponsor review)
3. S. He and M. M. Mench, (to be submitted pending sponsor review)

MEMS Sensor:

Fuel Cell Testing

Air Pollution Control:
10. S. He, G. Xiang, D. Li, et al., Environmental Progress, 21, 131 (2002).