MODELING COLD START OF POLYMER ELECTROLYTE FUEL CELLS

A Thesis in Mechanical Engineering by Leng Mao

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ABSTRACT

While substantial research efforts are presently directed toward performance and durability improvement of polymer electrolyte fuel cells (PEFC), PEFC cold start capability and survivability at subzero temperatures remains a challenge and has been scarcely researched.

In order to achieve a fundamental understanding of PEFC cold start, a mechanistic model is developed in this thesis to describe the complex physics involved, along with necessary experimental validation. First, a theoretical analysis focusing on the catalyst layer is performed to study the importance of coupled water and heat balance, as well as to elucidate the main effects of ice formation on fuel cell performance. Second, to fully describe the multi-scale physics involved in PEFC cold start and the coupled nature of water and heat transport, a comprehensive multi-dimensional, multi-component, multiphase, transient model is developed. The model accounts for ice/frost precipitation and growth in the cathode catalyst layer and gas diffusion layer and for water transport characteristics at very low temperatures. Governing equations of species, heat and charge transport are developed using a single-domain approach and solved with a finite-volume based computational fluid dynamics (CFD) technique. Validated by extensive experimental data, this computational model is used to identify key parameters that define PEFC cold start capability. Finally, effects of operating conditions, such as initial membrane water content, applied current load and start up temperature, are investigated using this model. PEFC cold start performance with different cell configurations or designs are also studied using this model.
# TABLE OF CONTENTS

LIST OF FIGURES ..................................................................................................... vii

LIST OF TABLES ....................................................................................................... x

ACKNOWLEDGEMENTS ........................................................................................... xi

Chapter 1 Introduction ............................................................................................... 1
  1.1 Background and Motivations ........................................................................... 2
  1.2 Experimental Study of the Water Freezing Effect on PEFC .......................... 5
  1.3 Current Strategies of PEFC Cold Start ........................................................... 7
    1.3.1 Warm Up with Self Heat Generation ................................................... 8
    1.3.2 Warm Up with External Heating .......................................................... 10
    1.3.3 Warm Up with In-Situ Chemical Heating ............................................ 11
    1.3.4 Remove Residual Water during Shutdown .......................................... 12
    1.3.5 Keep Residual Water from Freezing during Shutdown ....................... 14
  1.4 Literature Review of PEFC Models ............................................................... 15
    1.4.1 Existing Cold Start Models of PEFC .................................................... 16
      1.4.1.1 Lumped Fuel Cell Stack Model ................................................. 16
      1.4.1.2 Layered Fuel Cell Model ............................................................ 17
      1.4.1.3 Numerical Fuel Cell Model ........................................................ 18
      1.4.1.4 Statistically Based Cold Start Model ......................................... 19
    1.4.2 CFCD Models of PEFC ........................................................................ 20
      1.4.2.1 Water Transport .......................................................................... 21
      1.4.2.2 Heat transport ............................................................................. 23
      1.4.2.3 Transient Phenomena ................................................................. 25
  1.5 Multi-scale Phenomena in PEFC Cold Start .................................................. 26
  1.6 Summary and Objectives of the Present Research ......................................... 32

Chapter 2 Theoretical Analysis of PEFC Cold Start .................................................. 37
  2.1 Model of PEFC cold start ............................................................................. 37
    2.1.1 Water Balance ...................................................................................... 37
    2.1.2 Heat Balance ......................................................................................... 41
    2.1.3 Voltage Loss in the Presence of Ice Formation ..................................... 44
    2.1.4 A Complete Solution of Cold Start Problem ........................................ 48
  2.2 Results and Discussion ................................................................................... 51
  2.3 Conclusions ..................................................................................................... 55

Chapter 3 CFD Model of PEFC Cold Start ................................................................ 72
  3.1 CFD Model of PEFC Cold Start .................................................................... 72
<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.1.0 Model Assumptions</td>
<td>72</td>
</tr>
<tr>
<td>3.1.1 Governing Equations</td>
<td>73</td>
</tr>
<tr>
<td>3.1.1.1 Mass Conservation</td>
<td>73</td>
</tr>
<tr>
<td>3.1.1.2 Momentum Conservation</td>
<td>74</td>
</tr>
<tr>
<td>3.1.1.3 Species Conservation</td>
<td>76</td>
</tr>
<tr>
<td>3.1.1.3.1 Reactant Transport in GDL, CL and Flow Channels</td>
<td>76</td>
</tr>
<tr>
<td>3.1.1.3.2 Water Transport in GDL and Flow Channels</td>
<td>77</td>
</tr>
<tr>
<td>3.1.1.3.3 Water Transport through the Membrane</td>
<td>77</td>
</tr>
<tr>
<td>3.1.1.3.4 Water Transport in CL</td>
<td>80</td>
</tr>
<tr>
<td>3.1.1.4 Charge Conservation</td>
<td>81</td>
</tr>
<tr>
<td>3.1.1.4.1 Proton Transport</td>
<td>81</td>
</tr>
<tr>
<td>3.1.1.4.2 Electron Transport</td>
<td>82</td>
</tr>
<tr>
<td>3.1.1.5 Energy Conservation</td>
<td>83</td>
</tr>
<tr>
<td>3.1.1.6 Electrochemical Kinetics</td>
<td>84</td>
</tr>
<tr>
<td>3.1.2 Boundary Conditions</td>
<td>86</td>
</tr>
<tr>
<td>3.1.3 Initial Conditions</td>
<td>87</td>
</tr>
<tr>
<td>3.1.4 Numerical Implementation</td>
<td>88</td>
</tr>
<tr>
<td>3.2 Results and Discussion</td>
<td>89</td>
</tr>
<tr>
<td>3.3 Conclusions</td>
<td>96</td>
</tr>
</tbody>
</table>

Chapter 4 Effects of Operating Conditions in Isothermal Cold Start

<table>
<thead>
<tr>
<th>Subsection</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.1 Introduction</td>
<td>117</td>
</tr>
<tr>
<td>4.2 Purge Effects</td>
<td>119</td>
</tr>
<tr>
<td>4.2.1 Equilibrium Purge</td>
<td>119</td>
</tr>
<tr>
<td>4.2.2 Short Purge</td>
<td>122</td>
</tr>
<tr>
<td>4.2.2.3 Current Load</td>
<td>124</td>
</tr>
<tr>
<td>4.3 Conclusions</td>
<td>125</td>
</tr>
</tbody>
</table>

Chapter 5 Start up Temperature Effect

<table>
<thead>
<tr>
<th>Subsection</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.1 Introduction</td>
<td>134</td>
</tr>
<tr>
<td>5.2 Three Dimensional Modeling</td>
<td>136</td>
</tr>
<tr>
<td>5.3 Effect of Startup Temperature</td>
<td>137</td>
</tr>
<tr>
<td>5.3.1 Membrane water uptake</td>
<td>137</td>
</tr>
<tr>
<td>5.3.2 Vapor Phase Transport</td>
<td>138</td>
</tr>
<tr>
<td>5.3 Conclusions</td>
<td>140</td>
</tr>
</tbody>
</table>

Chapter 6 Effects of Cell Designs

<table>
<thead>
<tr>
<th>Subsection</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.1 Membrane</td>
<td>146</td>
</tr>
<tr>
<td>6.1.1 Membrane Thickness</td>
<td>146</td>
</tr>
<tr>
<td>6.1.2 Alternative Membrane Material</td>
<td>148</td>
</tr>
<tr>
<td>6.2 Catalyst Layer</td>
<td>148</td>
</tr>
<tr>
<td>6.2.1 Catalyst Layer Thickness</td>
<td>148</td>
</tr>
</tbody>
</table>
6.2.2 Optimization of the CL Composition ......................................................... 150
6.3 Conclusions ..................................................................................................... 151

Chapter 7 Conclusions and Future Work ................................................................. 157

7.1 Conclusions ..................................................................................................... 158
7.2 Outlook ........................................................................................................... 161
  7.2.1 Micro-scale phenomena ........................................................................ 161
  7.2.2 Optimization of Operating Conditions ................................................. 162
  7.2.3 Electrode Flooding Post Cold Start ...................................................... 163
  7.2.4 Experimental Validation ....................................................................... 164

Bibliography ............................................................................................................. 165
LIST OF FIGURES

Figure 1-1: Schematic of a polymer electrolyte fuel cell ..................................................34
Figure 1-2: Multi scale physics of PEFC cold start ..........................................................35
Figure 1-3: The catalyst layer of PEFC (adapted from Eikerling, M., Kornyshev, A. and Kulikovsky, A., The Fuel Cell Review, December 2004/January 2005) ..........................................................36
Figure 2-1: Water transport in fuel cell during cold start ................................................58
Figure 2-2: Water removal in the outflow ........................................................................59
Figure 2-3: Effects of ice formation on cathode overpotential .........................................60
Figure 2-4: Ice formation during cold start from -20°C ...................................................61
Figure 2-5: Temperature change during cold start from -20°C ........................................62
Figure 2-6: Cell Voltage evolution during cold start from -20°C ......................................63
Figure 2-7: Water balance during cold start from -20°C ..................................................64
Figure 2-8: Breakdown of heat generation during cold start from -20°C .........................65
Figure 2-9: Ice formation during cold start from -10°C ....................................................66
Figure 2-10: Temperature change during cold start from -10°C .....................................67
Figure 2-11: Temperature change during cold start from -10°C .....................................68
Figure 2-12: Water balance during cold start from -10°C ...............................................69
Figure 2-13: Breakdown of heat generation during cold start from -10°C .......................70
Figure 2-14: Effect of thermal mass on cold start from -10°C .......................................71
Figure 3-1: Schematic of the cell modeled .................................................................101
Figure 3-2: Mesh of the single-channel PEFC ...............................................................102
Figure 3-3: Independence study of the model (a) time step; (b) spatial mesh size ..........103
Figure 3-4: Discharge curve at constant current 40 mA/cm² .........................................104
Figure 3-5: Ice fraction in the cathode catalyst layer in X-Y plane ....................105
Figure 3-6: Ice fraction in the cathode catalyst layer in X-Z plane .....................106
Figure 3-7: Ice fraction in the cathode catalyst layer in Y-Z plane .....................107
Figure 3-8: Current Density Distribution in membrane ....................................108
Figure 3-9: Water Vapor Distribution in Gas Channel .....................................109
Figure 3-10: Water content contour in Y-Z plane at the center of membrane ....110
Figure 3-11: Temperature contour in X-Y plane .............................................111
Figure 3-12: Temperature contour in X-Z plane .............................................112
Figure 3-13: Temperature contour in Y-Z plane at the center of membrane .......113
Figure 3-14: Breakdown of the heat sources ...................................................114
Figure 3-15: Experimental Validation of the model .........................................115
Figure 4-1: Cold start after equilibrium purge ..................................................127
Figure 4-2: Voltage evolutions for cold start from -30°C after different equilibrium purge: (a) experiments and (b) simulations .............................................128
Figure 4-3: Cold start with short purge and equilibrium purge .........................129
Figure 4-4: Water content in MEA after short purge (Ballard Power System Inc. 
[87]) ................................................................................................................130
Figure 4-5: Current density profiles along the flow direction during cold start from -20°C after short purge .................................................................131
Figure 4-6: Ice growth profiles along the flow direction during cold start from -20°C after short purge .................................................................132
Figure 4-7: Cold start with different current load ..............................................133
Figure 5-1: Saturation pressure of water vapor at different temperatures .........141
Figure 5-2: PEFC cold starts under -20°C and -30°C ........................................142
Figure 5-3: Start up temperature effect ..............................................................143
Figure 5-4: Ice fraction contours of cold start from -20°C under different thermal boundary conditions ............................................................................................................. 144

Figure 5-5: Temperature distributions during cold starts from -20°C under different thermal boundary conditions .......................................................................................... 145

Figure 6-1: Effect of membrane thickness ................................................................................................................................. 153

Figure 6-2: Effect of the water diffusivity of membrane on cold start .......................................................... 154

Figure 6-3: Effect of catalyst layer thickness ......................................................................................................................... 155

Figure 6-4: Effect of catalyst layer composition and tortuosity factor ................................................ 156
LIST OF TABLES

Table 2-1: Electrochemical and transport properties ................................................. 57
Table 3-1: Summary of governing equations.......................................................... 98
Table 3-2: Geometric Parameters and Operating Conditions .................................... 99
Table 3-3: Electrochemical and Transport Properties ................................................ 100
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Chapter 1
Introduction

In recent years, fuel cells have been seriously considered as alternative power generation devices for transportation applications owing to their high efficiency and zero emission. A fuel cell converts chemical energy of a fuel directly into electricity, which ensures higher energy conversion efficiency and produces almost none of the sulfur and nitrogen compounds released by conventional generation methods. Among several types of fuel cells, the polymer electrolyte fuel cell (PEFC) has received the most attention and been investigated more thoroughly because it can operate at high power densities and low temperatures compared to other types of fuel cells [1]. These advantages of the PEFC make it particularly suitable for automotive application.

Although the driving forces for commercializing PEFC are strong, there are still several barriers to be overcome, such as the power limitation imposed by heat and water management. PEFC operational characteristics depend heavily upon temperature and water distribution, especially when phase change phenomena such as cathode flooding are involved. Thus, it is important to study the impact of thermal design and water distribution, which govern efficiency and performance of a fuel cell system.

In addition, when a PEFC operates in extremely cold weather, water produced from the oxygen reduction reaction cannot be removed fast enough from the fuel cell and will form ice or frost inside the catalyst layer and the gas diffusion layer. The ice/frost formation will plug the pores of these layers, blocking reactant transport. The ice or frost
formed in the catalyst layer will also cover the reaction site and reduce the electrochemical active area (ECA). All these factors will dramatically reduce the fuel cell operating voltage, even causing shutdown of the cell. Therefore, the quick startup capability of a PEFC becomes an important criterion for its commercialization. This issue is known to the automotive industry as “cold start”, which refers to the fuel cell operation starting from subzero temperatures to normal conditions at approximately 80°C.

To better understand the fundamentals of PEFC cold start, the primary concern of this research is to develop a multiphase fuel cell model to simulate this complicated process, which includes the interrelated transport phenomena of mass, species, charge and heat with phase change.

In this chapter, the background and motivations of PEFC cold start research are discussed first, then current strategies for cold start are reviewed, followed by a discussion of existing cold start models for fuel cell stack and related modeling work. Finally, the multi-scale physics of cold start is described in detail.

### 1.1 Background and Motivations

The polymer electrolyte fuel cell is an electrochemical device in which hydrogen and oxygen are combined to produce water, as shown in Figure 1-1. Reactant gases enter the fuel cell through a set of flow fields. The purpose of flow fields is to evenly distribute the reactant gases, as well as carry away the unused gases and product water. Once gases enter the fuel cell from gas channels, gases diffuse through a porous gas diffusion layer (GDL) towards the catalyst layer (CL), where the chemical reactions occur. The CL is
also a micro-porous structure of carbon particles coated with a finely dispersed catalyst, which promotes the kinetics of the electrochemical reactions. A micro-porous layer (MPL) made highly hydrophobic is often included between each GDL and CL to provide a transition to improve electric contact between the two layers and facilitate liquid water removal.

Anode and cathode are separated by a thin ionomeric membrane which conducts protons but insulates electrons. The humidification of the membrane directly influences proton conductivity, thus pre-humidification of the reactants is often needed in normal operation. Both CLs are applied or hot-pressed onto the membrane to form a membrane electrode assembly (MEA).

On the anode side, hydrogen dissociates into protons and electrons:

\[ 2H_2 \rightarrow 4H^+ + 4e^- \]  \hspace{1cm}  \text{(1-1)}

Protons travel through the membrane to the cathode and electrons are forced through an external circuit. On the cathode side, protons transported from the ionomeric membrane combine with electrons from the external circuit and oxygen, producing water at the cathode CL. That is:

\[ O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \]  \hspace{1cm}  \text{(1-2)}

As mentioned earlier, successful startup of a fuel cell under extreme weather conditions is a key issue to be overcome. For fuel cell vehicles, customers will expect to start the vehicle quickly, implying a very short period for the fuel cell to reach its full power. However, there are some limitations for the power output at startup. For instance, under subzero temperatures, the product water will turn into ice and plug the pores of the
CL and GDL, significantly lowering the performance and even causing the cell shutdown. With larger power output and faster ice formation, the fuel cell will be more quickly shutdown. This is an important issue not only due to customers’ desire for quick startup, but also because durability of a fuel cell is greatly affected by the startup cycle. The degradation caused by an unsuccessful cold start is much more severe than that caused by a successful one. In addition, reduction of the startup time offers other advantages to system configuration, such as reducing the need for pre-heating and external heating sources. For the direct hydrogen system, the current DOE requirement for the 2010 goal of cold startup from -20°C to 100% power is 30 seconds [2].

Therefore, a basic understanding of the startup process and improved fuel cell components to enhance the startup capability are of great importance. However, the physics of PEFC startup at subzero temperatures is very complex, as it involves the interplay of phenomena at disparate scales which vary from ice formation in micro-pores of the CL to heat flow through the whole stack. This is to be elucidated shortly.

In recent years, researchers have made great efforts to resolve this issue. Nevertheless, there are more patents than published articles on this topic, indicating a serious lack of knowledge in this area. The majority of proposed concepts and solutions are from system level perspective, which provides very limited insight and less useful fundamental data for feasible and effective methods. Hence, well-designed experiments and mathematic modeling should be developed to advance our understanding of cold startup.

Although it has become routine to use numerical models to simulate fuel cell operation and predict performance, there is very little literature addressing modeling of
cold start in PEFCs, and almost all of it uses lumped analysis of heat balance to explain this process, from which quite limited information can be obtained to improve our understanding of this complex process. This may be the reason most strategies are proposed though the system point of view. To find a creative and passive solution, it is absolutely necessary to develop a comprehensive model which includes more physical complexities and enables us to study material effects and improve component design.

In summary, current techniques proposed for cold start and modeling efforts are all at the system level, which indicates that an understanding of fundamental physics of cold start is virtually absent. This work attempts to identify the fundamental physics and establish a detailed model for PEFC cold start for the first time. Beginning with the understanding of multi-scale physics, a numerical model is developed to better understand these fundamentals and reveal the key parameters governing the cold start performance.

1.2 Experimental Study of the Water Freezing Effect on PEFC

The effect of water freezing on PEFC performance and degradation is studied by several groups through experimental studies.

Cho et al. [3] studied the changes of fuel cell characteristics using electrochemical impedance spectroscopy (EIS), cyclic voltammetry (CV) and Brunaer-Emmett-Teller porosity analysis (BET) upon thermal cycling from 80 to –10°C. They conclude that the volume change of CL upon freezing/thawing leads to the fuel cell degradation. The deformation of the CL structure causes an increasing ohmic loss due to deteriorated
contact between the membrane and the CL and an increasing polarization resistance due to the decrease of ECA and poor utilization of platinum catalysts. Methods of preventing the degradation by gas purge and solution purge are studied [4]. A much slower degradation rate is observed with these methods.

Oszcipok et al. [5] [6] used CV and BET in isothermal potentiostatic cold start to investigate the degradation effects. They found ice formation in CL, GDL and MPL, which leads to a significant performance loss through cold start cycle with a decreasing ECA of the cathode electrode. Besides the CL structure change which leads to the contact resistance increase between membrane and CL, structure change of the cathode GDL and MPL are also observed with the cold start cycling, which causes changes in the hydrophobicity. In addition, a statistical model is developed to investigate the importance of some operating parameters to cold start behavior, which will be discussed later in this chapter. However, in their latest paper [7], they conclude that a passive cold start up of a portable system is not viable due to the thermal mass of the peripheral components and to end-plate heat losses. Energy consumption for passive start up could be higher than external heating methods. Consequently, electrical heating is used to assist the fuel cell stack to 0°C to avoid the severe degradation caused by ice formation. Successful cold start practice is achieved from –20°C for a fuel cell stack in their experiments.

Yan et al. [8] investigate the effect of subzero temperatures on PEFC cold start performance by measuring the polarization curves of a 25cm² single cell at chamber temperatures between 80°C and –15°C. No successful start up can be achieved under subzero temperatures without purge at the fuel cell shutdown. After gas purge, a single cell is able to start at –5°C with insulation. With higher air stoichiometry and gas
temperature, a single cell is possible to start up at \(-10^\circ\text{C}\) with a low current as 100 mA/cm\(^2\), while it is failed to start up with 200 mA/cm\(^2\). They also observed MEA and GDL damage such as delamination of the catalyst layer from both the membrane and GDL through scanning electron microscopy (SEM) method. The study by Guo et al. [9] reveals the importance of the membrane water storage through PEFC freezing/thawing cycles. More severe damage is observed for a fully hydrated MEA than for a less hydrated one.

These studies all indicate that the fuel cell is difficult to start up from sub-freezing temperatures and significant degradation occurs through either freezing/thawing cycles or cold start cycles. A number of strategies are proposed to solve this problem and will be discussed in the following session.

### 1.3 Current Strategies of PEFC Cold Start

From the heat and water management point of view, many strategies have been proposed for rapid startup of PEFC from subzero temperatures. Realizing the cold start problem comes from the low temperature and ice formation inside the fuel cell, these strategies focus on raising the fuel cell temperature and removing residual water or reducing the initial ice before start.

Among the methods of raising the cell temperature, there are a few strategies for heating up the fuel cell by itself. Conventionally, an external heat source (e.g., a storage battery) or a heater is employed to heat up the fuel cell from subzero to normal operation temperature (about \(80^\circ\text{C}\)), as can be found in most of the literature. In addition, methods
of catalytically burning the fuel/oxidizer mixture to locally heat up the MEA are also provided in some patents. Usually, a cooling loop is employed to assist the warming up of the cell. To increase the temperature quickly and avoid the need for a large heat source, thermal mass of a fuel cell is always minimized and heat insulation is applied.

In terms of water management, purge systems connected to the fuel cell are proposed, which purge the fuel cell at a temperature above the freezing point to prevent initial ice formation during shutdown under a cold weather. To prevent ice formation below the freezing point during startup, some approaches are also suggested, such as using a lower current load in the cold startup to reduce the rate of reaction water produced, thus to prevent ice blockage; or introducing anti-freeze liquids (e.g. water/glycol mixture) into the fuel cell.

In the following, different strategies to resolve the cold start issues in PEFCs are further discussed in detail.

1.3.1 Warm Up with Self Heat Generation

Waste heat will be released during fuel cell operation; usually this amount of heat is comparable to the power generated. If it can be utilized to warm up the fuel cell above the freezing point before shutdown by the ice formation, the fuel cell can be startup successfully at no extra cost.

Fletcher et al. [10] discussed a “short-circuit” method to heat up fuel cell. He suggests that by decreasing the resistance of the external circuit connected to the fuel cell, the fuel cell is effectively short circuited for a period of time. Using the electrical current
generated, the fuel cell temperature could be raised to the normal operating temperature. Accordingly, the flow rate of the reactant also needs to increase to meet the higher current requirement. However, the disadvantage of this short-circuit operation is that an extremely high electrolyte resistance must be overcome at subzero temperatures.

Roberts et al. [11] proposed a strategy of “reactant starvation” to raise the fuel cell temperature. By operating the fuel cell at a high current density at which the reactant is consumed more quickly than it is supplied, an increased over-voltage is obtained at the electrode. As a result, more internal heat is generated to warm up the fuel cell. Also mentioned in the patent another advantage of this method is that the produced water can be minimized. However, severe degradation will be caused by the reactant starvation [12].

Takahashi [13] proposed another starting method in which the contact resistance between components in the main body of a fuel cell is increased by reducing the pressure applied to the main body. Internal energy losses are increased and thus the fuel cell temperature can be increased without using an external power source or heater.

All these methods try to make the fuel cell operate beyond its normal operating point to produce more heat to rapidly heat up the fuel cell. However, in this work it will be shown that the heat production is directly proportional to the water produced. The more heat generated, the more water produced. Therefore, there are no differences between applying these conditions and operating normally with different current loads, except that working at these conditions will cause additional damage to the fuel cell.
1.3.2 Warm Up with External Heating

An easy way to heat up the fuel cell is using some external devices to raise the fuel cell temperature. In this case, an extra power source is required.

The heating strategies can be classified as electric heating, reactants pre-heating and cooling loop heating. Gebhardt [14] discussed using a heating element to heat up a minimal area of a fuel cell unit, i.e. to electrically heat a portion of the fuel cell by an external source, then autothermally heat up the entire cell. A method proposed by Pettit [15] uses electrical heating to preheat the inlet gases, and Habrich [16] described a scenario in which the reactants are pre-heated by the reformer before entering the flow channels. Conventionally, a cooling loop is employed with an external heat source to warm the fuel cell stack during startup, as in the patents of Fuller et al. [17] and Wexel et al. [18].

The external heating source could be an electrical device or an external gas burner like the reformer.

In the patent of Reiser [19], a battery is used to provide the power under freezing condition and assist the fuel cell to warm up rapidly. Similar ideas are also presented by Mufford et al. [20] and Spach et al. [21]. From a simple analysis, the energy required for a temperature increase from -20°C to 0°C for a 200 cell stack is 1800 kJ. For a 10 kW heat source, the time to reach the freezing point is 180s.

The patents of Habrich [16], Tajima et al.[22], Yokoi et al. [23] and Stute [24], suggested that a fuel cell could get the required heat from high temperature combustion in an external gas burner through a heat exchanger. Matsubara et al. [25] proposed a method
in which the exhaust gas formed during the reforming process is selectively preheated and introduced into the fuel cell stack. Gebhardt et al. [26] described a fuel cell with a reformer starting first, and then utilizes the operating heat to heat up the fuel cell stack. Baumann et al. [27] proposed a reforming reactor heating up the gas to operating temperature, in which the fuel is burnt with the intermittently impinged oxygen catalytically.

Although external heating is one method used to warm up the fuel cell, additional space and cost will be included in the fuel cell system design, which is not desirable for automotive applications. It can be seen from the discussion above that the focus of these proposed strategies is on how to minimize the extra design costs.

1.3.3 Warm Up with In-Situ Chemical Heating

Besides raising the fuel cell temperature using heat generated from the operation itself and external heating sources, another method to heat up the fuel cell without introducing extra costs is using in-situ chemical heating. Instead of separating the fuel and air in the normal operation, mixing the fuel with air directly can generate extra heat to raise the temperature of fuel cell components.

Fuller and Wheeler [28] proposed a method of introducing a dilute hydrogen/air mixture into the cathode to generate heat at subflame temperatures, thereby warming up the fuel cell to a temperature at which the fuel cell operation may begin. The cathode structure should be sufficiently hydrophobic to prevent flooding and freezing of water thereby to assure ice-free passages for the fuel/oxygen mixture to enter and react.
Wheeler suggested further in his patent [29] that the temperature rise from the hydrogen/air reaction should be limited to about 150 F without flame, explosion or drying out the membrane by controlling the hydrogen gas stream to a small volume percentage of the overall mixture (around 1% by volume to less than 4% by volume in the cathode airflow at -40°C).

Rock and Plant [30] indicated that the MEA can be locally heated by the exothermal reaction between hydrogen and oxygen on either catalyst. Furthermore, they suggested that for the exothermic heating purposes, higher gas flow rates than normal operation usage should be supplied to the fuel cell to ensure a uniform distribution of the heat generated by the chemical reactions. Based on an initial temperature of below –25°C, they suggest that for a reaction at the anode, the oxygen content should be at least 2% by volume and less than about 7% by volume. Similarly for the cathode, hydrogen concentration should be 0.5-3.5% by volume in the cathode airflow upon startup.

In these methods, besides the possible danger from mixing fuel and air together, water is also produced at the same time proportional to the heat generated. Therefore, if water is not removed from the CL, it will freeze there and cause additional problems.

**1.3.4 Remove Residual Water during Shutdown**

Removal of the water from the CL is another important method for cold startup besides heating the fuel cell to a temperature above the freezing point. However, during cold start operation, it is hard to remove the product water mechanically. Hence, to store maximum production water to delay the ice/frost formation before freezing occurs and to
earn time for temperature increase, the initial condition before cold start should be optimized. Usually actions are taken at the shutdown of a normal operation prior to cold start, since it is much harder to remove water from the fuel cell once ice/frost forms.

Gas purge therefore becomes an effective method to improve startup performance by improving the initial condition before cold start. A typical process purges the oxidant and fuel passages using nitrogen at the shutdown prior to the cell temperature dropping below the freezing point, thus reducing the amount of water within the fuel cell before initiating the start operation.

Neutzler et al. [31] point out that water accumulated in the GDL and the flow channels may freeze and block fuel system lines, which will dramatically delay the startup of the fuel cell. They suggest that the shutdown procedure include the steps of reducing the fuel cell system temperature to make water vapor condense in the fuel cell; removing both liquid and gaseous water from the fuel cell; purging the reactant gas passages with a non-humidified gas; and reducing the system pressure to approximately atmospheric pressure.

Roberts et al. [32][33] also indicate the purge process should be conducted after disconnecting the fuel cell with the external circuit and at a temperature below the cell operating temperature, preferably as low as 10°C.

Similar to gas purge, an idea of vacuum drying is discussed by Fuss [34]. He describes a method of substantially dehydrating the fuel cell by evacuating the flow field of the fuel cell with a vacuum sufficient to evaporate and remove water from the fuel cell to prevent damage due to freezing. Water is more easily evaporated with a lesser vacuum from a warm fuel cell than from a cooler one, therefore he suggests that the fuel cell be
evacuated shortly after it is shut down from normal operation (e.g. about 80°C) and still warm (i.e. at least about 50°C).

The purge process needs to be optimized to minimize the remaining water in CL, GDL and gas channels while keeping the membrane hydrated. Although gas purge alone cannot solve the cold start problem, it greatly improves the cold start performance and enhances the possibility of successful startup. Moreover, it does not cause any damage to the fuel cell system. Therefore, it is considered an effective way to assist the startup operation.

### 1.3.5 Keep Residual Water from Freezing during Shutdown

Recognizing ice/frost formation as the key factor causing the cold start problem, an alternative method to avoid ice formation during the non-operation period is keeping the residual water from freezing, instead of removing it.

A simple method has been discussed by Molin et al. [35] integrating a heat storage device to the PEFC system by insulating the fuel cell. They suggest that a heat storage device be applied to the PEFC stack in order to use the waste heat produced by the PEFC stack.

By keeping the fuel cell operating at some minimum level such that internal resistance provides sufficient heat and excessive water can be removed by the outflow, ice formation can be minimized or even prevented. Roberts et al. [11] suggest a method of starvation to heat up the fuel cell by limiting the reactant flow, they also point out that the amount of reaction water produced during starvation is reduced, thus preventing ice
blockage in the fuel cell. However, at low level operation, it takes much longer time even forever to reach normal operation temperature.

Breault et al. [36] describe a “direct antifreeze cooled” fuel cell which does not require isolating an antifreeze cooling fluid from the cathode and anode catalysts within a sealed coolant system. Minimum free water is left within the system that may be frozen when the fuel cell is shutdown and subject to sub-freezing temperatures, thus the fuel cell can achieve a rapid startup without melting substantial amounts of frozen water. The direct antifreeze solution in their method should be non-volatile and not wet a hydrophobic substance such as "Teflon" at cell operating temperatures. It should be capable of being oxidized by fuel cell catalysts, such as alkanetriol. This sort of solution minimizes the movement of antifreeze as a vapor, reducing contact with the catalysts. Antifreeze at catalysts will also be oxidized to avoid catalyst poisoning.

1.4 Literature Review of PEFC Models

The literature on the modeling of PEFC cold start is scarce, and most uses a lumped analysis of heat balance to explain this process, yielding quite limited information to improve our understanding of this complex problem. At the stack level, heat transfer has been explored with several approaches. Mathematical analyses at the cell level have, to date, assumed the form of lumped parameter treatments for each component differing little from the stack model.
1.4.1 Existing Cold Start Models of PEFC

Three different cold start fuel cell/stack models are discussed in this section and all of them are transient models considering the energy and mass balances for the fuel cell/stack.

1.4.1.1 Lumped Fuel Cell Stack Model

Weisbrod et al. [37] discussed cold start dynamics by developing a global model of heat requirements and water transients during startup from sub-freezing temperatures. And cold startup experiments are conducted to validate the model in both auto-thermal condition and with coolant heated by wasted heat from the fuel processor.

An overall heat and water balance is solved for the fuel cell stack at the initial ambient temperature –40°C. Their major assumptions are: 1) the stack is without coolant system; the polarization curve under -10°C is estimated; 2) dry air is available from the compressor at 78°C (isentropic compression from –40°C) ; 3) gases leave at 100% relative humidity; and 4) the bipolar plates are thermally isolated from the end plates. Using this model, they estimated the stack temperature increases with and without an external heat source, and validated the temperature change predicted by the stack model with their experiments. They also predicted the fraction of GDL void volume occupied by ice formed from water produced in the reaction.

Based on their calculations, they concluded that air preheating provides small benefit. Furthermore, they provided some design guidelines to minimize startup time, such as reducing the thermal load of the end plates, operating the stack at a constant low
voltage to maximize the heat production, and requiring dry gas to feed the stream up to 0°C.

In this model, the transient nature of cold start and some physical effects such as ice formation were considered. However, the fuel cell stack was modeled as a lumped mass in the energy balance equation, therefore a temperature distribution could not be obtained. Although the ice fraction in GDL was predicted by water balance, its effect during cold start was not considered.

1.4.1.2 Layered Fuel Cell Model

Sundaresan [38][39] described a one-dimensional, transient, layered cell thermal model to simulate the sub-freezing cold start of a PEFC. Unlike a lumped model, the fuel cell/stack in this model has a multi layered structure in which individual cell components, such as membrane, GDL and CL, are considered as different layers. By applying the heat and mass balance to each layer, temperature distribution in a fuel cell/stack during cold start can be predicted. The heat source term includes: sensible energy flows for coolant, anode and cathode gases; latent heat released during phase changes (freezing under subzero condition and thawing above freezing point); heat losses to the environment; as well as internal heat generated by the electrochemical reactions and ohmic resistance.

The major assumptions made in this cell model are: 1) temperature distribution between layer centers is linear; 2) current density is homogeneously distributed over the active area; 3) net water drag is 0, i.e., the electro-osmotic drag through the membrane from anode to cathode and the back diffusion of product water from cathode to anode are
equal; 4) thermal conductivity for the materials and entropy used in the heat generation are not a function of temperature; 5) ideal gas law is used for gases; 6) condensation and vaporization are spontaneous and complete; 7) the membrane has constant resistance and contact resistance (thermal and electrical) between cell layers is neglected.

Using this layered cell model, the cell temperature distribution can be obtained, and this distribution can be used to observe the coldest layer temperature and determine whether it is below freezing even while the other layers are above freezing. Nevertheless, this one-dimensional model only solves for temperatures with the simplification of a uniform current density distribution, where the effects of species transport and ice formation are not considered. In addition, while ice formation is determined by local conditions, the temperature in each layer cannot be predicted by this layer-averaged model.

### 1.4.1.3 Numerical Fuel Cell Model

A transient three-dimensional heat and mass transfer model simulating PEFC cold start is presented by Yukio et al. [40]. The heat and mass balances are calculated along the gas flow direction, where the species transport includes the gas diffusion on the electrode and the backing layer, the membrane conductivity, the electro-osmotic transfer and the diffusion of water in the membrane. The major assumptions in this model are: 1) freezing water affects only the cathode; 2) water produced freezes immediately at the reactive area; 3) constant pressure; 4) water enters and leaves in vapor phase.
The cell voltage, current-density distribution, and temperature distribution of the membrane, separator, cooling water, and gas are calculated on the condition that the average current density and initial temperature are given. Their simulation is compared with experimental results. Based on the simulation, they conclude: 1) freezing starts from the downstream side of the cathode due to the higher vapor pressure there; 2) self-starting is possible for ambient temperature around -5°C, while below that temperature, external heating is necessary.

Although the heat transfer is solved in three dimensions, the water transport and the electrochemical reactions are considered as one dimensional. For water transfer, cathode water is the sum of the water produced during the reaction and the water brought from the anode by electric-osmotic drag, and freezing water is the cathode water deducted by the water carried away by cathode gas. But the membrane water uptake, critical in the water balance, has not been taken into account. The effective reaction area is assumed to decrease in proportion to the amount of frozen water; however, the proportionality coefficient is determined by fitting an experimental polarization curve, which limits this model in predicting cold start behavior.

1.4.1.4 Statistically Based Cold Start Model

Statistical software is employed by Oszcipok et al. [5] [6] to investigate the cold start behavior based on experimental data. The cumulated charge transfer density which directly corresponds with the amount of water produced was used to evaluate the cold start behavior. Potentiostatic single-cell experiments were conducted under the isothermal
condition and analyzed by the statistical model. The experimental results were fitted mathematically to study the effects of three parameters: reference power density which indicates the degree of degradation; the air flow rate and the initial membrane humidity.

From the regression results, they concluded that the initial start current mainly depends on the membrane humidity and the operational voltage; the current density drops dramatically once the maximum membrane humidity is reached. From their experiments, they also found degradation effects by ice formation in the porous structure leading to significant performance loss.

The drawback of this statistical model is that it is obtained by fitting experimental data, whose reliability strongly depends on the analysis and database. In Oszcipok’s model, a general polynomial equation is assumed for the relationship between cumulated charge transfer density and the three parameters. The regression does not adequately reflect the actual physics and some important parameters are neglected.

### 1.4.2 CFCD Models of PEFC

In recent years, computational fuel cell dynamics (CFCD) is employed to better understand the physics during PEFC operation by solving the complete set of transport equations governing mass, momentum, species, energy, and charge conservation. In the last few years, more physically complex models have been developed with less restrictive assumptions. Although no specific model dealing with cold start has been published, the current comprehensive CFCD models in PEFC provide us a solid ground to advance in
tackling this problem. A recent review of state of the art CFCD modeling is presented by Wang [41].

In the following, three sub-areas of PEFC modeling critical for the development of a multiphase cold start model are reviewed: (1) water transport, (2) heat transport, and (3) transient phenomena.

1.4.2.1 Water Transport

The key factor distinguishing cold start from normal operation is the ice/frost formation, which is directly related to the local water distribution. Also as mentioned before, fuel cell performance strongly depends upon membrane water content. Therefore water management is always one of the most critical and widely studied issues in PEFCs due to the conflicting needs to hydrate the polymer electrolyte and to avoid excessive water accumulated in porous electrodes and GDL. In cold start, the conflict becomes more severe as a result of ice formation inside the CL and GDL, more difficult to remove compared with the liquid water. Early modeling works [42]-[47] focused on fully humidified inlet reactants to ensure high proton conductivity of the electrolyte and the least ohmic loss. However, under low temperatures, fully humidified gas easily becomes oversaturated with water vapor and ice formation occurs in the cathode CL even at low operating current densities.

In cold start, the polymer membrane not only functions as a proton conductor but also plays a very important role in storing product water to delay and reduce the water desublimation in the CL. The physics of water transport through the polymer membrane under normal condition has been investigated thoroughly by many researchers. A diffusion model was first introduced by Springer et al. [43] for Nafion 117 membrane by
assuming equilibrium between the gas phase and the ionomer phase of water in the Nafion membrane. In this case, the membrane water content at the interface can be determined by the activity of water vapor. Hsing and Futerko [48] developed a two dimensional finite element model in which the membrane water content at the cathode/membrane interface was assumed to be fully hydrated and at the anode/membrane interface was assumed to be equilibrium with water vapor. More recently, Janssen [49] demonstrated 1-D and 2-D numerical models to account for water transport through the MEA under various humidification conditions of inlet gases. In his model, the CLs were excluded in the water transport calculation, and reacting species along the channel and in the through plane direction were calculated in one dimension.

Comprehensive models were developed using the CFD approach to reflect the different modes of water transport in various components of a PEFC, particularly the back diffusion and electro-osmotic drag through the membrane. Dutta et al. [50][51] uses an approximate analytical solution for water transport through the membrane by assuming a constant diffusion coefficient and drag coefficient and then embeds it into numerical solutions. This approach removes the MEA from the computational domain. However, the ionic resistance in the CL cannot be accurately taken into account. In addition, a PEFC model treating the MEA as an interface without thickness essentially ignores the membrane water storage capacity and therefore cannot be used in simulating important transient phenomena such as cold startup. In contrast, Wang and co-workers [47] [52] developed a unified water-transport model applicable throughout a PEFC including the MEA region. Different modes of water transport are incorporated in the unified water transport equation such as diffusion, convection, and electro-osmotic drag where phase equilibrium is assumed between different phases of water, i.e. the equilibrium water uptake curve in the membrane phase. Under this treatment, the water
transported through the membrane and absorbed by the membrane during cold start can be correctly captured.

1.4.2.2 Heat transport

In cold start, heat transport is extremely important because the PEFC temperature should be increased to above the freezing point in a short time to ensure sustainable operation. In self startup, the PEFC temperature rise is expected to be obtained through the waste heat generated from the cell. A PEFC produces waste heat in an amount comparable to its electric power output. Heat generation in a PEFC cold start comprises entropic heat of reactions, the irreversibility of the electrochemical reactions, ohmic resistance and phase change. The phase change term is due to water desublimation/melting as it is related to two-phase transformation. Also hydration of polymer membranes strongly depends on the temperature as the water vapor saturation pressure is an exponential function of temperature. Thus, thermal management in PEFC cold start is inherently coupled with water management and the two factors combine to ensure the startup capability of a PEFC.

Early efforts in simulating the thermal management were made by Nguyen and White and Fuller and Newman. A two-dimensional PEFC model is developed by Nguyen and White with one-dimensional heat transfer in the flow direction. In this model, the only heat source is from the phase change of water in the flow channel. Fuller and Newman developed a pseudo two dimensional thermal PEFC model with one dimensional mass transfer in the through-plane direction and one dimensional heat transfer in the flow direction. The enthalpy change of the overall electrochemical reaction is incorporated in their model. However, in these early models the temperatures of membrane and electrodes were not differentiated. In cold start, even a small temperature
variation in these regions can cause a huge difference in the water vapor transport. Furthermore, the major heat source terms were not specified in their models, such as the entropic and irreversible reaction heats. Rowe and Li [54] developed a one dimensional model in the through membrane direction and predicted the temperature variation in the through membrane direction under the various current densities and electrode thermal conductivities. However, the cathode CL is assumed to be fully hydrated and the membrane water content is linearly interpolated, which is not applicable to a low humidity operation like cold start.

Multidimensional thermal models were presented by many PEFC modeling groups. Maggio et al. [55] performed pseudo three-dimensional simulations by neglecting the temperature gradient in the flow direction. However, the heat source terms were also treated globally and not made location specific. Such treatment has also been used in the three-dimensional models developed by Shimpalee and Dutta [56] and Costamagna [57]. Assuming the membrane to be fully humidified, Berning et al. [58] presented a three-dimensional PEFC model including irreversible and entropic heat terms in the CLs and Joule heating in the membrane. Zhou and Liu [59] developed a three-dimensional PEFC model in which the entropic reaction heat was ignored.

Ju et al. [60]-[62] developed a three-dimensional model by taking into account all the heating sources. Their prediction indicates that the primary mechanism of heat removal from the CL is through lateral heat conduction along the in-plane direction to the current collector. Heat removed by gas convection inside the gas channel accounts for less than 5% under typical PEFC operating conditions. In the present work of modeling PEFC cold start; this thermal model is extended to include the phase change and transient effects.
1.4.2.3 Transient Phenomena

Dynamic characteristics of a fuel cell engine are of paramount importance for automotive application, particularly for the startup. In cold start, the situation becomes more complex because of the ice/frost accumulation at the electrodes due to desublimation.

Three primary processes govern the time response of a PEFC during normal operations [65]: electrochemical double-layer discharging; gas transport through channel and GDL; and membrane hydration or dehydration. The time constants for double-layer discharging and reactant gas transport through GDL are short enough to be ignored for automotive fuel cells. The slowest process is membrane hydration, for Nafion 112 and a reference current density of 1 A/cm², the membrane hydration takes about 25 s. Therefore, for low humidity cells where the membrane undergoes water uptake, the water accumulation term is essential for transient analysis.

Cold start of PEFC is a fully transient process. During startup at subfreezing temperatures, low humidity fuel/air is supplied and fuel cell operates at a very low current load to avoid freezing inside the cell. The membrane hydration takes much longer with such a low current. At the same time, heat is generated from the operation. Both water and heat transport in cold start should be taken into account for transient processes, where the water vapor is subject to desublimation and the cell temperature rises from subzero to normal operating temperature at around 80°C.
Raising the cell temperature to an operational level before shutdown by ice formation is the ultimate goal of a PEFC cold start. Therefore, transient response is essential for a successful PEFC cold startup.

Wang’s group is one of the first to study the transient phenomena during a PEFC operation. Um et al. [47] developed a model to simulate the transient response of a PEFC to a voltage step change under fully hydrated condition. More recently, Wang and Wang [63]-[65] extended the work of Um et al. to include the membrane hydration transient process for low humidity PEFC, showing a time response of the average current density to a step change in cell voltage in a low-humidity fuel cell. Significant undershoot and overshoot are found for the current density due to the transient phenomena of gas transport and membrane hydration. For membrane hydration during normal operation with a current density of 1A/cm\(^2\), the fuel cell transients occur over as long as 15 s. Transient of cold startup thus could take much longer compared with startup under ordinary conditions.

**1.5 Multi-scale Phenomena in PEFC Cold Start**

Although many strategies have been proposed to tackle the cold start problem, there are no feasible solutions due to the lack of fundamental knowledge. Aside from the scarcity of basic experimental data, few published models use a black-box approach to simulate cold start behavior, which does not take into account fundamental physical phenomena.
Physics governing PEFC cold start is characterized by several disparate length scales. These range from the microscopic scale of the ionomeric structure in the proton-conducting membrane and triple-phase boundary in the CL, to the component level (membrane and CL), to the cell level, as shown in Figure 1-2. All of these are associated with different physical phenomena.

At the microscopic scale, important physics include the state of water in the ionomer, proton and water transport mechanisms through the membrane\cite{66}-\cite{68}, ice/frost nucleation and growth from the triple-phase surface with mixed wettability, and the effect of ice formation on the membrane and the CL morphology during the cold start cycle.

The state of water and mechanism of proton conduction in the membrane can be explained by distinguishing between tightly bounded water near pore surfaces and liquid-like water in the interior of pores. During cold start, the liquid-like water freezes and conductivity of membrane drops dramatically below the freezing point. Water in the membrane can be loosely categorized as freezing water, bounded freezable and bounded non-freezable, but the effect of the state of water to proton transport is still unknown. Cappadonia et al. \cite{69}\cite{70} observed a change in activation energy of the conductance of Nafion 117 at transition temperatures between 225K and 260K depending on the water content. However, this behavior is not observed in our experimental measurements \cite{71}. To understand membrane behavior in cold start, knowledge of mutual interactions in molecules of ionomer, water and proton at low temperatures is needed.

To achieve good performance under low temperatures, higher proton conductivity of membrane is desired without ice formation in the cathode electrode. However, unlike
normal operation, water uptake by the membrane is a very important way to store product water and prevent freezing in the cathode CL, gaining more time for waste heat to warm up the fuel cell. Proton conductivity, which strongly depends on the degree of membrane hydration, is reduced as a trade off for a longer operational time. Therefore, to predict the PEFC cold start behavior it is critical to understand the characteristics of membrane water uptake under low temperatures.

During proton transport, each proton drags some number of water molecules along. This number, called the electro-osmotic drag coefficient, lies typically in the range of 1–2.5 for normal operations. It increases with decreasing equivalent weight (EW), defined as the weight of polymer relative to the number of acid sites. Water content dependence of electro-osmotic drag coefficient has also been extensively studied [72]-[75]. The electro osmotic drag is strongly affected by the presence of free water, implying that the drag coefficient known in normal operation may no longer be valid under cold start conditions.

The CLs, especially on the cathode side, are the heart of a PEFC. The functionality of a typical fuel-cell CL is elaborated by Eikerling et al. [76]. As shown in Figure 1-3, the electrochemical reactions occur at the three-phase interface between gas, electro-catalyst (supported on the electronically conducting phase of carbon) and the electrolyte (i.e. ionomer). A two-phase interface between electrolyte and electro-catalyst has also been proposed as the reaction surface where the electro-catalyst is supported on a carbon particle and covered by a thin layer of membrane electrolyte, with the gas species dissolved in the electrolyte. Both ideas consider that CLs have small pores and are highly hydrophobic, and it takes a high liquid pressure for water to invade.
Under low temperatures, the reaction kinetics is characterized by higher activation loss and lower reaction rate. Furthermore, the low water saturation pressure will cause the product water from the oxygen reduction reaction to freeze within the cathode CL easily, forming ice to block the reactant diffusion as well as covering the active reaction sites. At the microscopic scale, several questions need to be answered in order to understand the macro behavior of cold start. First, when does ice nucleation initiate? At a specific temperature, what is the vapor saturation level on which ice formation begins? This incipient time will partly determine the fuel cell temperature before the cell is shut down by ice formation. Second, where does it happen? Once vapor becomes oversaturated in the CL, ice nucleation occurs. Is this nucleation also determined by the local surface condition? Third, how does it grow? The morphology of ice formed directly affects how fast the active reaction site will be covered and the reactant diffusion will be blocked.

At the component level, major issues associated with cold start are: (1) the rate of water adsorption or desorption in the membrane at very low temperatures; (2) ice/frost filling of the CL; (3) O₂ transport limitation; (4) pore expansion and collapse upon phase change; and (5) the interfacial delamination between the membrane and CL during thermal cycling.

Because of the low vapor saturation pressure, water carried away by the outflow is very limited. Water produced at the cathode CL is partially absorbed by the ionomer if it is not fully hydrated, and the remainder will freeze in the CL. This process strongly depends on the water transport in the porous CL and also in the ionomer phase. Besides the morphology of frozen ice, the pore size and structure of the CL also affect the cold
start behavior. On the other hand, the formed ice will cause pore expansion and some unrecoverable mechanical damage in the MEA.

As mentioned before, the formed ice will block the reactant transport, but how it comes into play is still unclear. As a result of ice blockage of reactant diffusion and active reaction site coverage, the distribution of reaction current is non-uniform both along the thickness of the CL and along the flow direction.

At the cell level, the heat flow and current/water distributions play major roles in cold start characteristics. By minimizing the thermal mass of each component and using warming up circulation loops or external assist heating, the cold start performance can be greatly enhanced.

Moreover, these multiscale phenomena are intimately coupled; for example, the ice/frost nucleation and growth at the microscopic scale strongly affects the O₂ transport process through the CL and hence the operating time of cold start at the cell level. On the other hand, the transport phenomena occurring at the cell level, prior to and during cold start, determine the temperature and water distributions, which in return control ice/frost nucleation and growth at the microscopic scale of the cathode CL, and ice filling or melting in the CL at the component level.

The coupled nature of micro- and macro-scale phenomena in PEFC cold start explains why the cold start discharge behavior is controlled not only by the operating conditions such as the purge procedure, discharge current density and the ambient temperature, but also by the microscopic properties of materials such as the wettability of the CL pore walls and pore size distribution in the CL.
Figure 1-2 illustrates important physical phenomena occurring at various stages of PEFC cold start. Four stages are defined in the figure along with the power and temperature profiles, i.e. shutdown, cool down, cold start, and post cold start. After shutdown, a purge process will remove liquid water from the gas channels, thus avoiding ice formation and damage in them. In addition, the purge process will evaporate some liquid water from the GDL, CL and membrane in order to create a reservoir to store water generated during cold start. During cool down, residual water vapor inside the fuel cell will condense inside micropores of the CL, thus occupying a fraction of the open pores in the CL. The liquid water trapped inside the CL micropores will turn into ice once the cell temperature drops below the freezing point.

The cool-down process is followed by cold start in which the fuel cell is discharged in either galvanostatic or potentiostatic mode. The current load produces both waste heat (desired) and product water (undesired). The amount of heat generation, after overcoming the cell thermal mass, must promote the cell temperature rise above and beyond the freezing point before the CL is completely filled up with ice and hence shut down. This constitutes a successful self start. Clearly, the self start condition hinges upon the delicate balance between heat generation (and resulting temperature rise) and water production. In addition, the cell thermal mass and heat flow through the GDL between the CL and land play a pivotal role in self-start. If water production completely fills up the CL and shuts down the electrochemical reaction before the cell temperature raise beyond the freezing point, the cell voltage experiences a drop down and the cold start fails unless there is external assist heating.
Once the fuel cell successfully starts, the ice inside the micropores is melted. However, the trapped liquid water must then be evaporated and become accessible for gas transport before the CL is restored to its full function. To this end, the fuel cell must reach a sufficiently high temperature (i.e. >50°C). Before reaching this temperature level, no high current load may be applied without producing a drastic drop in the cell voltage. Therefore, it is evident that cold start has profound implications to post cold start events.

1.6 Summary and Objectives of the Present Research

Cold startup of a PEEC, a tremendous barrier in fuel cell commercialization for automotive applications, is being investigated with great effort worldwide. Many patents have been filed proposing different strategies to tackle this problem. In warming up the fuel cell system, self startup strategies are suggested by operating the fuel cell at extreme conditions to increase the waste heat, while most patents tend to increase the temperature using assist heating methods. To prevent ice formation inside the fuel cell, purging the system at shutdown to remove the residual water is suggested in some strategies. Also methods of using anti-freezing solutions in PEFC to avoid freezing below the freezing point are discussed.

Although dozens of patents have been filed in discussing methods of cold startup, not a single patent has been found discussing an inherent solution to cold start, such as material and MEA improvement. This may be mainly due to the lack of knowledge in the micro physical process; most of the strategies suggested are from the macro point of view, which are far from feasible and effective methods.

The physical phenomena during cold start range from ice nucleation in the CL and proton transport in the ionomer at the micro scale to heat flow through a fuel cell
stack at the macro scale. To better understand the physical processes during cold start, there is an imperative need for a comprehensive model which includes the interrelated transport phenomena of mass, species, charges and heat. Few efforts have been made in modeling cold start, partly due to its complexity. Several existing fuel cell stack models use lumped analysis to study the thermal behavior; none of them contains fundamental physics.

In this research, our objectives are to:

- Elucidate the fundamental phenomena via modeling in conjunction with fundamental experiments. By simulating the cold start process with a detailed model and validating the results against experimental data, a much better fundamental understanding of the cold start can be achieved. For example, the distribution and evolution of ice formed inside the electrode and its effects can be shown by simulations. Key parameters dominating the cold start can be identified from modeling along with guided experiments.

- Optimize fuel cell design and operating conditions for cold start. By comparing simulation results for different fuel cell designs and at different operating conditions, the fuel cell system can be optimized for cold start operation. New designs may be proposed from the simulations, and operating conditions can be refined. The detailed model cannot only provide innovative ideas but also demonstrate their effects directly. Comparing with the experimental data, some feasible and effective solutions improving cold start performance can be obtained.
Figure 1-1: Schematic of a polymer electrolyte fuel cell
Figure 1-2: Multi scale physics of PEFC cold start
Figure 1-3: The catalyst layer of PEFC (adapted from Eikerling, M., Kornyshev, A. and Kulikovsky, A., The Fuel Cell Review, December 2004/January 2005)
Chapter 2
Theoretical Analysis of PEFC Cold Start

Based on the water and heat balance, an analytical model is developed in this chapter to describe PEFC cold start behavior, especially ice formation and its effects during cold start. The conditions and key parameters that affect frost/ice formation are analyzed; also discussed are the effects of formed ice during cold start.

2.1 Model of PEFC cold start

The following assumptions are made in the present analytical model: (1) fuel cell treated as a lumped thermal mass with a uniform temperature; (2) incompressible and ideal gas mixtures; (3) isotropic and homogeneous GDL, CL and membrane; (4) immediate and homogenous ice formation in CL when the water vapor pressure exceeds the saturation pressure; (5) negligible ice formation in the GDL due to the limited vapor transport at low temperatures; (6) outflow saturated with water vapor; and (7) negligible potential drop due to ohmic resistance in the electronically-conductive solid matrix of GDL and catalyst layers, as well as bipolar plates.

2.1.1 Water Balance

Water transport mechanism in the PEFC cathode during cold start is schematically shown in Figure 1-3. To prevent the fuel cell from shutdown by the ice
formed inside the catalyst layer, product water is preferred to be diffused into the membrane or transported out into GDL and/or gas channel, thereby keeping the catalyst layer free of ice.

When the water production rate exceeds the removal rate from the catalyst layer and the gas becomes oversaturated, residual water will desublimate and form ice in the pores of the CL. Water can be removed from the CL either by membrane absorption or vapor phase transport to the GDL. The ice formation rate in the catalyst layer (i.e. the water accumulation rate \( \dot{n}_{\text{acc}}^{\text{H}_2\text{O}} \)) can be estimated by assuming instant desublimation of water accumulated in the catalyst layer that cannot be transported into the membrane or GDL. That is,

\[
\dot{n}_{\text{acc}}^{\text{H}_2\text{O}} = \dot{n}_{\text{CL}}^{\text{H}_2\text{O}} - \dot{n}_{\text{mem}}^{\text{H}_2\text{O}} - \dot{n}_{\text{GDL}}^{\text{H}_2\text{O}}
\]

\[\text{2-1}\]

Including the drag effects, water generation rate in the cathode catalyst layer can be expressed as the sum of production water from the oxygen reduction reaction and the dragged water from anode side:

\[
\dot{n}_{\text{CL}}^{\text{H}_2\text{O}} = \frac{IA}{2F} \left(1 + n_d \right)
\]

\[\text{2-2}\]

Humidified gases are always used to ensure that the membrane is hydrated under normal operations. But during cold start, the main goal is to prevent or reduce the ice formation. Dry gases are used to minimize water accumulation inside the cell prior to cool-down, and furthermore, the ionomer is considered a water buffer because it can uptake some water when it is not fully hydrated and thereby store part of the production water to decrease the amount of water subject to desublimation in the catalyst layer.
Assuming equilibrium between membrane water content and activity of the surrounding gas, the water uptake curve is expressed by Springer et al. [43] [78].

Considering that the membrane becomes fully hydrated from an initial state, the maximum amount of water absorbed by the membrane can be expressed as:

\[ n_{\text{mem}} = \frac{\rho_{\text{dry}} (\lambda_{\text{sat}} - \lambda_0)}{E W} \cdot \delta_{\text{mem}} A \]  \hspace{1cm} (2-3)

where \( \lambda_0 \) is the initial water content in the ionomer, \( \lambda_{\text{sat}} \) is the maximum membrane water content when in equilibrium with saturated vapor. For a Nafion@112 membrane with initial water content of 4, this maximum water storage capacity of the membrane is equal to 1.7 mg/cm². However, for very small water diffusivity characteristic of very low temperatures, the membrane water storage cannot be fully utilized. By assuming the membrane as a semi-infinite slab, a similarity solution can be used to estimate for the water transport rate into the membrane, i.e.:

\[ \dot{n}_{\text{mem}} = \frac{\rho_{\text{dry}} \sqrt{D_{\text{mem}} (\lambda_{\text{CL}} - \lambda_0)}}{E W \sqrt{\pi t}} A \]  \hspace{1cm} (2-4)

Beside membrane absorption, water vapor can also be transported from the CL to the GDL. Due to the temperature difference in the through-plane direction, it may desublimate in the GDL. However, water transported from the CL to the GDL is limited by the low vapor saturation pressure under subfreezing condition. In addition, water transferred out of the CL also becomes more difficult when ice forms inside. Therefore the amount of water freezing in the GDL is very small under low temperatures and is neglected in this study. That is, the water vapor being transported to the GDL from CL is the water being removed through the outflow.
Under subzero temperatures, the maximum rate for water to be removed through the cathode exhaust can be obtained by assuming the outflow is always saturated with water vapor, such that:

\[
\dot{n}_{\text{outflow}}^{H_2O} = \dot{n}_{\text{outflow}}^{H_2O}
\]

where the Goff-Gratch equation \[71\] is adopted in this work for the saturation pressure of water vapor over ice \( p_{\text{sat}}^{\text{H}_2\text{O}} \). Due to the low saturation pressure at a low temperature, this amount is quite small compared with the water production rate. Figure 2 shows the water removal rate compared with the water production rate for a PEFC discharging at 100mA/cm\(^2\). A stoichiometry of 2 has been used with air supplied at the cathode inlet. If pure oxygen is used, the water removal rate would be about 5 times smaller than air. The water removal rate from the cathode outlet is much smaller than the water production rate, especially at subzero temperatures. Therefore, it is impossible to remove all the product water through the outflow during subzero startup.

From Eq. 2-1, Eq. 2-2, Eq. 2-4 and Eq. 2-5, the rate of water accumulation in the CL can be obtained. Before the CL gets saturated with water, there is no ice formation inside the fuel cell \( \dot{n}_{\text{ice}}^{H_2O} = 0 \). The water accumulated will first be stored in the CL until the water saturation is reached.

\[
\rho_{\text{dry}} \left( \lambda_{\text{CL}} - \lambda_0 \right) \frac{\delta_{\text{CL}}}{E W} \dot{e}_{\text{mc}} = \int_0^t \dot{n}_{\text{acc}}^{H_2O} dt
\]

In cold start, the saturation pressure in the catalyst layer is reached in a short time
because the catalyst layer is a thin layer and saturation pressure is extremely small at low
temperature. Similar to the membrane, the water storage capacity of the ionomers in the
cathode catalyst layer is

\[ n_{CL}^{H_2O} = \frac{\rho_{sat}(\lambda_{sat} - \lambda_0)}{\beta_{CL}} \delta_{CL} \varepsilon_{ac} A \]  \hspace{1cm} (2-8)

A 10 µm catalyst layer can store up to 0.083 mg/cm² water when the ionomer
content is 0.25 and initial water content is 4.0. Once the water saturation is reached in the
CL, the ice will precipitate at the rate of water accumulation, i.e. \( \dot{n}_{ice}^{H_2O} = \dot{n}_{acc}^{H_2O} \). The ice
fraction is defined as the volume fraction of the ice to the void space in the CL, which is

\[ s = \frac{V_{ice}}{V_{void}} \]  \hspace{1cm} (2-9)

Thus, by assuming homogenous ice formation, ice fraction in the catalyst layer
can estimated from desublimation rate, that is

\[ s = s_o + \int_{s_o}^{t} \dot{n}_{ice}^{H_2O} V_{ice} dt = s_o + \int_{s_o}^{t} \left( \dot{n}_{CL}^{H_2O} - \dot{n}_{mem}^{H_2O} - \dot{n}_{GDL}^{H_2O} \right) V_{ice} dt \]  \hspace{1cm} (2-10)

When the fuel cell temperature reaches the freezing point, ice starts to melt in the
catalyst layer, absorbing latent heat of melting, which will be discussed in the next
session.

\textbf{2.1.2 Heat Balance}

To ensure a successful self-start, the fuel cell should raise its temperature beyond
the freezing point before being shutdown by ice in the CL. The duration a PEFC can
operate is determined by the rate of ice filling the CL pores and the thermal capacity of
the cell.

Self startup depends on the waste heat produced from ORR while water is created. The waste heat produced in a PEFC can be subdivided into reversible heat, irreversible heat and heat released during phase transition, which is

$$\dot{Q}_{\text{total}} = \dot{Q}_{\text{rev}} + \dot{Q}_{\text{irrev}} + \dot{Q}_{\text{phase}}$$

Considering a H₂/air fuel cell operated at the temperature \( T \), pressure \( P \), and the current density \( I \) on the electrode surface area, \( A \). The reversible heat release, \( Q_{\text{rev}} \), can be written as:

$$\dot{Q}_{\text{rev}} = \left( -T \Delta S \right) \frac{I}{2F} A = \left( -T \frac{\partial U_o}{\partial T} \right) IA \tag{2-12}$$

where \( \Delta S \) represents the entropy change of the overall reaction, \( U_o \) is the thermodynamic equilibrium potential of the reaction with all reactants and products in gas phase. For the PEFC, the equilibrium potential is written as:

$$U_o = 1.23 - 9.0 \times 10^{-4} (T - 298.15) \tag{2-13}$$

In addition, the irreversible heat generation due to the cell operated at a different lower voltage, \( U_{\text{cell}} \), than the equilibrium \( U_o \) is simply given by:

$$\dot{Q}_{\text{irrev}} = \left( -\frac{\Delta G}{2F} - U_{\text{cell}} \right) IA = \left( U_o - U_{\text{cell}} \right) IA \tag{2-14}$$

where \( \Delta G \) is the free energy change of the H₂/O₂ reaction and the cell voltage \( U_{\text{cell}} \) can be obtained from Eq. 2-26. This irreversible heat generation is due to the electrochemical reactions and ohmic resistance.

In cold start, there is another special heat source term due to phase change, such
as releasing heat during desublimation and absorbing heat when the ice starts to melt.

\[ \dot{Q}_{sg} = \dot{n}_{ic}^{H_2O} h_{sg} \]  

where \( h_{sg} \) is the enthalpy change of water between the solid phase and the vapor phase and \( \dot{n}_{ic}^{H_2O} \) is the desublimation/melting rate. Combining Eq. 2-11, Eq. 2-12, Eq. 2-14 and Eq. 2-15, the total heat generation, \( Q_{total} \), is thus given by

\[ \dot{Q}_{total} = \left( U_o + \frac{h_{sg}}{2F} - T \frac{\partial U_o}{\partial T} \right) IA - U_{cell} IA \]  

The first term on the right side of Eq. 2-16 is the maximum chemical power available from the overall reaction, the second term is the actual electrical power produced by a fuel cell. And the sum of the first two terms in the brackets \( U_o + \frac{h_{sg}}{2F} \) actually represents the thermal potential of the \( \text{H}_2/\text{O}_2 \) reaction with production water being ice.

The heat losses from the cell to the surroundings \( \dot{Q}_{loss} \) are through the outflow and from bipolar plates and cell edges, which can be generally expressed as:

\[ \dot{Q}_{loss} = (\dot{m}C_p)_{outlet} T - (\dot{m}C_p)_{inlet} T_0 + h_0(A(T - T_0)) \]  

where \( h_0 \) is the convection heat transfer coefficient. When a cell is thin and the end effects are negligible, the spatial uniformity in temperature is a good approximation. By applying the energy balance over the entire cell with the assumption of spatially uniform cell temperature, the temperature of a PEFC during the cold start can be calculated from:
where the left side of the equation refers to the sensible heat of the cell component. During the melting, cell temperature is fixed at the freezing point, from which the ice fraction can be obtained using Eq. 2-18.

2.1.3 Voltage Loss in the Presence of Ice Formation

The effect of freezing on the fuel cell electrochemical performance is similar to that of flooding. Freezing affects the fuel cell performance by hindering the oxygen transport and reducing the active reaction sites. The difference between the freezing problem and the flooding problem is that liquid water can be continually transported from the cathode and a steady state solution exists for the flooding problem; while in the freezing problem, the ice precipitated inside the CL cannot be removed, thereby the fuel cell cold start is an inherently transient problem.

The blockage of species diffusion can be simply described by the effective diffusion coefficient $D_{\text{eff}}$:

$$D_{\text{eff}} = D (\varepsilon_{\text{CL}} (1-s))^{1.5}$$  

where $D$ is the diffusion coefficient in open space, $\varepsilon_{\text{CL}}$ is the catalyst layer porosity. Not only the reactant but also the water inside the catalyst layer becomes difficult to transport, which promotes the desublimation.

The coverage effect can be expressed as the active reaction area decreasing, which is:
In the present work, a linear relationship (i.e. \( n = 1 \)) is assumed between the fraction of surface coverage and the ice volume fraction. In fact, this relationship depends strongly on the micro-scale morphology of ice formed in the CL. If a sheet-like shape is formed, the surface could be totally covered by a small volume fraction of ice, thereby rendering \( n \) to be very large. On the other extreme, if the ice morphology is needle-like, the exponent becomes small. Experimental work is ongoing in our laboratory to determine Eq. 2-20.

These two effects of formed ice cause the electrochemical reaction to slow down and finally shutdown the fuel cell. Electrochemical kinetics is governed by Butler-Volmer equation. The cathode potential can be expressed in terms of Tafel kinetics, i.e.

\[
j = a_i \alpha \bigg( \frac{c_{\text{O}_2}^{\text{CL}}}{c_{\text{O}_2}^{\text{eff}}} \bigg) \exp(-\frac{RT}{\alpha_F \eta_c})
\]

Based on the experimental data given by Parthasarathy et al. [77], the temperature dependence of the ORR kinetic parameter is approximated as:

\[
i_o(T) = i_o(353.15K) \exp \left[ -11000 \left( \frac{1}{T} - \frac{1}{353.15} \right) \right]
\]

This correlation indicates that under low temperatures, the electrochemical reaction becomes more sluggish.

The consumption rate of oxygen is proportional to the current density. Under the assumption that the reaction current density is uniform throughout the catalyst layer, the
oxygen concentration follows a quadratic distribution in the through-plane direction, as given by:

\[
\frac{\partial}{\partial x} \left( D_{O_2} (e_{CL} (1-s))^{1.5} \frac{\partial c_{CL}^{O_2}}{\partial x} \right) = \frac{j}{4F} = \frac{I}{4F \delta_{CL}} \tag{2-23}
\]

where \( x=0 \) at the interface of the catalyst layer and membrane and \( x=\delta_{CL} \) at the interface of the catalyst layer and GDL. The concentration of the oxygen at the reaction site can be expressed as a function of the oxygen concentration in the flow channel and the oxygen flux to the catalyst layer, that is

\[
c_{CL}^{O_2} = c_{c}^{O_2} - \frac{I}{4F} \left( \delta_{GDL} - \frac{D_{O_2} e_{GDL}^{1.5}}{D_{O_2} e_{GDL}^{1.5} (e_{CL} (1-s))^{1.5}} \right) \tag{2-24}
\]

Taking the average value of the oxygen concentration in the cathode catalyst layer and plugging it into Eq. 2-21, one can obtain the cathode overpotential as a function of the current density and the ice fraction in the cathode catalyst layer. That is,

\[
\eta_c = -\frac{RT}{\alpha_c F} \ln \left( \frac{1}{(1-s) a_0 \delta_{CL}} \cdot \frac{c_{CL}^{O_2} + c_{CL}^{O_2} - \frac{I}{4F} \left( \delta_{GDL} + \frac{2 \delta_{CL}}{3 D_{O_2} e_{GDL}^{1.5}} \right)}{c_{c}^{O_2}} \right) \tag{2-25}
\]

where the two terms related to \((1-s)\) represent the two effects of ice formation as the reduction in the ECA and the hindering of oxygen transport respectively.

The effects of ice formation are plotted in Figure 2-3, showing the cathode overpotential as a function of the ice fraction for a fuel cell operated at 100mA/cm² under -20°C. At such a low current density, the mass limitation becomes less severe because of
the small oxygen consumption rate. As shown in Figure 2-3, the difference of using air (10.11 mol/m$^3$) and pure oxygen (48.14 mol/m$^3$) is small. And the overpotential decreases sharply at high ice fraction, indicating that the fuel cell is shutdown by the ice coverage on the ECA as well as complete blockage of the reactant.

Generally, the cell voltage can be estimated by subtracting the activation loss and ohmic losses from the equilibrium potential subtracting.

$$U_{cell} = U_a - \eta_a + \eta_c - IR$$ \hfill 2-26

As mentioned earlier, the mass transport limitation is unimportant because the current applied during cold start is usually very small. The ohmic loss comes from the protonic resistance of the electrolyte in both membrane and CL, the contact resistance, the electronic resistance of the CL, GDL and current collector. However, the contact resistance and electronic resistance are small and thereby neglected in the present work. The protonic resistance in the anode CL is also negligible because HOR occurs primarily at the CL/membrane interface. Assuming the ORR reaction occurs uniformly in the cathode CL, the ohmic loss can be expressed as:

$$IR = I \left( \frac{\delta_{mem}}{\kappa_{mem}} + \frac{\delta_{CCL}}{2\kappa_{CCL}^{1.5}} \right)$$ \hfill 2-27

where $\kappa_{mem}$ and $\kappa_{CCL}$ are the protonic conductivities of the ionomer evaluated at different water contents in the membrane and catalyst layer, respectively.

It can be seen from Eq. 2-25 that during cold start, ice formation in the CL causes the cathode overpotential to increase through reducing the active reaction area and blocking the oxygen transport. As a consequence, the fuel cell voltage drops down.
2.1.4 A Complete Solution of Cold Start Problem

The PEFC cold start problem can be mathematically fully described by three processes: ice formation derived from the water balance; temperature rise based on energy balance; and the cell voltage drop-down as a function of ice formation. During cold start, the ice formation blocks the oxygen transport from the gas channel to the reaction sites and partially covers the ECA with ice sheets. Simultaneously, heat production from the oxygen reduction reaction raises the cell temperature, which in return alters the ice formation. These coupled phenomena have been analyzed by assuming a uniform cell temperature and homogenous ice formation in the catalyst layer in the present model.

The cold start process can be divided into four distinct stages:

1. When the fuel cell starts to operate and water is produced at the cathode to increase the water vapor concentration in the gas until saturation. In this stage, no ice precipitation occurs.

2. Once water saturation is reached in the gas phase in the CL, further product water will precipitate in the CL. At the same time, the waste heat produced will warm up the fuel cell. In this stage, the fuel cell could be shutdown if the CL pores are filled completely with ice before the cell temperature rises beyond the freezing point.

3. If the fuel cell temperature successfully rises to the freezing point before the CL is shutdown by ice, the ice in the CL starts to melt, absorbing the waste heat produced from the cell and keeping the cell temperature at the freezing point.

4. When the CL is totally free of ice, the cell temperature begins to rise again
until the normal operation temperature at which point the cell cooling must be initiated to maintain a steady operation.

Detailed analysis of each stage follows.

Stage 1:

In the first stage where the cell temperature is below zero, the water balance equation is solved using Eq. 2-7. In this period, there is no desublimation because gas in the CL is not saturated with water vapor. If the time interval for stage 1 is defined as \( t_0 \), one has:

\[
\int_{0}^{t_0} \dot{n}_{acc} H_{2O} dt = \frac{\rho_{dry} (\dot{\lambda}_{sat} - \dot{\lambda}_0)}{E} \delta_{CL} e_{acc}
\]

The cell temperature can be solved from the energy balance equation, Eq. 2-18, where phase change of water does not occur. If the cell temperature increases up to the freezing point in this period, the fuel cell can be successfully start up without ice formation. But, this is rarely the case with realistic fuel cell design and operating conditions.

Stage 2:

Ice starts to precipitate from the over-saturated gas inside the cathode CL once the vapor saturation is reached and the cell temperature is still below the freezing point. There are two possibilities in the second stage depending on whether the cell temperature can reach the freezing point before ice fills up the pores in the CL.

If the temperature cannot rise to the freezing point before the catalyst layer is filled up with ice, i.e. ice fraction reaches the unity, and the fuel cell will be shutdown, marking the end of this second stage or cold start. The shutdown time can be estimated by Eq. 2-29
Otherwise, time needed for the fuel cell temperature rising up to the freezing point can be calculated by solving the energy balance, that is, \( T(t_1) = T_{\text{freeze}} \). At this point, the ice fraction reaches its maximum value \( s(t_1) \). To have a successful self startup, \( t_1 \) should always be less than \( t_{\text{shutdown}} \). The cell temperature and ice fraction evolution can be calculated by solving the energy and water balance equations coupled with the cell voltage expression with effects of ice formation.

Stage 3:

The third stage begins when the freezing point is reached and ends when the ice formed in the CL completely melts \( (s(t_2) = 0) \). In this stage, formed ice absorbs heat and starts to melt. The cell temperature is constant at the freezing point in this third stage, \( T = T_{\text{freeze}} \), due to phase transition. The ice melting rate can be calculated from the energy balance:

\[
-Q_{\text{sg}} = \dot{Q}_{\text{rev}} + \dot{Q}_{\text{rev,irrev}} - \dot{Q}_{\text{loss}} \tag{2-30}
\]

Therefore, the ice fraction evolution can be obtained as follows:

\[
s = s(t_1) + \int_{t_1}^{t_2} \frac{-(\dot{Q}_{\text{rev}} + \dot{Q}_{\text{rev,irrev}} - \dot{Q}_{\text{loss}})}{\varepsilon_{\text{CL}} V_{\text{CL}} h_{\text{sg}}} v_{\text{ice}} \, dt \tag{2-31}
\]

In this melting stage, part of the waste heat is absorbed by ice melting. There is a mathematical possibility that the product heat is insufficient to melt all ice. In that case the cell will remain at the freezing point with only partial ice being melted.

Stage 4:
The fourth stage starts when the ice completely disappears in the CL. In this stage, the fuel cell temperature starts to rise from the freezing point to the normal operating temperature, which can be obtained by Eq. 2-18.

**2.2 Results and Discussion**

The analytical model presented in the preceding section is employed to study and understand the physics governing PEFC cold start. Simulations are performed to assess the effects of the start up temperatures, the initial water content in the membrane, and the thermal mass of bipolar plates. In these simulations, both anode and cathode gas streams have constant flow rates corresponding to a stoichiometric flow ratio of 2 at the current density of 100 mA/cm$^2$ and the inlet pressure of 1.0 atm. The cell parameters used in the calculations are listed in Table 2-1. The startup current density is 100 mA/cm$^2$ in all calculations.

The analytical solution of cold start with a start up temperature -20ºC is presented in Figure 2-4 - Figure 2-8 . The initial water content in the membrane corresponds to that cell is purged with gas of 50% relative humidity. Figure 2-4 and Figure 2-5 show the ice formation and temperature evolution during the cold start, respectively. From the plots, it can be seen that the fuel cell temperature cannot rise to the freezing point before the ice fraction reach the unity, which means the fuel cell is shut down by ice formation in the CL. It can be seem from Figure 2-4 that there is no ice precipitation during the first 33 seconds of cold start. Once the gas is saturated with water vapor in the CL, desublimation occurs and ice starts to form in the pores of the cathode CL. The corresponding cell
voltage evolution in this startup is shown in Figure 2-6. The initial rapid increase is mainly owing to the decrease in the protonic resistance of the membrane upon water uptake, especially for ionomers in the cathode CL, as shown in Eq. 2-31. When ice starts to appear inside the CL, the activation loss increases as a result of the oxygen blockage and ECA reduction as illustrated in Figure 2-3. However, when the ice fraction is low, the cell voltage continues to increase due to the improvement of the membrane proton conductivity with more water uptake and less ORR kinetics with rising cell temperature. The effect of ice formation becomes significant only when the ice fraction approaches the unity, as characterized by the sharp drop in cell voltage. Figure 2-7 shows the water fluxes in and out of the cathode CL during cold start where a positive value indicates a source and the negative represents a sink. The water produced from the ORR together with the water dragged from the anode can be either transported into the membrane and GDL or freezes inside the CL. From the plot, it is obvious that the outflow can only remove a very small amount of water due to the small flow rate and the low vapor saturation pressure at subzero temperatures. Before the vapor saturation is reached, the product water is absorbed by ionomers in CL. The increasing water content in the CL leads to a larger water flux into the membrane. Once the water content in the catalyst layer reaches its peak, i.e. equilibrium with saturated water vapor, the flux starts to decrease as can be seen from the similarity solution in Eq. 2-4. As a result, the residual water precipitating as ice inside the CL increases. At about 105 seconds, the catalyst layer is filled with ice and the fuel cell is shutdown by the ice formation. The breakdown of heat generation is plotted in Figure 2-8, where a positive value means a heat source and a negative value is a heat loss. The sensible heat, i.e. the heat warming up the fuel cell, is
the difference between the total heat generation and the heat loss. The reaction heat accounts for about 50% of the total heat generation and the entropic heat accounts for 25%. The Joule heat is high initially due to the large protonic resistance of the electrolyte, and it decreases with further discharge as more product water being absorbed by the ionomer. After 33 seconds, there is latent heat released from the desublimation process. At the end of discharge, the reaction heat which is proportional to the cathode overpotential increase dramatically due to the CL filling up with ice. The heat losses, both from the bipolar plate and through the exhaust gas, are proportional to the temperature difference between the fuel cell and the ambient. The waste heat brought out by the outflow is small and negligible although it increases as the cell temperature rises.

Cold start from -20°C is unsuccessful because the temperature cannot reach the freezing point before the cathode CL being filled up with ice. Increasing the start up temperature is more likely to achieve a successful start up which reduces not only the heat loss to the environment but also the heat needed for the fuel cell to reach the freezing point. As presented in Figure 2-9 - Figure 2-13, a PEFC start is studied by the analytical model with the same configuration and conditions except the ambient temperature is -10°C. In Figure 2-9, the cold start process can be clearly divided into 4 stages: (1) In the first 33 seconds, water vapor builds up in the gas in the CL until it becomes saturated. (2) Then ice starts to form and reaches its peak at 58 seconds when the cell temperature rise to the freezing point. (3) After that, the ice starts to melt and the temperature remains at the freezing point, as shown in Figure 2-10. (4) Once the ice completely melts, the temperature rises again to the normal operating condition. The temperature increase below the freezing point is faster than that above the freezing point, which is due to the
latent heat released during ice formation and increasing heat loss to the environment when cell temperature becomes higher. Figure 2-11 shows that the cell voltage keeps increasing during the cold start from -10°C, which is mainly owing to the ohmic resistance decrease and fast kinetics with a rising temperature. However, due to the ice formation, the voltage increase is depressed between 33 and 58 seconds. From the water balance during cold start in Figure 2-12, it is similar to the -20°C case except that during the thawing the ice melted contributes to the water generation in CL. The breakdown of the heat generation is given in Figure 2-13. The most noticeable difference between cold starts from -10°C and -20°C is the heat absorbed by the ice during thawing process. There is a small increase of the reaction heat during desublimation, suggesting the effect of ice formation on cathode overpotential, and its decrease during the melting and thereafter is due to the fast reaction kinetics. The heat loss from the bipolar plates decreases as the cell temperature rises and levels when cell temperature remains at the freezing point.

It is of interest to study the thermal effects on cold start. Reducing the thermal mass of a fuel cell, particularly the bipolar plates, is another way to improve cold start performance by increasing the cell temperature more quickly. Fuel cells with graphite bipolar plates of thickness 0.5mm, 1mm and 1.5 mm are simulated using the present model. To include the effect of heat loss to the environment, a constant heat transfer coefficient 20 W/m²K is used for the heat loss through the bipolar plates to the surroundings. From the temperature evolution curves shown in Figure 2-14, the fuel cell with less thermal mass, or thinner bipolar plates, is more likely to start up successfully, as can be seen from the slope of temperature increase. For a fuel cell with 1.5mm graphite bipolar plates, the temperature cannot rise to the freezing point from -20 °C before the CL
being filled up with ice; therefore the fuel cell cannot successfully start up. Comparing the thermal curves for 0.5mm and 1.0mm bipolar plates, it is seen that the time needed to melt the ice is shorter with less thermal mass because the amount of ice formed is smaller. Furthermore, the heat loss to the surroundings is also of great importance by comparing the thermal curve of 1.0mm bipolar plates. With a larger heat transfer coefficient 50 W/m²K, the fuel cell with the same configuration cannot start up successfully from -20°C, suggesting that thermal insulation will improve the cold start performance. In a stack environment, the heat transfer coefficient $h_0$ represents the cell-to-cell heat loss. Therefore, end cells feature higher $h_0$ and hence are more difficult to start; the cells in the middle of a stack are characterized by smaller $h_0$ and consequently are easier to start.

2.3 Conclusions

Water transport and subsequent ice formation control PEFC cold start behavior. Production water from the ORR and dragged water from the anode accumulate at the cathode electrode. If this amount of water cannot be removed fast enough, water vapor gets saturated and desublimates into ice. The effects of ice formation manifest in two aspects: coverage of the electrochemically active reaction surface and blockage of the oxygen transport. These two effects decrease the fuel cell voltage and even cause the shutdown of the fuel cell.

The criterion of a successful start up is that the cell temperature rises above the freezing point before the cathode electrode is completely filled with ice. Although the water storage capacity of the membrane is relatively large, only a small fraction is
utilized due to the sluggish water transport in the membrane at subzero temperatures characteristic of cold start. Water produced at the cathode CL can either transport into the membrane and the GDL or accumulate and form ice in the CL. Once the gas in the CL becomes oversaturated, water will desublimate into ice, where the desublimation rate depends on the water accumulation and removal rate from the catalyst layer. Before the catalyst layer being filled up with ice, the cell temperature must rise beyond the freezing point to ensure a successful start up. The cold start process is divided into four stages for a successful cold start, according to the temperature and ice formation evolutions.

An analytical solution of PEFC cold start is obtained in this work and is employed to study the effects of operating conditions and design parameters are investigated using this analytical model. At different startup temperatures, the cold start behavior varies. For a higher startup temperature, the energy required to heat up the fuel cell to the freezing point is lower, also the heat loss to the environment is less due to a small temperature difference thereby more likely to start up successfully.

Thermal effect is investigated to improve the cold start performance. Reducing thermal mass and applying thermal insulation lead to a quicker temperature increase with the same amount of waste heat released. The water management is another way for improvement which will be discussed in Chapter 4.

In general, the analytical model is helpful for us to understand the cold start process. However, to really understand the interactions between the different transport processes and phase change phenomena, a detailed multi-dimensional model and further validation is required.


<table>
<thead>
<tr>
<th>DESCRIPTION</th>
<th>UNIT</th>
<th>VALUE</th>
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<tbody>
<tr>
<td><strong>Cell Configuration</strong></td>
<td></td>
<td></td>
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</tbody>
</table>
| Anode/Cathode Bipolar Plates Thickness | m        | $1.0 \times 10^{-3}$  
| Anode/Cathode Bipolar Plates Thickness | m        | $0.5 \times 10^{-3}$  
| Anode/Cathode Bipolar Plates Thickness | m        | $1.5 \times 10^{-3}$  
| **Anode/Cathode GDL Thickness** | m        | $3.0 \times 10^{-4}$  
| **Anode/Cathode CL Thickness** | m        | $1.0 \times 10^{-5}$  
| **Membrane Thickness [Nafion® 112]** | m        | $5.1 \times 10^{-4}$  
| **Anode/Cathode GDL Porosity** |          | 0.6             
| **Anode/Cathode CL Porosity** |          | 0.5             
| **Volume Fraction of Membrane in CL** |          | 0.20            
| **Equivalent Weight of Membrane [Nafion® 112]** | kg/mol   | 1.1             
| **Dry Density of Membrane [Nafion® 112]** | kg/m$^3$ | $1.98 \times 10^3$  
| **Electrochemical Kinetics** |          |                |
| **Anode Reference Exchange Current Density (353.15 K)** | A/m$^3$  | $1.0 \times 10^9$  
| **Cathode Reference Exchange Current Density (353.15 K)** | A/m$^3$  | $1.0 \times 10^4$  
| **Anode Transfer Coefficient** |          | 2              
| **Cathode Transfer Coefficient** |          | 1              
| **Faraday Constant** | C/mol    | 96487.0        
| **Transport Parameters** |          |                |
| **H$_2$O Diffusivity in Membrane** | m$^2$/s  | $1.0 \times 10^{-12}$  
| **Membrane Proton Conductivity** | S/m      | 1.0             
| **Electro Osmotic Drag Coefficient** |          | 0.5            
| **Thermal Properties** |          |                |
| **Anode/Cathode GDL Heat Capacity** | J/K-m$^3$ | $5.68 \times 10^5$  
| **Anode/Cathode Catalyst Heat Capacity** | J/K-m$^3$ | $1.69 \times 10^6$  
| **Membrane Heat Capacity** | J/K-m$^3$ | $1.65 \times 10^6$  
| **Anode/Cathode Bipolar Plate Heat Capacity** | J/K-m$^3$ | $1.57 \times 10^6$  
| **Latent Heat of Desublimation** | J/mol    | $5.1 \times 10^4$  
| **Heat Transfer Coefficient between Cell & External** | W/K-cm$^2$ | $2.0 \times 10^3$  
| **Specific Volume of Ice** | m$^3$/mol | 2.0             
| **Operating Conditions** |          |                |
| **Discharge Current** | A/m$^2$  | 1000.0         
| **Initial Water Content in Membrane** |          | 3.0             
| **Heat transfer coefficient with environment** | W/K-m$^2$ | 50.0             
| **Startup Temperature** | K        | 253.15$^\circ$  

*: default value if not specified
Figure 2-1: Water transport in fuel cell during cold start
Start-up Temperature (°C)

Water Production/Flow Rate (mg/cm²s)

Water production rate at 100 mA/cm²

Water removal rate in out flow

Figure 2-2: Water removal in the outflow
Figure 2-3: Effects of ice formation on cathode overpotential
Figure 2-4: Ice formation during cold start from -20°C
Figure 2-5: Temperature change during cold start from -20°C
Figure 2-6: Cell Voltage evolution during cold start from -20°C
Figure 2-7: Water balance during cold start from -20°C
Figure 2-8: Breakdown of heat generation during cold start from -20°C
Figure 2-9: Ice formation during cold start from -10°C
Figure 2-10: Temperature change during cold start from -10°C
Figure 2-11: Temperature change during cold start from -10°C
Figure 2-12: Water balance during cold start from -10°C
Figure 2-13: Breakdown of heat generation during cold start from -10°C
Figure 2-14: Effect of thermal mass on cold start from -10°C
Chapter 3

CFD Model of PEFC Cold Start

While the theoretical analysis presented in the preceding chapter sheds light on the basic physics governing cold start of a PEFC, a predictive, multi-dimensional model is desirable for quantification of heat and water transport phenomena as well as their interactions. This chapter attempts to develop such a physical model and solves it using a computational fluid dynamics (CFD) technique. Simulation results will be given to demonstrate the fundamental physics included in this model and validated against the experimental data.

3.1 CFD Model of PEFC Cold Start

CFD technique has been widely used in fuel cell research to facilitate the physical understanding. However, no efforts have been made in modeling the PEFC operation at subzero temperatures. This thesis work is the very first attempt in modeling the PEFC cold start with CFD technique.

3.1.0 Model Assumptions

The basic assumptions of the proposed transient CFD model are listed below,

- Negligible gravity effect;
- Ideal gas mixtures;
• Incompressible gas due to small pressure gradients;
• Laminar flow due to small flow velocities;
• Isotropic and homogeneous porous layers, characterized by an effective porosity and a permeability;
• Instantaneous desublimation of water after over saturation at the freezing point.

### 3.1.1 Governing Equations

A single-domain approach is employed for PEFC cold start modeling. In this approach, PEFC operation is described by mass, momentum, species, charge and energy conservation principles. In the cold start model, phase change phenomena and its impact are further considered. With the major assumptions mentioned above, the governing equations are given as following.

#### 3.1.1.1 Mass Conservation

The continuity equation in the cold start model reads as:

\[
\frac{\partial (\varepsilon \rho_s)}{\partial t} + \frac{\partial (\varepsilon \rho)}{\partial t} + \nabla \cdot (\rho \vec{u}) = S_m \tag{3-1}
\]

The mass conservation equation for the cold start model is different from the equation of single phase. The density \( \rho \) is the fluid mixture density and \( \rho_s \) is the density of solid ice. \( \varepsilon \) is the volume fraction for the fluid mixture and can be written as
\[ \varepsilon = \varepsilon_0 (1-s) \], where \( \varepsilon_0 \) is the initial porosity of a porous layer and \( s \) is the ice fraction in the pore spaces. Therefore, it is not a constant as in normal operations but a variable. Similarly, the fraction occupied by ice can be expressed as \( \varepsilon_s = \varepsilon_0 s \). To ensure flux continuity at the porous GDL-channel interface, the superficial fluid velocity vector \( \vec{u} \) is used in the mass conservation equation. Because the ionomer is not included in the control volume, source term \( S_m \) stands for the mass transport through the ionomer in the CL. In the anode it includes the \( \text{H}_2 \) consumed in the HOR reaction, water transport through the membrane by diffusion and electro-osmotic drag, as shown in Eq. 3-2.

\[
S_{m,a} = -M_{\mu_s} \frac{j}{2F} + M_w \left[ \nabla \cdot \left( D_{w,m} \nabla C_w \right) - \nabla \cdot \left( n_d \frac{i_x}{F} \right) \right] \tag{3-2}
\]

In the cathode, it includes proton being brought into the reaction through the membrane, water transport through the membrane and mass crossover, as shown in Eq. 3-3. The mass source of anode and cathode should be balanced unless some water is stored in the membrane due to diffusion or electro-osmotic drag and mass crossover. More details can be found in [79]

\[
S_{m,c} = M_{\mu_o} \frac{j}{4F} - M_{\mu_c,o} \frac{j}{2F} + M_w \left[ \nabla \cdot \left( D_{w,m} \nabla C_w \right) - \nabla \cdot \left( n_d \frac{i_x}{F} \right) \right] \tag{3-3}
\]

### 3.1.1.2 Momentum Conservation

For flow in a porous medium, the fluid velocity is caused by the pressure gradient (with the gravity effect neglected), and it is described by Darcy’s law
To be valid both in a porous medium and an open channel, the momentum equation can be generalized as:

\[ \ddot{u} = -\frac{K}{\mu} \nabla p \]  \hspace{1cm} (3-4)

In the equation, \( \ddot{u} \) and \( p \) denote the superficial fluid velocity vector and pressure, respectively. This equation reduces to the extended Darcy’s law within the porous media with a small permeability. Inside the flow channel porosity is set to unit and permeability equal to infinity.

Due to the ice formation during cold start, part of the available pore space is occupied by solid ice, thus the cross sectional area available for fluid flow is less than the total pore space. This phenomenon can be described by the concept of relative permeability \( k_r \), which defines the ratio of actual permeability of flow at a given ice fraction to the total intrinsic permeability of the porous medium. Similar definition appears in the flooding problem [80]. In this work, relative permeability is proportional to the cube of ice fraction by assuming the porous layers are homogeneous. Therefore, the permeability \( K \) can be written as:

\[ K = k_r K_0 = (1-s)^3 K_0 \]  \hspace{1cm} (3-6)
3.1.1.3 Species Conservation

3.1.1.3.1 Reactant Transport in GDL, CL and Flow Channels

In the PEFC modeling, expressing the model equations in terms of molar concentrations provides further advantage, since the source and sink terms arising from electrochemical reactions in the above equation can be conveniently expressed in molar fluxes. Species conservation equation in terms of molar concentration can be written as:

\[
\frac{\partial (\rho c_i)}{\partial t} + \nabla \cdot (\rho \vec{u} c_i) = \nabla \cdot (D_i^{eff} \nabla c_i) + S_i^r
\]

The first term in the left hand side of the equation stands for the transient accumulation of the species. The second term is the convection term. On the right hand side of the equation, the first term defines diffusion in fluid phase and the last term on the right hand side denotes a source/sink term in the CL arising from electrochemical reactions which is proportional to the current load, which is

\[
S_i^r = - \frac{s_i^j}{nF} j
\]

where \( s_i^j \) is the stoichiometry coefficient of the species \( i \) in the reaction, and \( n \) is the number of electrons transferred.

Note that the species diffusion coefficient in the equation is the effective diffusion coefficient, which is modified via Bruggeman correlation [81] to account for the effects of porosity and tortuosity of porous electrodes and CL.

\[
D_i^{eff} = \varepsilon^{1.5} D_i^j
\]
3.1.1.3.2 Water Transport in GDL and Flow Channels

Similar to the reactant transport, water conservation equation in terms of molar concentration can be written specifically as:

$$\frac{\partial}{\partial t} \left( \rho C_{H_2O} \right) + \nabla \cdot \left( \bar{u} C_{H_2O} \right) = \nabla \cdot \left( D_{g,eff}^{H_2O} \nabla C_{H_2O} \right) + \delta_{H_2O}$$  \hspace{1cm} (3-10)

The water diffusion coefficient in the equation also is the effective diffusion coefficient. Furthermore, in the region where the ice forms, diffusion of water vanishes. That is:

$$D_{g,eff}^{H_2O} = e^{1.5} D_g^{H_2O} \quad \text{when no ice presents} \quad (s = 0)$$
$$D_{g,eff}^{H_2O} = 0 \quad \text{when ice presents} \quad (s > 0)$$  \hspace{1cm} (3-11)

3.1.1.3.3 Water Transport through the Membrane

As discussed in the previous section, water transport in the polymer membrane has unique characteristics and requires special attention. Furthermore, several modes of water transport in the membrane must be accounted for, in order to predict the water distribution accurately. For this purpose, the “unified water transport” model by Um [82] [83] is incorporated into the present PEFC cold start model.

The unified water transport through the membrane model of Um [82] employs the following conservation equation:

$$\frac{\partial}{\partial t} \left( \rho_{mem} C_{mem}^{H_2O} \right) = \nabla \cdot \left( D_{mem,eff}^{H_2O} \nabla C_{mem}^{H_2O} \right) - \nabla \cdot \left( \frac{n_d}{F} I_e \right)$$  \hspace{1cm} (3-12)
Here, the assumption that the fluid velocity is zero in the membrane has been made. This equation precisely describes two important modes of water transport through the polymer membrane, electro-osmotic drag and diffusion.

$\varepsilon_{mem}$ is the ionomer fraction in the membrane, usually taken as unity. The water molar concentration, $C_{mem}^{H_2O}$, represents an equivalent total water concentration that is in thermodynamic equilibrium with the membrane having a local water content of $\lambda$,

$$C_{mem}^{H_2O} = \frac{\rho \lambda}{EW} \tag{3-13}$$

where $\rho$ and $EW$ are the density and equivalent molecular weight of the membrane, respectively. The water content, $\lambda$, is the number of water molecules per sulfonic acid group within the membrane. The one-to-one relationship between the membrane water content and the water concentration is given by the water uptake curve, shown in Figure 1-4.

The water activity is defined as:

$$a = \frac{C_{mem}^{H_2O}}{C_{sat}^{H_2O}} = \frac{C_{mem}^{H_2O} RT}{p_{sat}} \tag{3-14}$$

where Goff Gratch equation [84] is adopted in this work for the saturation pressure of water vapor over ice $p_{sat}$. In the membrane phase, the membrane water uptake curve is extrapolated for water activity less or equal to 1 as follows:

$$\lambda = 0.043 + 17.18a - 39.85a^2 + 36.0a^3 \quad \text{for } 0 < a \leq 1 \quad \text{(i.e. } C_{mem}^{H_2O} \leq C_{sat}^{H_2O}) \tag{3-15}$$

The above correlation was fitted by Springer et al. [43] to the experimental data of the polymer membrane in equilibrium with water vapor. In this model, the amount of
water above saturation is supposed to form ice immediately; in other words, the maximum water content in the membrane is 14.

By utilizing this equivalent water concentration as the primary variable in the membrane instead of the physically more meaningful water content, the water equation and concentration are ensured to be continuous across the electrode-membrane interface, which can be written as:

\[
\frac{\partial (\varepsilon_{\text{mem,eff}} C^{H_2O})}{\partial t} = \nabla \cdot (D_{\text{mem,eff}}^{H_2O} \nabla C^{H_2O}) - \nabla \left( \frac{n_e}{F} I_e \right)
\]

3-16

The left hand side is the transient term, where the effective factor is defined as:

\[
\varepsilon_{\text{mem,eff}} = \varepsilon_{\text{mem}} \frac{dC^{H_2O}_{\text{mem}}}{dC^{H_2O}} = \varepsilon_{\text{mem}} \frac{1}{EW_{\text{sat}}} \left( \rho + \lambda \frac{d\rho}{d\lambda} \right) \frac{d\lambda}{da}
\]

3-17

The first term on the right hand side of Eq. 3-16 describes the diffusion mechanism. The water diffusion coefficient for the equivalent water concentration in the membrane is expressed as:

\[
D_{\text{mem,eff}}^{H_2O} = D_{\text{mem}}^{H_2O} \frac{dC^{H_2O}_{\text{mem}}}{dC^{H_2O}} = D_{\text{mem}}^{H_2O} \frac{1}{EW_{\text{sat}}} \left( \rho + \lambda \frac{d\rho}{d\lambda} \right) \frac{d\lambda}{da}
\]

3-18

Here, \(C^{H_2O}_{\text{mem}}\) is the true membrane water concentration and equal to \(\rho \lambda / EW\), where \(\rho\) is the membrane density and \(EW\) the membrane equivalent molecular weight (i.e. the membrane weight per mole of SO_3^- (functional) group).

The actual water diffusion coefficient, \(D_{\text{mem}}^{H_2O}\) is given by the following equation:

\[
D_{\text{mem}}^{H_2O} = \begin{cases} 
3.1 \cdot 10^{-7} \lambda \left( e^{0.284\lambda} - 1 \right) e^{-2346/T} & \text{for } 0 < \lambda \leq 3 \\
4.17 \cdot 10^{-8} \lambda \left( 1 + 161 \cdot e^{-4\lambda} \right) e^{-2346/T} & \text{otherwise}
\end{cases}
\]

3-19
This water transport equation for the membrane region is conformable to the general equation expressed in Eq. 3-10, provided that the electro-osmotic drag term is combined into the source terms. Thus, a single equation describing water transport throughout a PEFC becomes possible.

### 3.1.1.3.4 Water Transport in CL

The water transport equation in the CL can be written as:

\[
\frac{\partial (e_c C_{mc}^H)}{\partial t} + \frac{\partial (e_{mc} C_{mc}^H)}{\partial t} + \nabla \cdot \left( \bar{u} C_{mc}^H \right) = \nabla \cdot \left( D_{mc}^H \nabla C_{mc}^H \right) + \nabla \cdot \left( D_{mc}^H \nabla C_{mc}^H \right) + n_c^H \frac{\partial C_{mc}^H}{\partial t} + \frac{j_{mc}^H}{n_c} \]

where \(e_{mc}\) stands for the ionomer fraction in the CL and \(D_{mc}^H\) is the actual water diffusivity of ionomer in the CL. The source/sink term, \(S_c^H\), includes not only the production from electrochemical reactions but also the sources introduced by electro-osmotic drag and phase change.

\[
S_c^H = -\nabla \left( \frac{n_c I_c}{F} \right) - \frac{S_c^H}{n_c} \frac{j_{mc}^H}{n_c} + \dot{q}_{mc}^H
\]

The first term on the right hand side of Eq. 3-21 represents the electro-osmotic drag of the water across the membrane phase. It is directly proportional to the gradient of ionic current, \(I_c\). The electro-osmotic drag coefficient depends on the water content of the membrane, but in this study a constant drag coefficient is used.

The last term represents the phase change effect, which can be calculated by:
where the freezing rate $r_{\text{freeze}}$ is large enough to make $C_{H^2O}^{\text{freeze}}$ very close to $C_{sat}^{\text{H}_2O}$ and the melting rate $r_{\text{melt}}$ is thus determined by the heat conservation where the temperature is fixed at the freezing point until all the ice is melted.

Following the derivation for water transport in the membrane, the water transport equation can be written as:

$$
\dot{q}_{\text{sg}}^{\text{H}_2O} = \begin{cases} 
0 & \text{when } C_{H^2O}^{\text{freezing}} \leq C_{sat}^{\text{H}_2O} \\
 r_{\text{freeze}} (C_{sat}^{\text{H}_2O} - C_{H^2O}^{\text{freeze}}) & \text{when } C_{H^2O}^{\text{freezing}} > C_{sat}^{\text{H}_2O} \text{ & } T < T_{\text{freezing}}^{H^2O} \\
 r_{\text{melt}} (C_{H^2O}^{\text{melt}} - C_{H^2O}^{\text{sat}}) & \text{when } T = T_{\text{freezing}}^{H^2O} \text{ & } s > 0 \\
 0 & \text{when } T \geq T_{\text{freezing}}^{H^2O} \text{ & } s = 0 
\end{cases}
$$

The effective catalyst porosity $\varepsilon_{\text{CL,eff}}$ is defined as:

$$
\varepsilon_{\text{CL,eff}} = \varepsilon + \varepsilon_{mc} \frac{dC_{\text{mem}}^{\text{H}_2O}}{dC_{H^2O}^{\text{mem}}} = \varepsilon + \varepsilon_{mc} \frac{1}{EW} \frac{RT}{P_{\text{sat}}} \left( \rho + \lambda \frac{d\rho}{d\lambda} \right) \frac{d\lambda}{da}
$$

The effective water diffusion coefficient for the equivalent water concentration in the CL can be expressed as:

$$
D_{\text{CL,eff}}^{\text{H}_2O} = D_{g,eff}^{\text{H}_2O} + \varepsilon_{mc}^{1.5} D_{\text{mem}}^{\text{H}_2O} \frac{dC_{\text{mem}}^{\text{H}_2O}}{dC_{H^2O}^{\text{mem}}} = D_{g,eff}^{\text{H}_2O} + \varepsilon_{mc}^{1.5} D_{\text{mem}}^{\text{H}_2O} \frac{1}{EW} \frac{RT}{P_{\text{sat}}} \left( \rho + \lambda \frac{d\rho}{d\lambda} \right) \frac{d\lambda}{da}
$$

### 3.1.1.4 Charge Conservation

#### 3.1.1.4.1 Proton Transport

The charge conservation equation follows that:
This means that the gradient of the current density comes from the electrochemical reaction. The current density can be expressed as \( I_e = -\kappa_e^{\text{eff}} \nabla \phi_e \). Therefore, the electrolyte phase potential equation can be written as:

\[
\nabla \cdot \left( \kappa_e^{\text{eff}} \nabla \phi_e \right) + S_\phi = 0 \tag{3-27}
\]

In the above equation, \( \phi_e \) denotes the electrolyte phase potential, and \( \kappa_e^{\text{eff}} \) the effective ionic conductivity in electrolyte membrane, which is modified via Bruggeman correlation to account for the electrolyte phase volume fraction and tortuosity. And \( S_\phi \) is the source/sink term, which can be expressed as \( S_\phi = j \). The intrinsic ionic conductivity of electrolyte is a function of water content and temperature \([71]\), as given by:

\[
\kappa_e = \exp \left[ 2222 \left( \frac{1}{303} - \frac{1}{T} \right) \right] \left( 0.005139 \lambda - 0.00326 \right) \text{[S/cm]} \tag{3-28}
\]

### 3.1.1.4.2 Electron Transport

The electron phase potential equation can be written as:

\[
\nabla \cdot \left( \sigma_s^{\text{eff}} \nabla \phi_s \right) + S_\phi = 0 \tag{3-29}
\]

In the above equation, \( \phi_s \) denotes the electron phase potential, and \( \sigma_s^{\text{eff}} \) the effective electron conductivity. The source/sink term can be written as \( S_\phi = -j \), which indicates the sum of current flow by protons and by electrons are constant and always
equal to the applied current load. In the electrode, the current transfers from one to the other by electrochemical reactions.

### 3.1.1.5 Energy Conservation

Temperature is a critical parameter to the PEFC cold start since it directly determines a startup successful or not. In the analytical solution presented in the preceding chapter, a lumped thermal model is adopted, assuming that the temperature in the PEFC is not a function of location but only a function of time. However, for the PEFC cold start, it is the local temperature that determines ice formation in the CL. Although the spatial temperature variation may be only a few degrees, it makes a large difference in determining whether a PEFC will start or not.

The energy conservation equation can be expressed as Eq. 3-30:

\[
\frac{\partial (\varphi \rho C_p T)_{\text{cell}}}{\partial t} + \frac{\partial (\varphi \rho C_p T)_{\text{g}}}{{\partial t}} + \nabla \cdot \left( \rho C_p u T \right) = \nabla \cdot \left( k_{\text{eff}} \nabla T^{\text{H,C}} \right) + S_T
\]

where the first two terms on the left hand side stand for heat accumulation or dissipation with time for porous matrix and fluid inside respectively. The third term on the left hand side is the convection term. The first term on the right hand side of the equation stands for the diffusion term or heat dissipation in space. The last term is the heat source/sink term due to electrochemical reaction, proton and electron transport and phase change per unit volume.

As discussed in the analytical model, heat generation in the electrodes includes entropic heat of reactions, the irreversible heat of electrochemical reactions, Joule heat
and latent heat from phase change during freezing and melting, which can be expressed as:

\[
S_T = f \left( \eta - T \frac{\partial U_a}{\partial T} \right) + \frac{i_e^2}{\kappa_{\text{eff}}} + q_{\text{v},0} h_{\text{v}}
\]  

where \( q_{\text{v},0} \) is the phase change in unit volume [mol/(m^3s)] and the resistance heat from the electron transport in electronic phase is neglected. Eq. (3-31) provides pointwise heat generation expression, and its integral over the entire cell will result in the global formula identical to Eq. 2-16.

In the membrane, only ohmic resistance exits, i.e.

\[
S_T = \frac{i_e^2}{\kappa_{\text{eff}}}
\]  

In normal operating condition, it is our goal to minimize the waste heat generation to obtain a high efficiency. However, during the cold start, we want to maximize this waste heat to warm up the fuel cell to ensure successful and rapid startup.

**3.1.1.6 Electrochemical Kinetics**

The electrochemical reactions take place at the CL, where the reactants are consumed and water is produced. At the same time, the current carried transfer between electron phase and electrolyte phase. While the transfer current density, or the reaction rate is determined by the electronic phase potential and the electrolyte phase potential. The relationship is known as Butler-Volmer equation:
In PEFC, the hydrogen oxidation reaction (HOR) and oxygen reduction reaction (ORR) occur at the anode and cathode of a PEFC, respectively, as shown in Eq. 1-1 and Eq. 1-2.

The anode exhibits facile electro kinetics and hence a low surface overpotential, therefore it can be expressed by a linear kinetic rate equation:

\[ j = a_i o \left\{ \exp\left(\frac{\alpha_a F}{RT} \eta\right) - \exp\left(\frac{-\alpha_c F}{RT} \eta\right) \right\} \]  

where the sum of transfer coefficients, \( \alpha_a + \alpha_c \), is equal to 2 for HOR

The cathode has relatively slow kinetics with higher surface overpotential, so that it can adequately be described by Tafel kinetics:

\[ j_c = a_i ref \left( \frac{C^{O_2}_{ref}}{C^{O_2}_{ref}} \right)^{1/2} \left( \frac{\alpha_a + \alpha_c}{RT} F\eta \right) \]  

and \( \alpha_c \) is equal to 1 for ORR.

The surface overpotential in the above equations is defined as:

\[ \eta = \phi_e - \phi_i - U_o \]  

where \( \phi_i \) and \( \phi_e \) denote the potentials of the electronic and electrolyte phases, respectively. \( U_o \) stands for the thermodynamic equilibrium potential, which is zero on the anode but a function of temperature at the cathode:

\[ U_o^{anode} = 0 \]
\[ U_o^{cathode} = 1.23 - 9.0 \times 10^{-4} (T - 298.15) \]
where \( T \) is in Kelvin (K) and \( U_o \) is in Volts (V). Under the assumption of perfectly conductive electronic phase of anode and cathode CL, \( \phi \) becomes zero for the anode and is equal to the cell voltage for the cathode.

It is not precisely known how solid ice blocks the access of electrons, protons and reactants to active reaction sites and hence reduces the oxygen reduction rate. In this work, directly proportional reduction of active reaction surface with the ice fraction is assumed, that is:

\[
a = (1 - s) a_o \tag{3-38}
\]

where \( a_o \) is the total catalyzed and hence electrochemically active surface area per unit of CL volume. Hence, \( a_o \) is a function of Pt loading in mg/cm\(^2\) and the CL thickness.

### 3.1.2 Boundary Conditions

The governing equations presented above require appropriate boundary conditions. In the single domain approach, only the external boundary conditions are required. The boundary conditions for flow and species transport equations are described as zero flux for the entire boundary except at the channel inlets and outlets. For the energy conservation equation, the boundary condition is set as constant at startup temperature except channel outlets. Zero flux condition is applied for the electrolyte phase potential, while for the electronic phase potential, a reference point is set at the anode side and a constant flux (constant current density) is applied at the cathode.

At the inlets, the species concentrations are specified as follows:
and the inlet velocity of the fuel and oxidant are defined as:

\[ u_{anode}^{in} = U_{a,in}; \quad u_{cathode}^{in} = U_{c,in}; \]  \hspace{1cm} 3-40

which are determined by the reference current density \( I_{\text{ref}} \) and the stoichiometrical flow ratio, which is defined as the ratio of the amount of reactant supplied to that required for the electrochemical reaction. Given the electrode cross-sectional area is \( A_{\text{rxn}} \) and inlets area of anode and cathode are \( A_{a,\text{in}} \), \( A_{c,\text{in}} \) respectively, the flow stoichiometry can be expressed as:

\[
\xi_a = \frac{C_{\text{anode}}^{\text{H}_2} U_{a,in} A_{a,\text{inlet}}}{I_{\text{ref}} A_{\text{rxn}} / 2F}; \quad \xi_c = \frac{C_{\text{cathode}}^{\text{O}_2} U_{c,in} A_{c,\text{inlet}}}{I_{\text{ref}} A_{\text{rxn}} / 4F}
\] \hspace{1cm} 3-41

### 3.1.3 Initial Conditions

Initial temperature is set as the startup temperature throughout the whole cell. The reactant species in the gas channel and GDL are set the same as the inlet gas at each side initially. Generally, the initial water content in the membrane is determined by fitting the measured impedance into our ionic conductivity curve of the electrolyte, as shown in Eq. 3-28. When the purge is longer enough, the initial water content can be considered in equilibrium with the purge gases. The water concentration in the CL is set at equilibrium with the membrane water activity.
Phase potential in the electrolyte is set as 0 initially everywhere and the electron phase potential at each side is set as the thermodynamic potential of the half cell reaction respectively.

### 3.1.4 Numerical Implementation

The conservation equations are discretized using a finite-volume method and solved within the commercially available CFD software, Fluent®, by customizing its User Defined Functions (UDF). The software utilizes well-known SIMPLE algorithm and an algebraic multigrid method to efficiently solve the resulting set of discretized linear equations.

The resulting set of governing equations is summarized in Table 3-1. Single channel geometry is employed in this study, which is sketched in Figure 3-1 and the mesh used in the simulation is plotted in Figure 3-2. The geometric parameters and operating conditions are listed in Table 3-2. The electrochemical properties and transport parameters used in simulations are given in Table 3-3.

Before comparisons are made to the experiments, a time-step and grid independence study of the model is performed by varying the time step and mesh density for a cold start at -20°C with an initial membrane relative humidity equal to 0.575. The cell voltage evolution curve is compared because it is an integral indication which reflects the impact of the multi-components transport and ice formation effects. From the results plotted in Figure 3-3, the model indicates satisfactory independence of both spatial mesh density and time-step.
3.2 Results and Discussion

The transient model proposed in the previous section has been developed to describe the governing physics in PEFC cold start. The detailed information predicted by this model will be discussed here, such as water, temperature and current density distributions, as well as the ice fraction distribution. The simulation results are validated against available experimental data [71] to demonstrate the model’s validity.

A cold start from a temperature of -20°C is simulated in a single-channel fuel cell with a 30µm Gore PREMEA membrane. In order to minimize the ice formation, dry gases are used for both inlets and the flow stoichiometry for each inlet is 2 at the reference current density.

The analysis in Chapter 2 demonstrates the importance of the membrane water storage. Therefore the initial membrane water content is an important measure of the fuel cell initial condition prior to cold start. In practice, a uniform initial water content of ionomer $\lambda_0$ can be realized by using a purge gas with relative humidity controlled at certain levels and purging the fuel cell for extended time, say several hours. In so doing, the membrane $\lambda_0$ reaches thermodynamic equilibrium with the RH of purge gas. The effect of initial condition caused by purge process will be discussed in detail in the next chapter. In this simulation, the relative humidity of purge gas is 0.75.

For a constant discharge current 40 mA/cm², the simulation result of the voltage change with time is compared with experimental data in Figure 3-4. As it can be seen from the figure, voltage drops suddenly at around 210s after discharge, indicating an unsuccessful cold start. In the first few seconds, there is no ice formation inside the cell.
When the CL is saturated with water vapor and the membrane cannot uptake any more water, the extra water will desublimate immediately. The ice formed inside blocks the reactant transport and covers the active reaction site, so that the overpotential has to increase to achieve a higher reaction rate to maintain the total current output, thereby causing a sudden voltage drop. In the experiment, the current load increases gradually from 0 to 40 mA/cm$^2$, while in the simulation a stepwise increase is applied. To match the total amount of product water, the simulation starts at the middle of current increase. From Figure 3-4, the simulation result matches well with the experimental data in terms of the shutdown time and the voltage evolution behavior during the cold start. However, the slope of voltage drop, indicating the effect of ice formation on cold start, is different. Hence further investigation of the micro scale physics such as the morphology of frozen ice in the CL is required.

Ice fraction evolution in the cathode CL during discharge is plotted in Figure 3-5, Figure 3-6 and Figure 3-7 with different views. Top view of ice fraction contour in the symmetric plane is shown in Figure 3-5. With further discharge, the ice fraction in the cathode CL increases. Under the immediate desublimation assumption, ice fraction in the CL is mainly determined by the local water production. Along the flow direction, current density decreases as a result of the reactant consumption in this direction. Therefore the ice fraction near the inlet grows faster at the beginning of cold start. The maximum value of ice fraction is reached at a small distance from the inlet because of the dry gas supplied. As more and more ice forming inside the cathode CL covers the reaction area and blocks the reactant transport, the current density distribution along the flow direction changes and hence the ice growth rate.
The front view of the ice fraction growth in the cathode CL is shown in Figure 3-6. The four groups are at four different discharge stages. In each group, contours at three locations are displayed, which are the cross sections of the inlet, half length and the outlet. By comparing the three plots in a group, it is obvious that catalyst layer at the inlet always have the highest ice fraction among these three locations. However, by comparing the same location in each group, the ice fraction grows faster near the inlet initially, while the ice fraction at the middle and outlet grows faster at the late stage due to the massive ice coverage near the inlet. For the in-plane direction, the upper part which is under the land has higher ice fraction since the heat dissipation is faster through the land and less water can be stored in the vapor phase at a lower local temperature. And for the through-plane direction, it is interesting to see that the highest ice fraction is not located at the interface between the cathode CL and membrane. During cold start, a fuel cell runs at a very low current density to reduce the water production rate. For such a low current density, the mass transport limitation in the through-plane direction is unimportant, while the proton transport in the ionomers becomes the limiting step for transfer current density. Therefore, the transfer current density is always higher near the membrane, unless the mass transport is substantially affected by the ice blockage. Although the water production rate is higher near the membrane, the ice formation rate does not follow the same pattern due to the water absorption by the membrane. If that is the case, ice grows faster at the interface between cathode CL and GDL and an ice-sheet is formed there which blocks the reactant transport and thereby shutdown the fuel cell before the whole catalyst layer is filled up with ice.
Figure 3-7 shows the side view of the ice fraction at the center of cathode CL. It clearly demonstrates the distribution of ice fraction, which decreases along the flow direction except for a small region near the inlet. At the final stage of cold start, i.e., after discharge for 210 seconds, the ice fraction near the inlet is close to 1. Along the in-plane direction, due to the low temperature near the land, ice fraction in the upper section is always higher than the lower section.

Directly affected by the ice formation, the current density contour at the center of membrane is shown in Figure 3-8. The average current density applied in the simulation is 40 mA/cm², or 400 A/m². Current density distribution in the flow direction is determined by the reactant concentration, proton conductivity and active reaction area. In the early stages with less ice coverage, the current density distributes quite uniformly along the flow direction as there exists only a small gradient due to the reactant consumption. The ice effect on current density distribution is small due not to only the small ice fraction but also to the low average current density applied, which makes the reactant transport limitation less severe.

When ice fraction approaches unity near the inlet at the final stage of cold start, the current density dramatically increases in the region with less ice coverage to compensate for the active reaction area loss, as can be seen in the last two contours. Due to the dryness of inlet gas, there is a very small region with less ice coverage where reaction can still proceed at the late stage of discharge. At final stage of cold start, the ice formation dominates the current distribution, where the cell operation is limited by the active ECA and transfer of oxygen to the reaction sites. The region near the inlet is shut down first with minimum current output, where highest ice fraction is reached. The
variation in the lateral direction at the late stage of cold start is due to the ice effect, while at the early stage it is due to the electron transport, which is discussed in detail by Meng and Wang [85].

The water distribution in the fuel cell gas channels is shown in Figure 3-9. Water produced in the cathode CL diffuses through the GDL to the cathode gas channel. The water vapor concentration increases along the flow direction in both gas channels. The saturation pressure of water over ice is low at subzero temperatures. For -20°C, the saturation concentration of water vapor is 0.049 mol/m³; therefore water vapor in the cathode gas channel easily reaches the saturation point. The small unsaturated portion near the inlet is due to the dry gas supply. At the fuel cell shutdown, this unsaturated portion is extended to about half length of the flow channel. That is because near the inlet the cathode CL is filled up with ice and no water can be produced there due to ice coverage. As the reaction is pushed to the downstream with less ice coverage, the local temperature increases as will be shown later in the discussion. As a result, the saturation pressure of water vapor also increases in downstream of the flow. At the anode gas channel, instead of increase all along in the flow direction, there is a water rich region corresponding to the unsaturated region in the cathode side. With a large amount of ice formed inside the cathode CL in this region, the osmotic drag decreases as a result of the reaction surface coverage, while back diffusion to the anode is less effected since the water inside the cathode CL is already saturated.

The water content at the center of membrane during discharge is shown in Figure 3-10. The membrane water content increases with further discharge. However, the water content is far from the maximum value due to the slow water diffusion in the
membrane at -20ºC. Before shutdown, the water content increases along the flow direction due to higher water vapor concentration in the downstream of cathode gas mixture. Although the water production rate is higher near the inlet, the excessive water desublimates immediately into ice and cannot diffuse into the membrane. Therefore, the ice fraction is higher near the inlet, while the water content in the membrane is higher near the outlet. At the final stage of discharge, the water content exhibits a different behavior from the early times, as shown in the last contour. At the shutdown the ice is already filled up the cathode CL near the inlet, therefore the current density near the outlet become higher to compensate for the active reaction area loss. The increase of current density causes more water being dragged to the cathode. Although there is more water produced at the same time, the water vapor is already saturated in the cathode CL and back diffusion is not affected by the water accumulation. Thus, in this region membrane actually loses water due to the higher local current density when the anode is dried out.

Closely related to the current density distribution, the temperature distribution during cold start is shown in Figure 3-11, Figure 3-12 and Figure 3-13 with different views. The temperature difference across the fuel cell is very small due to the huge applied thermal mass and large thermal conductivity of each cell component. From Figure 3-11, the temperature distribution is quite uniform in flow direction due to the relatively even distributed current and the major variation in temperature is in the through-plane direction. However at the final stage of cold start, the temperature rises near the outlet, following the same behavior as the local current density. The lowest
temperature occurs near the inlet, where local current density drops greatly due to the highest ice fraction.

Figure 3-12 shows the front view of the temperature distribution at the inlet, middle and outlet, respectively. It is apparent that the component warming up fastest is the CL, where the electrochemical reaction occurs. From the plots, it is easy to see that most of the heat dissipates through the current collector where a huge temperature gradient can be observed in the GDL near the interface with current collector.

As shown in Figure 3-13, the temperature in the upper part of the membrane is lower where the heat dissipates directly through the current collector adjacent to the GDL. When sufficient ice forms inside the electrode, the electrochemical reaction is pushed to the active reaction area with less ice covered. Therefore, the temperature has a maximum value near the outlet where the reaction is most active.

From the breakdown of the heating sources, as shown in Figure 3-14, it is easy to tell that most heat released during cold start is reaction heat. The entropic heat is fairly constant throughout the cold start which accounts for about 20% of the total heat generation. Since the membrane reaches equilibrium with the purge gas of humidity 0.75 before cold start, the proton conductivity is high initially and varies little with the increase of water content in ionomer. Thus the Joule heat, mainly due to the ohmic resistance in ionomer, is relatively small and constant. At the shutdown of fuel cell, there is a sharp increase in heat generation, it is simply because the local current density near the outlet increases as a result of the ice formation near the inlet. The activation loss and ohmic loss increases correspondingly. In this higher current density region, back
diffusion of water is not sufficient to balance the electro-osmotic drag. Therefore more water is accumulated at the cathode and ice is formed at a faster rate.

The model is validated against an extensive set of experimental data under various conditions (various purge practice, startup current density and temperature) and with different fuel cell designs (various membrane thickness), as shown in Figure 3-15. The product water is used as the cold start performance indicator, as will be explained in the next chapter. The experimental database comes partly from Tajiri et al. [86] and partly from Nissan Motor Co. Ltd. It is seen from Figure 3-15 that the model achieved ±20% agreement with experimental data for a wide range of operating and design parameters, except for a handful of points. The effect of these parameters will be discussed in detail in the subsequent chapters.

### 3.3 Conclusions

A transient model coupling multi-component, multiphase transport is developed in this work to describe PEFC cold start where ice/frost formation and its effects on cold start are considered. Cold start of a PEFC from -20°C with constant current is simulated using this model. The voltage evolution and total discharge time are predicted reasonably well using the present model. Some important physics are disclosed and explained through the simulation.

During cold start, water transport is the direct reason for ice formation. Production water from electrochemical reaction and dragged water from anode accumulate at the cathode electrode. Due to the small saturation value of water vapor and slow water
diffusion in the membrane at subzero temperatures, the water at the cathode cannot be removed fast enough and forms ice inside the micro-pores. As a result of the current density distribution, the ice fraction near the inlet is higher than that near the outlet.

The effect of ice formation can be summarized as two aspects: coverage of the active reaction surface and blockage of the reactant transport. These two effects substantially decrease the fuel cell performance and even cause the shutdown of the fuel cell. This ice effect can be clearly seen from the current density distribution.

To successfully startup a PEFC from subfreezing temperature requires that the cell temperature rises above the freezing point before the reactant transport to the reaction site is totally blocked or the reaction surface is fully covered by ice. Heat analysis of PEFC cold start is conducted by discussing different heat sources, where the reaction heat, or the activation loss, is the major contributor. Hence the temperature distribution is directly related to the current distribution. However, with a large thermal mass and without any thermal insulation, there is only very small increase in the cell temperature.

The present model provides us a useful tool for understanding the governing phenomena in cold start and predicting its performance. The operating conditions such as current load and initial water content in the ionomer controlled by the purge process have huge impacts on cold start performance and fuel cell characteristics such as membrane and catalyst design and operating conditions are of paramount importance. Optimization of fuel cell design, material characteristics and operating parameters holds the key to obtaining better performance of PEFC cold start. Using this model, the study pursuing improved cold start capability is conducted in the following chapters.
Table 3-1: Summary of governing equations

<table>
<thead>
<tr>
<th>Equation Type</th>
<th>Equation</th>
</tr>
</thead>
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<tr>
<td><strong>Continuity</strong></td>
<td>( \frac{\partial (\varepsilon, \rho_s)}{\partial t} + \frac{\partial (\varepsilon \rho)}{\partial t} + \nabla \cdot (\rho \vec{u}) = S_m )</td>
</tr>
<tr>
<td><strong>Momentum</strong></td>
<td>( \frac{1}{\varepsilon} \left[ \frac{\partial (\rho \vec{u})}{\partial t} + \frac{1}{\varepsilon} \nabla \cdot (\rho \vec{u} \vec{u}) \right] = \nabla \cdot \left( \mu_{\text{eff}} \nabla \vec{u} \right) - \nabla p + \rho \vec{g} - \frac{\mu}{K} \vec{u} - \rho_s \frac{d \varepsilon_s}{dt} \vec{u} )</td>
</tr>
<tr>
<td><strong>Species</strong></td>
<td>( \frac{\partial (\varepsilon C^i)}{\partial t} + \nabla \cdot (\vec{u} C^i) = \nabla \cdot \left( D_{\text{eff}} \nabla C^i \right) + S^i )</td>
</tr>
<tr>
<td><strong>Charge</strong></td>
<td>( \nabla \cdot \left( \kappa_s \sigma_{\text{eff}} \nabla \phi_s \right) + S_\phi = 0 )</td>
</tr>
<tr>
<td><strong>Energy</strong></td>
<td>( \frac{\partial (\rho_{\text{cell}} C_{\text{cell}} T)}{\partial t} + \frac{\partial (\rho_{\text{g}} C_{\text{g}} T)}{\partial t} + \nabla \cdot \left( \rho C_{\text{g}} \vec{u} T \right) = \nabla \cdot \left( k_{\text{eff}} \nabla T^{\text{H,O}} \right) + S_T )</td>
</tr>
</tbody>
</table>

**Electrochemical Reactions:**

\[ \sum_i s_i M_i^z = ne^- \]

In PEFC, there are:

- (Anode) \( \text{H}_2 - 2\text{H}^+ = 2e^- \)
- (Cathode) \( 2\text{H}_2\text{O} - \text{O}_2 - 4\text{H}^+ = 4e^- \)
Table 3-2: Geometric Parameters and Operating Conditions

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<td>Reference Current Density (with short purge)</td>
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Figure 3-1: Schematic of the cell modeled
Figure 3-2: Mesh of the single-channel PEFC
Figure 3-3: Independence study of the model (a) time step; (b) spatial mesh size
Figure 3-4: Discharge curve at constant current 40 mA/cm²
Figure 3-5: Fig. 3 Ice fraction in the cathode catalyst layer in X-Y plane
Figure 3-6: Ice fraction in the cathode catalyst layer in X-Z plane
Figure 3-7: Ice fraction in the cathode catalyst layer in Y-Z plane
Figure 3-8: Current Density Distribution in membrane
Figure 3-9: Water Vapor Distribution in Gas Channel
Figure 3-10: Water content contour in Y-Z plane at the center of membrane
Figure 3-11: Temperature contour in X-Y plane
Figure 3-12: Temperature contour in X-Z plane
Figure 3-13: Temperature contour in Y-Z plane at the center of membrane.
Figure 3-14: Breakdown of the heat sources
Figure 3-15: Experimental Validation of the model
Chapter 4

Effects of Operating Conditions in Isothermal Cold Start

Operating conditions such as initial cell conditions and current density have substantial influences on cold start performance and transport characteristics. Optimization of these operating parameters is essential to improve cold start capability of the fuel cell. To distinguish the effects of different operating conditions without the complication of cell temperature rise, isothermal start up cases are designed by applying a large thermal mass to the fuel cell. In this way, the temperature rise in the fuel cell is negligible and the fuel cell can be considered working at the constant start up temperature. The fate of a fuel cell under isothermal cold start is always shutdown; however, by comparing the product water generated before cell shutdown, the intrinsic capability of cold start can be quantified. Thus, fundamental data independent of the cell’s thermal mass or stack system design can be obtained from these well-designed isothermal cold start scenarios. Using the present model, cold start operations from various purge practices and under different current loads are investigated below. These parametric studies are performed for a GORE PREMEA Membrane of 30µm in thickness. All the simulations in this chapter are under isothermal conditions where the temperature throughout a fuel cell is fixed at the initial startup temperature.
4.1 Introduction

The initial water content of membrane reflects the membrane water storage potential and hence directly determines the cold start performance. Gas purge, as an effective method to remove the residual water from a fuel cell and alter the membrane water content, has been commonly adopted for automotive applications to improve cold start performance. Usually the purge process occurs right after fuel cell shutdown, so as to minimize the water undergoing freezing inside the fuel cell under low temperatures. For practical reasons as well as to prevent membrane dry-out, dry gases, usually N₂, are used to purge the fuel cell for a short period in practical applications. However, a short-time purge cannot effectively remove all of the water remaining in the fuel cell, particularly inside the CL. Therefore there is initial ice formed inside the fuel cell prior to cold start. This initial ice reduces the water storage capacity of the CL and also affects the reaction and species transport during cold start. For fundamental research purposes, a purge process called equilibrium purge has been adopted in this study, in which we use the purge gas with well-controlled relative humidity for a sufficiently long time (typically greater than 2 hours) until all liquid water in the CL and GDL is removed and the membrane water content reaches equilibrium with the relative humidity of purge gas. Equilibrium purge enables consistency in the initial condition of the water distribution, hence ensures consistent and reproducible cold start data.

As mentioned in Chapter 2, the total product water and heat generation are proportional to the current density applied. Therefore, cold start operation under constant current density are studied in both experiments and simulations. The current load, which
determines the water production rate and heat generation rate, is of paramount importance to the cold start performance. A large current density produces water fast and immediately passivates the CL, while a small current density generates heat slowly and needs a much longer time to warm up the fuel cell.

In this work, the cold start performance is evaluated by the total product water and the initial condition is measured by the initial water content of membrane. The total product water during operation, in mg/cm², is chosen as the performance indicator because it is directly correlated with the amount of heat produced. The total product water is the product of current density and operational time. Higher product water indicates more heat could be produced and hence a better chance for successful startup.

The water in the membrane plays the most important role in storing product water from the CL. Therefore, the initial membrane water content is the best measurement of the initial condition. In equilibrium purge, this initial water content can be easily inferred from the relative humidity of purged gas used. This is another salient advantage of employing equilibrium purge to study cold start fundamentals. However for short purge, the water content has to be estimated from the in-situ high-frequency measurement of the membrane resistance and then using the membrane conductivity-water content correlation. The maximum water content of membrane \(\lambda_{sat}\) is reached when it is in equilibrium with saturated vapor, therefore the potential of water storage in the membrane during cold start is measured by \(\Delta\lambda=(\lambda_{sat} - \lambda_0)\), where \(\lambda_0\) is the initial water content after purge.
4.2 Purge Effects

Purge is a useful method to reduce the initial ice inside the fuel cell before cold startup. Generally, the fuel cell is purged at the shutdown prior to cool-down. Thus the ice formed in cold weather until the next start is reduced.

Equilibrium purge uses gases with well controlled humidity purge for a long time. After that, there is no liquid water in the GDL and CL and the membrane reaches equilibrium with the purged gas. By using purge gases with different humidity, the effect of initial membrane water content on cold start can be obtained.

In the short purge of automotive practice, dry gases are used to maximize water removal and only purged for a very short time. Thus there is initial ice formed inside the fuel cell before start up. By comparing the cold start performance after dry purge with that after equilibrium purge, the effect of initial ice formation can be determined.

4.2.1 Equilibrium Purge

Figure 4-1 shows the product water achievable before shutdown for cold start after equilibrium purge. It clearly shows that the purge process has an important impact on cold start. Cold start after equilibrium purge with less humidified gases can hold more product water, which indicates a better performance with smaller initial water content of membrane. As can be seen in Figure 4-1, when the purged gas is fully humidified, or the membrane becomes fully hydrated after purge, no water can be stored in the membrane. Most of the product water and water dragged from anode can only be stored in the CL, therefore the fuel cell is shutdown when the cathode CL is filled up with ice. With a
larger water storage potential, the cell can operate much longer because the product water can be stored in the membrane.

Notice that the increase of product water with the membrane water storage potential is not linear. Under a low start up temperature such as -20ºC, the total product water storage can be decomposed into two parts, in the membrane and catalyst layer respectively, as can be seen from Figure 4-1. After equilibrium purge, there is no liquid water in the porous layer. The total water storage in the cathode CL can be fully utilized, which includes the ice formation in the open pore space plus the water absorption by ionomer portion in the CL. There is a small amount of product water stored in the ionomers of the CL, which increases linearly with the water storage potential, as shown by the region between the two dash lines in Figure 4-1. Therefore, it is the membrane that is responsible for the nonlinearity between the product water and water storage potential. This can be explained by the slow water uptake process of the membrane. A large water storage potential facilitates the membrane water uptake, which leads to more water stored in the membrane and defers the fuel cell shutdown. In return, this additional time gained allows more water to be transported from the CL to the membrane. Therefore, the product water storage and the water storage potential are non-linearly related.

The effects of purge can be found not only in the cold start duration but also in the power output, which is characterized by the rapid increase in the voltage at the beginning of cold start, as can be found in Figure 4-2. The reason is believed to be the decrease of the ohmic loss. The ohmic loss originates primarily from protonic resistance. For the PEFC operation, the anode HOR occurs exclusively at the interface of cathode CL and membrane due to the fast kinetics of HOR. Therefore, it is the protonic resistance in the
cathode CL and membrane that accounts for the ohmic loss. Assuming the transfer current density uniformly distributed in the cathode CL, the protonic resistances of membrane and cathode CL are $\frac{\delta_{\text{MEM}}}{\kappa(\lambda)}$ and $\frac{\delta_{\text{CCL}}}{2\kappa(\lambda)\varepsilon_{mc}}$ respectively. In the expression, $\kappa(\lambda)$ is the proton conductivity in the electrolyte which is a strong function of the water content, $\varepsilon_{mc}$ is the ionomer volumetric fraction in the cathode CL, $n$ is the tortuosity index, $\delta_{\text{MEM}}$ and $\delta_{\text{CCL}}$ are the thickness of membrane and cathode CL respectively. Although the thickness of the cathode CL is smaller than that of the membrane, the protonic resistance of the cathode CL is always higher due to less ionomer content.

After equilibrium purge with gases of different humidity, the water content of membrane reaches equilibrium with purge gases. If the purge gases are not fully saturated, the membrane will absorb water during cold start. Since proton conductivity of the electrolyte is a strong function of the water content, the ohmic loss decreases as a result of the membrane water uptake. Therefore, the cell voltage increases before being drastically affected by the ice formation, as can be seen in Figure 4-2. A sharp increase of the voltage is observed at the beginning of cold start due to the water absorption in the ionomer portion of the cathode CL, followed by a moderate increase to the peak of cell voltage caused by the slow water uptake of the membrane. The water content of ionomer in the catalyst layer increases quickly because the catalyst layer is a porous structure and the ionomer easily reaches equilibrium with the water vapor in the gas mixture. On the contrary, the membrane uptake is limited by the water diffusivity in the ionomer.
With different purge conditions, the initial protonic resistance and hence the magnitude of the voltage drop varies with different water content. From Figure 4-2, it can be seen that the initial increases of cell voltage have different magnitudes with different purge conditions. Plot (a) is the experimental data for the voltage evolution for cold start under -30ºC. Plot (b) shows the simulation results. The simulation well catches the magnitude of the initial voltage drop. The differences of duration between the experiments and the simulation come from the gradually increased current applied in the experiments. In the simulation, a step change of the current leads to the sudden drop of the initial voltage.

4.2.2 Short Purge

The comparison of cold starts after equilibrium purge and short purge is shown in Figure 4-3. It clearly shows that the purge process has an important impact on cold start.

By comparison with the equilibrium purge, it can be seen from Figure 4-3 that the short purge holds less product water, or has less operating time. This is because the initial ice left in CL after short purge not only reduces the water storage capacity of the electrode but also offers less time for the membrane to store water. The difference between cold starts after these two purge conditions actually lies in the utilization of the water storage potential in the ionomeric membrane.

Unlike equilibrium purge, short purge cannot reach an equilibrium state. Moreover, the initial water content in the MEA after purge is not uniformly distributed in the flow direction. After short purge, the MEA near the inlet loses most water because the
supplied dry gases have more potential to remove water and at the downstream the water cannot be removed from the MEA when the gas mixture in gas channel is already saturated. This non-uniformity has a huge impact on the current density distribution in the flow direction and thereby the cold start performance. Generally, local current density depends on the ECA and reactant concentration, as well as the transport of protons and electrons. However, the decisive factor at different stages of cold start changes along flow direction with different ice fraction and water content in ionomer. By studying impact of non-uniformity on cold start performance, innovative method of purge process and MEA design can be proposed based on this understanding to maximize the startup capacity of PEFC.

A typical water distribution in MEA after dry purge is shown in Figure 4-4 [87]. MEA near the inlet is almost dry after purge while the outlet is hardly affected by the purge. A simulation using this water distribution as the initial startup condition is performed by the present model for startup from -20°C. However, to demonstrate the purge effects, a fuel cell with 60cm in length is used in the simulation according to the purge results in Figure 4-4. The predicted current density distribution along the flow direction is plotted in Figure 4-5. At the inlet, the current density is very low because the membrane is dry after the purge. And near the outlet the current is affected by the initial ice formation. Therefore, there is a peak of the current density along the flow direction. This specific location is featured by the combination of high reactant concentration, no ice formation and hydrated membrane, which coincides with the location of ice front. From this plot, it can be found that the effect of ice formation is not very significant until shutdown. At the late stage of cold start, the portion at the downstream of the ice front is
shutdown first due to the initial ice formation and fast water production rate. Figure 4-6 shows the ice growth inside the cathode CL during cold start. The ice front propagates slowly towards the inlet and fills up quickly in the cathode CL. Compared with the distributions of current density and ice formation after equilibrium purge in Chapter 3, the initial non-uniformity after short purge has tremendous impact on the cold start performance. These results suggest that in the automotive application, short purge should be optimized to remove residual water more efficiently and uniformly.

4.2.2.3 Current Load

By using a lower current load, the fuel cell can better utilize the water storage potential in the membrane and CL to store more product water, thereby more heat generated from the reaction can be used to warm up the fuel cell for a successful start up. A fuel cell can even operate at a very low current density without ice formation. However, at such a low current, it is impossible to either meet the power supply requirement or to warm up the fuel cell in a short period of time. Hence it is important to find an appropriate current density at a given temperature to minimize the start up time.

Current density during cold start has significant impact on the fuel cell cold start operation. A lower current operation is more likely to last longer, but the problem is that lower current load produces less heat. Therefore, it takes longer to warm up the fuel cell, which is not advantageous in automotive applications.

Simulation results of cold start with short purge discharged at two different current loads, 100 and 40 mA/cm², are plotted in Figure 4-7. It is shown that the total
product water before cell shutdown at the lower current is much larger than that with the high current because lower water production rate under the low current density allows much more time for water to diffuse into the membrane or be taken out by outflow instead of freezing in the CL. The difference in the product water between the two cases with different current density is mainly due to the membrane water uptake. Discharged at a lower current, the fuel cell can store more water in the ionomer before being shutdown by ice.

High current load will cause fuel cell shutdown very quickly with a small portion of the membrane water storage capacity being utilized; while low current has a longer operating time which is not favored in automotive applications. Although this method of trading total heat generation with time is not desirable, it indicates that utilization of water storage capacity is quite different with various current loads. Therefore, applying different current loads with time during cold start may reach an optimal combination of start up time and total heat generation. The present model is useful to identify such optimal strategies.

4.3 Conclusions

In this chapter, the CFD model is used to predict the effects of operating conditions on PEFC cold start, with the focus on operating conditions such as purge conditions and applied current. The simulation results not only match with the experimental data, as shown in Figure 3-15, but also well explain the experimental practice by various groups in Section 1.2. Cho et al. [4] and Guo and Qi [9] show a
severe degradation with a fully hydrated fuel cell and a much better performance with less membrane hydration after gas purge or solution purge. Yan’s experiments [8] show that the fuel cell can only start up with a current density as low as 100 mA/cm² from -10 °C and no successful start up without gas purge.

With purge at the shut down, not only the ice formation prior to the start up but also the water content in the membrane is reduced. Therefore, more water can be stored in the membrane and cathode CL during cold start, which leads to a much better performance. Although the current density applied is proportional to the heat generation for a same time interval, it also produces more water in proportion. The membrane water absorption rate is only a function of the cell temperature; therefore higher current density leaves less time for water transport into the membrane and leads to a poorer cold start performance.
Figure 4-1: Cold start after equilibrium purge
Figure 4-2: Voltage evolutions for cold start from -30ºC after different equilibrium purge: (a) experiments and (b) simulations.
Figure 4-3: Cold start with short purge and equilibrium purge
Figure 4-4: Water content in MEA after short purge
(Ballard Power System Inc. [87])
Figure 4-5: Current density profiles along the flow direction during cold start from -20ºC after short purge.
Figure 4-6: Ice growth profiles along the flow direction during cold start from -20ºC after short purge
Figure 4-7: Cold start with different current load
Chapter 5

Start up Temperature Effect

Startup temperature is a key parameter defining cold start capability, in addition to the startup time. A PEFC can start up easily from -5°C, but with much more difficulty from -30°C. Although the startup temperature cannot be controlled, investigation of this effect helps to understand fundamental processes controlling cold start.

5.1 Introduction

Ambient temperature is of paramount importance to the PEFC cold start. For this reason cold start capacity is always described by the time required for the fuel cell to reach the normal operating condition from a certain temperature. For instance, the DOE target of cold start for 2010 is 30 sec from -20 ºC.

The temperature is so important because many key parameters governing fuel cell operation are strong functions of temperature, such as the electrochemical reaction kinetics, the species transport characteristics (especially the water transport in the ionomeric membrane), and the heat dissipation to the surroundings. For cold start particularly, the initial temperature not only affects the operating parameters but also defines the difficulty of achieving a successful startup. From the analysis in Chapter 2, the fuel cell temperature rise determines whether fuel cells start up successfully or not.
For a very low startup temperature such as -20 °C or -30 °C, the water transport in the vapor phase is unimportant because the water vapor saturation is low. The cold start ability is thus limited by the water storage in the membrane and cathode CL. Therefore, the most important parameter in determining the cold start performance is the membrane water uptake. However, with increasing startup temperature, the vapor phase transport becomes more important. The saturation pressure of water vapor is plotted in Figure 5-1 with temperature. It can be clearly seen that the vapor saturation increases dramatically with the temperature when the temperature is close to the freezing point. Thus, more water can be removed from the fuel cell by the exhaust gases. More importantly, more water can be transported from the cathode CL to GDL in the vapor phase. Due to the temperature gradient across the CL and GDL in the fuel cell operation, ice will form inside the GDL as a result of the drop in the water saturation pressure. As mentioned in Chapter 2, the water storage capacity in GDL is high compared to that of the membrane and CL. Under very low temperatures, the GDL water storage capacity is rarely used. At a temperature close to the freezing point, the GDL water storage can be utilized because of the vapor phase transport mechanism, therefore the fuel cell cold start performance will be greatly improved.

The purpose of this study is to identify the dominant mechanisms for cold start behavior at different startup temperatures or different stages of a cold start with temperature rise. Subsequently we can optimize cold start operation by using different strategies in each different temperature range, or by drawing different power output at different temperatures.
In this chapter, the startup temperature effect is studied using the present 3D model. The necessity of employing a 3D model is discussed in the following section. The startup temperature in this study ranges from -30 ºC to -10 ºC. The simulation results are validated against the experimental data to show the controlling mechanisms of cold start in each different temperature range.

5.2 Three Dimensional Modeling

When temperature distribution and thermal effects are important, a three-dimensional model must be developed to describe fuel cell cold start.

The through plane direction is the most important dimension in the cold start model because it describes the water transport in the membrane, CL and GDL. It is critical in predicting ice formation in the CL and its effect, which is the governing physics of PEFC cold start.

Along the flow direction, the species concentration, both reactants and product, varies due to the electrochemical reaction and species transport. As a result, the ice formation is not uniformly distributed along the flow direction. For a large-size cell, areas that are plugged by ice formation will then impose more stringent operating conditions on unplugged sections of the MEA; i.e. the current density in a partially blocked cell is redistributed to the remaining operable active areas. The increased local current density and water production exacerbate kinetic and transport deficiencies in remaining operating areas and further polarize the cell in a cascading failure that may lead to cell voltage reversal and possible cell damage.
Therefore, a 2D model which includes the through-plane direction and flow direction is required in the isothermal condition. However, when thermal effects play an important role, such as in the vapor phase transport, the third dimension along the in-plane direction must also be considered.

Most of the heat generated during cold start operation dissipates through the bipolar plates due to their high thermal conductivity. Therefore, the heat flow is primarily along the in-plane direction, i.e. lateral conduction through GDL. Since local temperature is crucial to ice formation in CL and GDL, 3D modeling is required under the non-isothermal condition.

5.3 Effect of Startup Temperature

A lower startup temperature requires more waste heat and thus longer fuel cell operation to reach the freezing point. Furthermore, the electrochemical reaction kinetics and transport properties all decrease dramatically with temperature, making the fuel cell operation much more difficult. Therefore it is of great interest to understand the governing physics at different startup temperatures effects and thereby to improve the cold start capability under low temperatures.

5.3.1 Membrane water uptake

Cold starts under -20°C and -30°C are studied thoroughly with different purge conditions. The simulation results are plotted in Figure 5-2. The shutdown time of cold
start under -20°C is longer than that under -30°C. The difference is mainly due to the slower water uptake of the membrane under lower temperature. Therefore, less water can be stored in the membrane and the CL is filled up with ice more quickly. When the membrane is fully hydrated, the cold start performances under these two temperatures become the same because only the CL can store water before shutdown.

5.3.2 Vapor Phase Transport

With low vapor saturation pressures at -20°C or -30°C, the vapor phase transport is unimportant. At a temperature level as low as -20°C, the vapor saturation pressure difference between GDL and electrode caused by the temperature difference is very small, without mentioning that the temperature difference itself is very small. When the cell temperature is higher, vapor phase transport may play a very important role, which will remove more water out of the CL. More importantly, temperature variation in the fuel cell may cause water freezing in GDL instead of filling up only the cathode electrode.

In Figure 5-3, cold starts under three different thermal boundary conditions are compared. Along the three boundary conditions, the isothermal condition means the fuel cell operates at a constant temperature throughout, which corresponds to the experimental condition in the lab using a single cell with large thermal mass. The constant temperature denotes that the bipolar plate temperature is kept constant at the startup temperature but the catalyst layer temperature is slightly higher due to heat generation from the cell. This thermal boundary condition simulates the end cell in a fuel cell stack where the external wall of the bipolar plate remains at the startup temperature. The simulation with heat flux
boundary condition at the external wall reflects the situation of a cell in the middle of a
stack where the heat transfer coefficient corresponds to the heat transfer coefficient
between cells. It is clear that the non-isothermal case with flux boundary condition has
the best performance, while the isothermal case is the worst.

By comparing the isothermal case and the constant boundary temperature case,
the vapor phase transport mechanism can be clearly identified. From the ice fraction
contours in Figure 5-4, it is obvious that there is more ice formed inside the GDL in the
non-isothermal case with constant boundary temperature. In this case, the temperature
gradient across the fuel cell is very small, about 0.5 °C. However, this small temperature
gradient promotes ice formation inside the GDL and improves the cold start performance.
Another important observation in Figure 5-4 is that under higher startup temperature, the
difference in product water increases as the vapor phase flux driven by the temperature
gradient increases. That is also part of the reason why the non-isothermal case with heat
flux boundary condition has the best performance. The fuel cell with flux boundary
condition can raise its temperature quickly, therefore the water removal from the CL in
vapor phase increases. Meanwhile, water transported into the membrane also increases as
a result of the temperature rise. Therefore, the difference between the two non-isothermal
cases is caused by both membrane water absorption and vapor phase transport.

For the flux boundary case, the cell temperature increases while the inlet gases are
still at the startup temperature. Therefore, a large thermal gradient can be observed near
the inlet in Figure 5-5. As a result, the vapor phase transport is further enhanced in this
region, which can be seen by comparing the ice fraction in the two non-isothermal cases.
5.3 Conclusions

The effect of startup temperature on the fuel cell cold start performance is found to be significant in this chapter. The major reasons accounting for the dramatic effect of the startup temperature are summarized as membrane water absorption and vapor phase transport. The membrane water absorption dominates the low temperature region where the water saturation pressure is low. If the startup temperature is close to the freezing point, vapor phase transport becomes increasingly important as the GDL water storage capacity can be partially utilized.
Figure 5-1: Saturation pressure of water vapor at different temperatures
Figure 5-2: PEFC cold starts under -20°C and -30°C
Figure 5-3: Start up temperature effect
Figure 5-4: Ice fraction contours of cold start from -20°C under different thermal boundary conditions
Figure 5-5: Temperature distributions during cold starts from -20°C under different thermal boundary conditions.
Chapter 6
Effects of Cell Designs

From the discussion in the preceding chapters, it is obvious that water and heat management in a fuel cell determine the cold start behavior. In addition to optimizing the operating conditions, designs of important fuel cell components are also critical to the cold start performance. In this study, membrane, CL and bipolar plates are the main focus of study. By choosing different materials and design parameters, the cold start performance is investigated using the present model. The simulation results are compared with experimental data, whenever possible, to explain these effects.

6.1 Membrane

Since the membrane plays such an important role in storing product water generated in the cathode CL especially under low temperatures, the impact of its design and material properties is of great interest.

6.1.1 Membrane Thickness

In all previous cold start simulations and experiments, a membrane of thickness 30μm is used. To improve cold start performance, a simple idea of enlarging the membrane water storage capacity by increasing its thickness is attempted by both experiments and simulations. A 45μm Gore membrane is chosen to perform the test.
The simulation results with a 45μm membrane are shown in Figure 6-1, which are in comparison with simulation results of a 30μm membrane. As can be seen, the membrane thickness effect is not appreciable because the membrane water absorption is the limiting step. The water transported into the membrane is not fast enough to fully utilize the water storage potential of the membrane. Therefore, enlarging the water storage capacity of the membrane by using a thicker membrane does not improve the water removal from the cathode CL. From results in Figure 6-3, the thicker membrane shows a better performance only when the purged gas humidity is low because it is difficult for water to diffuse from the cathode to the anode with a thicker membrane. When the initial water content is low in the membrane, more water can be stored in the membrane due to both larger flux driven by the water activity difference and longer operational time. Therefore in this case, the overall cold start performance can benefit from a thicker membrane despite the limited back diffusion of water.

Therefore an optimal membrane thickness exists for cold start from a certain temperature, beyond which the membrane thickness will no longer improve the cold start performance. Of course, for a membrane with higher water diffusivity, this optimal thickness will increase. If the membrane water diffusivity is infinitely large, the water transported into the membrane will be proportional to the membrane thickness. On the contrary, where a membrane cannot uptake any water, the thickness would have no effects. Better utilization of the water storage capacity appears to be more important than simply enlarging the capacity.
6.1.2 Alternative Membrane Material

To better utilize the membrane water storage, alternative membranes with better water transport properties are studied. The simulation results are shown in Figure 6-2. With the larger water diffusivity in the ionomeric membrane, more water can be absorbed by the membrane during the cold start and a longer operational time can be achieved. This indicates that the optimal thickness of the membrane increases as the water diffusivity of membrane increases.

6.2 Catalyst Layer

The cathode CL is the most important component during cold start because it is the place where water is produced. Fuel cell shutdown occurs when ice formation inside the cathode CL blocks the reactant transport and reduces the reaction site. To obtain a longer operational time, we can either speed up water removal from the cathode CL or increase water storage capacity of cathode CL, as long as its usage increases proportionally. Possibilities of increasing the CL thickness and optimizing the CL composition for an enhanced cold start performance are studied in this chapter.

6.2.1 Catalyst Layer Thickness

Water is produced at the cathode CL during cold start. To delay the shutdown by ice formation inside the cathode CL, the water storage capacity of the cathode CL is expanded by increasing its thickness.
The effect of the CL thickness is simulated by the present model. Figure 6-3 shows the simulation results with the baseline configuration parameters for PEFC with 10\(\mu\)m CL and 15\(\mu\)m CL respectively. When the catalyst layer becomes thicker, not only is the water storage capacity enlarged, but also more time is gained for water to enter the membrane. The increase of total product water is in part due to increased CL water storage capacity, and in part contributed from water absorption by the membrane within the extra time gained from increasing the CL thickness.

However, if the oxygen reduction reaction is limited by the reactant transport instead of proton transport, ice/frost first forms near the interface of the electrode and GDL because this location has higher local water production rate, and the water absorption of membrane is towards the membrane. This ice formation blocks oxygen transport and further degrades performance, with less water produced near the membrane until shutdown of the cell. In this case, the peak of the ice formation is towards the interface between the cathode CL and the GDL. If the blockage effect of ice formation, i.e. the tortuosity coefficient, is small, as in all previous simulations, the ice formation inside the cathode CL is quite uniform at the shutdown of cold start. Otherwise, there will be sheet-like ice formed at the cathode CL/GDL interface blocking the oxygen transport, leading to fuel cell shutdown without ice filling up the whole electrode. In this case, increasing the CL thickness may not improve the cold start or may even cause worse performance because of the further distance for water uptake by the membrane.

Therefore if the membrane water absorption is considered as a fairly constant factor, the effectiveness of the CL thickness strongly hinges on the local water production rate, or the current density distribution in the cathode CL. This fact provides us an
important clue for PEFC cold start improvement, which is optimizing CL composition such as ionomer loading, carbon loading and Pt loading to control the current density distribution. In the next section, the effect of ionomer distribution along the CL thickness is investigated.

6.2.2 Optimization of the CL Composition

The catalyst layer is very important in cold start, since the cell is shut down when oxygen transport is blocked and/or the active reaction area is totally covered by ice. Increasing the CL thickness is useful if the CL capacity can be fully utilized, i.e., the cell is shutdown after all the pores in CL are filled with ice. To realize this in the CL configuration, especially the ionomer fraction, Pt loading and carbon loading along the thickness must be engineered. The objective is to have ice formed faster near the CL/membrane interface, thereby to avoid forming a thin ice film at the front face blocking the oxygen transport before all CL pores become filled up.

The effect of the ionomer loading in the through plane direction is studied by comparing simulation results with different ionomer loading profiles. A constant loading and two linear loadings with reversed trends are applied in the simulations. To illustrate the reactant blockage effects of ice formation, the effects of tortuosity factors are also studied by using two constants, 1.5 and 2.5 respectively. Figure 6-4 shows the voltage evolutions during the cold starts for different cases. In these simulations, the effect of ionomer loading is the only interest. Therefore, the carbon loading changes corresponding to the ionomer loading to keep the porosity constant and the ECA, which
is the three phase interface, is also considered as a constant for different ionomer loading. From the figure, it is clear that the ionomer loading has tremendous effect on the cold start performance. With a higher ionomer loading towards the membrane, more water is produced near the membrane due to the high current density. The water produced near the membrane facilitates the water uptake and slows down the ice formation. And as a result of faster ice accumulation near the membrane, the reaction in cathode CL could continue because the reactant airway is not blocked by massive ice near the GDL.

### 6.3 Conclusions

In this chapter, the effects of fuel cell components designs on cold start are studied to improve the cold start performance. During the cold start, fuel cell water storage potential is far from full utilization due to the sluggish water transport at low temperatures. It is more important to better utilize the water storage capacity rather than to simply increase the capacity itself. A thicker membrane does not enhance the water removal from the cathode CL or make it even worse by hindering the water diffusion from the cathode to the anode. On the contrary, a membrane with larger water diffusivity offers much better performance with more water stored in the membrane.

CL, as the most important component in fuel cell cold start, is investigated for improvement. By increasing the thickness of the CL, not only more water can be stored in the CL itself but also longer operational time can be obtained for water transport into the membrane. However, its effectiveness depends on the utilization of the CL water storage potential. To better utilize the CL water storage potential, formation of ice film at
the interface of GDL/CL must be prevented because it blocks the oxygen transport and causes the fuel cell shutdown. The CL composition is studied to achieve better utilization by enhancing the local water production rate near the membrane.
Figure 6-1: Effect of membrane thickness
Figure 6-2: Effect of the water diffusivity of membrane on cold start
Figure 6-3: Effect of catalyst layer thickness
Figure 6-4: Effect of catalyst layer composition and tortuosity factor
Chapter 7
Conclusions and Future Work

PEFC cold start, the start up capability of a PEFC under extreme low temperatures, is well known as one of the key issues for fuel cell vehicle commercialization. The product water from the reaction, together with the residual water left in the fuel cell will form ice, greatly affecting the fuel cell performance due to the reactant blockage and the coverage of active reaction sites. This limitation becomes a technical challenge not only because of the practical needs for a quick start up under low temperatures but also due to the PEFC degradation through cold start cycles.

To better understand the fundamental physics, a transient model coupling multi-component, multiphase transport is developed in this thesis to describe PEFC cold start, where ice/frost formation and its effects on PEFC cold start are fully considered. It is evident that in addition to the operating conditions fuel cell component designs have huge impacts on cold start performance. Optimization of fuel cell design, material characteristics and operating parameters holds the key to obtaining better performance in PEFC cold start. Taking advantage of the detailed information provided by a mathematical tool, the present model helps us understand the governing phenomena of transport and electrochemical kinetics coupled with phase change in cold start, and provides assistance in design optimization.
The impact of different operating conditions and cell configurations are predicted using the present model and validated against the experimental data. A brief summary of the conclusions drawn from this thesis work are given below.

### 7.1 Conclusions

Due to its critical importance, PEFC cold start has become one of the most interesting problems in recent years. Many strategies have been proposed to solve this challenge but no intrinsic solution has been presented. Few technical papers can be found, due to the poor understanding of the governing physics. PEFC cold start is a complex process as it involves intimately coupled physics in disparate length scales, from micro-scale water and proton transport in membrane and ice nucleation at the three phase interface in CL, to micro-scale heat transport in a fuel cell or even a stack. The objective of this thesis work, as explained in Chapter 1, is to advance the physical understanding by using a mathematical model in conjunction with experimental validation.

In Chapter 2, a simple analysis of cold start is performed with a lumped model. This analytical model is used to illustrate the ice formation and its effects on the fuel cell performance. It is found that cold start performance can be measured by the amount of product water since the total heat generation, which is proportional to the product water, defines the chance for a successful start. Since the fuel cell is shut down when the CL is filled up with ice, it is preferable to remove water from the CL during cold start. However, the product water before shutdown is much smaller than the water storage potential of fuel cell components due to the slow water transport at low temperatures.
For a fuller understanding of cold start under several situations, a more comprehensive transient, 3D numerical model is developed to study the PEFC cold start in Chapter 3. By using a single-domain approach with CFD technique, the PEFC cold start operation is described by mass, momentum, species, charge and energy conservation principles coupled with phase change phenomena. Detailed information is revealed by the simulation results. It is found that the ice formation has tremendous effect on the distribution of water, temperature and current density. In turn, the ice formation is also a result of the local distributions of the water and temperature. It is found that the membrane plays a very important role in removing the water from the CL. The reaction heat accounts for about 60% percent of the total heat generation and most of the heat is dissipated through the bipolar plate due to its high thermal conductivity. However, because of the large thermal mass of the bipolar plate, the temperature rise is small.

To achieve a better cold start capability, the impact of operating conditions on cold start is studied using the present model in Chapter 4. Purge, as an effective method commonly adopted in the automotive industry to create a favorable initial condition before cold start, is thoroughly investigated in this research. A purge procedure called equilibrium purge, specifically developed to serve the research purposes, is compared with a practical purge using dry gas. The cold start performance after equilibrium purge is better due to the absence of initial ice and uniform distribution of water content. The important role played by the membrane in terms of water storage during cold start is discovered through numerical simulations. The differences of initial water content of membrane and ice fraction in porous layer caused by different purge conditions leads to the variation in the amount of water stored in the membrane, thereby the modified fuel
cell performance. Another operating condition, the current density applied during cold start, also has a large effect on the performance. A higher current can generate heat more quickly; however it also results in a faster water production rate and less time for membrane water storage, which will cause an early shutdown of the fuel cell. For a single cell without any insulation, the total heat generation is higher for a lower current density because it can operate for a longer time. Therefore, it is a trade off between the power generation and startup time.

The startup temperature, as the key parameter for PEFC cold start, is investigated in Chapter 5 by comparing the results of cold start under different temperatures from both simulations and experiments. The difference confirms the slower water transport because of low temperatures. However, at a startup temperature near the freezing point, the vapor phase transport becomes more important and can no longer be neglected as at -20°C or -30°C. At higher temperatures, more water is transported from the CL to the GDL in vapor phase because of the dramatically increased water vapor saturation pressure; hence the PEFC startup performance will be greatly improved. The relationship between temperature and water transport in PEFC cold start is better understood through the simulation and experimental validation.

To find a feasible solution to the cold start problem, the effects of fuel cell designs such as material and thickness of the membrane and CL are studied in Chapter 6 using the present model. It is evident that better utilization of the water storage capacity is the key to improved cold start capability. Increased membrane thickness is not effective due to the slow water transport in the membrane, whereas an alternative membrane material with higher water diffusivity shows a much better performance. The simulation results
reveal that the fuel cell cold start can benefit much from a thicker CL. However, there are possibilities that an ice film may form at the CL/GDL interface, blocking the oxygen transport, without utilizing the full potential of CL water storage. Therefore, it is critical to optimize the CL composition to prevent ice film formation at the CL/GDL interface. By investigating the effects of ionomer loading, it is found that with a higher ionomer loading near the membrane, water is produced faster at the CL/membrane interface, which facilitates membrane water storage and lowers water production rate near the CL/GDL interface, thereby obtaining better performance.

7.2 Outlook

Although the present model is demonstrated to be useful in advancing our understanding, much further research is necessary in order to fully understand the problem and find the ultimate solution to PEFC cold start.

7.2.1 Micro-scale phenomena

As stated in the first chapter, cold start is a complex problem which includes physics at various length scales that are intimately related.

Water is produced at the three-phase interface during the fuel cell operation such that the ice crystals first nucleate and grow at the interface. The pattern and morphology of ice formation could be quite different with different CL materials. In the present model, a linear relationship is assumed for the ECA and porosity reduction. However, this
approximation may not be valid for ice formation inside the CL with various morphologies. This factor must be further considered and implemented in future models.

The state of water in the membrane under low temperatures is another theoretical question to be cleared. Water transport in the membrane is demonstrated to be the most important process in removing the product water from the CL during cold start. The state of water in the membrane under low temperatures determines the water uptake, water diffusivity and proton conductivity and thereby the cold start performance.

Therefore, a better understanding of the microscopic phenomena such as the ice growth inside the CL and membrane water state is absolutely necessary for further understanding and optimization of PEFC cold start.

### 7.2.2 Optimization of Operating Conditions

From the forgoing discussions in this thesis work, it can be seen that the cold start performance strongly depends on the operating conditions such as the purge practice, applied current and start up temperature.

The importance of purge is studied in Chapter 4. The purge process itself is a difficult problem to be tackled for fastest and most efficient water removal without drying out the membrane. From Chapter 4, it is found that the non-uniform distribution in water content along the flow direction has great impact on cold start. Therefore, a uniform water content distribution is favorable for cold start and achievement of this by gas purge must be further studied for the purge practice. In order to alleviate the problem of ice formation while keeping the polymer electrolyte membrane hydrated and obtain the
best combination of purge time and startup time, the purge process should be carefully designed.

In the thesis work, constant current discharge is used throughout cold start. However in practical applications, a constant current may not be the best solution because the fuel cell startup ability increases as its temperature increases. A current load profile, i.e., different current loads at different temperatures, may greatly improve cold start performance by achieving the desired temperature in a short time.

7.2.3 Electrode Flooding Post Cold Start

The main focus of this thesis work is to analyze cold start behavior by studying isothermal cold start under different operating conditions and cell designs. However during a successful cold start, when the cell temperature is successfully raised to the freezing point, the ice formed will start to melt and form liquid water inside the fuel cell. This amount of water together with the product water from the electrochemical reaction will accumulate inside the porous layer. If liquid water cannot be removed fast enough, it will cause flooding in the fuel cell and this flooding condition is more severe than the normal operation because of ice melting. In the presence of liquid water, the water transport through the porous media is driven by the capillary force. To understand this effect, the two phase transport phenomena in catalyst layer and gas diffusion layer should be further investigated.
7.2.4 Experimental Validation

The experimental data used in the model validation under different operating conditions are limited to the fuel cell shutdown time and cell voltage evolution. However, to completely take advantage of the detailed information obtained from numerical simulation that elucidates the complex physics underlying cold start, more experimental data at a distribution level is required.

In Chapter 4, cold start with a non-uniform distribution of initial water content and initial ice fraction along the flow direction is simulated. This initial condition of cold start after purge, as well as the distribution of current and water content, can perhaps be measured along the flow direction. By validating against the distribution data, the present model can be further refined. This methodology is also suitable for other directions. With these validations, the model can yield more physical results in predicting cold start behavior.

In addition, the present model can be improved to explain the degradation phenomena during the cold start. Therefore experimental data that reveals the degradation of PEFC through cold start cycles should be obtained for development of a realistic theory for degradation mechanisms.
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EDUCATION

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